Strontium isotopes in melt inclusions from Samoan basalts: Implications for heterogeneity in the Samoan plume

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Abstract

We measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on 41 olivine-hosted melt inclusions from nine Samoan basalts using laser ablation multi-collector (LA-MC) ICPMS. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are corrected for mass bias after eliminating major isobaric interferences from Rb and Kr. The external precision averages ± 320 ppm (2σ) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on natural Samoan basalt glass standards of a similar composition to the melt inclusions.

All of the Sr-isotope ratios measured by LA-MC-ICPMS on Samoan melt inclusions fall within the range measured on whole-rocks using conventional methods. However, melt inclusions from two Samoan basalt bulk rock samples are extremely heterogeneous in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70459–0.70926), covering 70% of the variability observed in ocean island basalts worldwide and nearly all of the variability observed in the Samoan island chain (0.7044–0.7089). Seven melt inclusions from a third high $^3\text{He}/^4\text{He}$ Samoan basalt are isotopically homogeneous and exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.70434 to 0.70469.

Several melt inclusions yield $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than their host rock, indicating that assimilation of oceanic crust and lithosphere is not the likely mechanism contributing to the isotopic variability in these melt inclusions. Additionally, none of the 41 melt inclusions analyzed exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than the least radiogenic basalts in Samoa ($^{87}\text{Sr}/^{86}\text{Sr}=0.7044$), within the quoted external precision. This provides an additional argument against assimilation of oceanic crust and lithosphere as the source of the isotopic diversity in the melt inclusions.

The trace element and isotopic diversity in Samoan melt inclusions can be modeled by aggregated fractional melting of two sources: A high $^3\text{He}/^4\text{He}$ source and an EM2 (enriched mantle 2) source. Melts of these two sources mix to generate the isotopic diversity in the Samoan melt inclusions. However, the melt inclusions from a basalt with the highest $^3\text{He}/^4\text{He}$ ratios in Samoa exhibit no evidence of an enriched component, but can be modeled as melts of a pure high $^3\text{He}/^4\text{He}$ mantle source.

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1. Introduction

Ocean island basalts (OIBs) erupted at hotspots are thought to be the surface expression of buoyantly upwelling mantle plumes that sample the mantle's compositional heterogeneities at various depths and times

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[1,2]. The Samoan islands and seamounts, formed by a mantle plume impinging on the Pacific plate just north of the Tonga Trench, form a time-progressive hotspot track [3,4] which conforms reasonably well to Morgan's hotspot model [5]. Samoan lavas exhibit the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the largest $^{87}\text{Sr}/^{86}\text{Sr}$ variation (0.7044–0.7089) measured in fresh OIBs [4,6], making them ideal for prospecting for diverse Sr-isotope compositions in melt inclusions.

Olivine-hosted melt inclusions in Samoan lavas provide snapshots of diverse magma chemistry before complete melt aggregation, providing an opportunity to see more of the isotopic heterogeneity which exists in the melt source but that is not detectable in whole rocks. However, the chemical variability in melt inclusions may be generated by a number of processes that obscure source variation, including pre-entrapment fractional crystallization, post-entrapment diffusive re-equilibration, crustal assimilation, and degree, type and depth of melting [7–16].

Studies delineating Pb-isotope diversity in melt inclusions have demonstrated that heterogeneous melt source compositions are an important factor in generating compositional variability [17–21]. A landmark Pb-isotope study of melt inclusions hosted in basalts from Mangaia Island in the Cook Islands revealed significantly more isotopic heterogeneity than is found in whole rocks from the island [17]. The results indicate the presence of an unradiogenic Pb-isotope endmember in the melt inclusions not discernable in whole-rock basalts. Problematically, this unradiogenic Pb endmember has been poorly characterized, owing partly to the large uncertainties associated with in situ Pb-isotope measurements: Pb-isotope data from melt inclusions generally are limited to $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope projections (due to the inability to collect precise ^{204}Pb data on silicate melt inclusions), which place DMM (depleted MORB mantle, low $^3\text{He}/^4\text{He}$, low $^{87}\text{Sr}/^{86}\text{Sr}$), FOZO (*Focus Zone*, high $^3\text{He}/^4\text{He}$, low $^{87}\text{Sr}/^{86}\text{Sr}$), PHEM (*Primitive Helium Mantle*, high $^3\text{He}/^4\text{He}$, middle-range $^{87}\text{Sr}/^{86}\text{Sr}$) and EM2 (enriched mantle 2, low $^3\text{He}/^4\text{He}$, high $^{87}\text{Sr}/^{86}\text{Sr}$) in such close graphical proximity that they cannot be unequivocally resolved. The true pedigree of the unradiogenic Pb endmember in Mangaia is still unknown, and could be similar to any of these four endmembers.

An advantage to the Sr-isotope system is that the EM2 endmember has dramatically higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.7089) [4] than the DMM (0.7026) [22], PHEM (0.7045) [23] and FOZO (0.7030) [24] mantle endmembers, and can be readily differentiated from the three less radiogenic endmembers. PHEM hosts signifi-

cantly more radiogenic Sr than DMM and FOZO and is easily resolved from these two components. Unfortunately, DMM and FOZO exhibit similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and it will be difficult to differentiate between these two components as potential sources of the isotopic diversity in melt inclusions.

We present Sr-isotope data from olivine-hosted melt inclusions recovered from Samoan basalts, some of which lie near the EM2 mantle endmember, with the goal of better understanding the puzzling unradiogenic component sampled by melt inclusions. To this end, we also contribute Sr-isotope data measured on melt inclusions from a recently discovered high $^3\text{He}/^4\text{He}$ basalt from Samoa [25]. Our strategy is to analyze Sr isotopes in melt inclusions from EM2 and high $^3\text{He}/^4\text{He}$ endmember basalts from Samoa, to constrain the role of the various components—EM2, PHEM, DMM and FOZO—that may be contributing to the Sr-isotope diversity in the Samoan plume.

2. Methods

A detailed description of the protocol used for in situ measurement of Sr isotopes in basaltic glasses (and melt inclusions) by LA-MC-ICPMS is provided in the Supplementary data. In order to measure Sr-isotope ratios in situ, we use a 213 nm NewWave laser ablation system coupled to a Thermo-Finnigan Neptune MC-ICPMS, located in the Plasma Facility at Woods Hole Oceanographic Institution (WHOI). During analytical runs, the laser is run in aperture mode with 100% power, a pulse rate of 20 Hz and a spot size of 120 μm . The raster pattern varies depending on the size and shape of the melt inclusion, and the line speed is 4 $\mu\text{m}/\text{s}$. Surface contamination is removed by pre-ablation using the same raster and spot size, but with a pulse rate of 5 Hz, 45% power and a raster speed of 30 $\mu\text{m}/\text{s}$.

During each analytical session, we measure intensities on masses 82 through 88. Raw data are exported to an offline data correction program (TweaKr) for correcting the Rb and Kr isobaric interferences. Runs with low intensities (i.e., <1 V on mass 88, due to small size or low Sr content) were discarded as they are prone to large systematic errors [26]. Masses 85 and 88 are pure Rb and Sr, respectively, with no significant known interferences, and require correction only for mass fractionation. We correct for Kr interferences on masses 84 and 86 so that the mass fractionation-corrected $^{84}\text{Sr}/^{86}\text{Sr}$ value is canonical (0.0565725). The protocol for correcting mass 87 for the Rb interference is the following: A Samoan basalt glass with known $^{87}\text{Sr}/^{86}\text{Sr}$, from analysis by conventional Thermal Ionization Mass Spectrometry

Table 1

Corrected and normalized $^{87}\text{Sr}/^{86}\text{Sr}$ melt inclusion and whole-rock data, including Rb/Sr ratios and raw exported Neptune data (in volts)

Sample name and grain #	Disc #	Mass 82 meas'd-V	Mass 83 meas'd-V	Mass 84 meas'd-V	Mass 85 meas'd-V	Mass 86 meas'd-V	Mass 87 meas'd-V	Mass 88 meas'd-V	$^{85}\text{Rb}/^{87}\text{Rb}$ required	$^{87}\text{Sr}/^{86}\text{Sr}$ corr'd ^a	$^{87}\text{Sr}/^{86}\text{Sr}$ corr'd ^b	Int. prec.	Rb/Sr	Int. prec.	# Cycles	Type	Oliv Fo
AVON3-78-1 (whole rock):											0.70890		0.1255				
78-1Z	Year1	0.0013	0.0011	0.0193693	0.158083	0.263023	0.250903	2.25759	2.58966	0.70791	0.70784	87	0.0746	1.82	14 ^e	C	84.6
78-1#7 ^d	Disc1	0.0020	0.0022	0.0193323	0.164332	0.188415	0.199670	1.60867	2.58811	0.70927	0.70926	123	0.1081	2.47	9	H	84.6
78-1#9 ^d	Disc1	0.0019	0.0021	0.0178511	0.111482	0.163039	0.159876	1.38845	2.58811	0.70733	0.70732	103	0.0850	1.90	6	H	84.4
78-1#6 ^d	Disc2	0.0031	0.0034	0.0297219	0.341900	0.308400	0.354647	2.62064	2.58593	0.70846	0.70843	99	0.1397	2.63	32	H	83.6
78-1#9 ^d	Disc2	0.0031	0.0034	0.0316443	0.384820	0.340724	0.395010	2.89882	2.58593	0.70873	0.70870	94	0.1421	3.08	30	H	82.8
78-1#10 ^d	Disc2	0.0030	0.0031	0.0241696	0.094343	0.202069	0.179689	1.70410	2.58663	0.70845	0.70842	104	0.0593	3.21	16	H	83.6
78-1#4 ^d	Disc3	0.0049	0.0057	0.0638080	0.704962	0.756968	0.817352	6.43584	2.58694	0.70869	0.70866	44	0.1179	0.60	40	G	85.2
78-1inside	Disc3	0.0048	0.0049	0.0311385	0.155536	0.152840	0.165959	1.25071	2.58564	0.70689	0.70686	139	0.1337	2.20	16	C	84.3
78-1B	Disc3	0.0044	0.0043	0.0327454	0.189114	0.222802	0.230356	1.86119	2.58675	0.70791	0.70788	127	0.1089	5.76	10	C	84.2
78-1C	Disc3	0.0041	0.0043	0.0408646	0.414636	0.401444	0.448986	3.40453	2.58675	0.70866	0.70863	38	0.1304	1.96	24	C	83.9
78-1D	Disc3	0.0048	0.0048	0.0313504	0.130366	0.156852	0.158811	1.28485	2.58675	0.70699	0.70696	119	0.1091	3.79	14	C	85.3
AVON3-71-2 (whole rock):											0.70594		0.0754				
71-2C ^d	Year1	0.0015	0.0012	0.0241555	0.131881	0.348997	0.301171	2.99950	2.58977	0.70488	0.70481	50	0.0469	4.99	10 ^e	G	88.8
71-2C ^e	Disc3	0.0049	0.0051	0.0423813	0.151006	0.357484	0.309961	3.00928	2.58772	0.70487	0.70484	60	0.0539	2.09	19	G	88.8
71-2Da	Year1	0.0014	0.0012	0.0190549	0.143364	0.258958	0.241512	2.22256	2.58977	0.70555	0.70549	53	0.0687	3.92	12 ^e	C	90.1
71-2i_mil ^d	Disc1	0.0041	0.0042	0.0293387	0.151118	0.188888	0.190950	1.57393	2.58696	0.70605	0.70602	42	0.1028	0.89	19	G	90.7
71-2#6_sao1	Disc1	0.0040	0.0044	0.0392836	0.237282	0.399731	0.376067	3.39132	2.58675	0.70532	0.70529	63	0.0750	2.45	32	C	90.3
71-2#6_sao2	Disc1	0.0038	0.0039	0.0311684	0.151330	0.259691	0.241924	2.18859	2.58675	0.70511	0.70508	90	0.0741	3.15	15	C	90.5
71-2pentagon	Disc1	0.0035	0.0036	0.0274768	0.164455	0.221630	0.220515	1.86556	2.58653	0.70603	0.70600	69	0.0944	1.40	35	C	91.1
71-2#5 ^d	Disc3	0.0049	0.0055	0.0608667	0.440578	0.704362	0.672560	5.98503	2.58694	0.70537	0.70534	34	0.0792	1.23	40	G	91.0
71-2#5 ^e	Disc3	0.0049	0.0057	0.0600272	0.456791	0.688053	0.667289	5.84446	2.58694	0.70537	0.70534	34	0.0841	1.21	40	G	91.0
71-2#6 ^d	Disc3	0.0050	0.0053	0.0461581	0.261970	0.420138	0.399032	3.54513	2.58674	0.70602	0.70600	53	0.0794	1.35	40	G	85.7
71-2#6 ^e	Disc3	0.0050	0.0054	0.0511361	0.320998	0.514222	0.489758	4.35389	2.58674	0.70600	0.70598	32	0.0793	1.19	40	G	85.7
71-2Z	Disc3	0.0041	0.0042	0.0286629	0.120538	0.176062	0.169532	1.46336	2.58809	0.70576	0.70573	97	0.0882	2.60	21	C	86.1
71-2N	Disc3	0.0041	0.0043	0.0326106	0.171904	0.249420	0.242412	2.09517	2.58778	0.70554	0.70551	48	0.0879	2.74	26	C	90.5
71-2imi_run2	Disc3	0.0046	0.0048	0.0392641	0.162916	0.326152	0.292704	2.74335	2.58778	0.70520	0.70518	112	0.0638	2.80	12	C	91.0
71-2V	Disc3	0.0034	0.0037	0.0358138	0.196791	0.370738	0.339729	3.15166	2.58754	0.70461	0.70459	122	0.0668	4.32	13	C	87.4
OFU-04-06 (whole rock):											0.70458		0.0458				
OFU-04-06-13 ^d	Ofu	0.0012	0.0004	0.0123598	0.087599	0.202878	0.179279	1.74009	2.58774	0.70458	0.70457	226	0.0541	6.04	6	H	79.8
OFU-04-06-15 ^d	Ofu	0.0008	0.0006	0.0166800	0.116272	0.260130	0.231639	2.23575	2.58791	0.70443	0.70443	128	0.0556	1.62	13	H	77.3

OFU-04-06-25 ^d	Ofu	0.0009	0.0008	0.0272537	0.215485	0.450579	0.407078	3.87445	2.58797	0.70455	0.70454	60	0.0595	3.24	20	H	77.2
OFU-04-06-26 ^d	Ofu	0.0007	0.0006	0.0135577	0.076760	0.200599	0.173323	1.72195	2.58771	0.70443	0.70443	86	0.0476	2.73	16	H	76.5
OFU-04-06-28 ^d	Ofu	0.0007	0.0006	0.0138764	0.082936	0.207139	0.180426	1.77796	2.58777	0.70435	0.70434	164	0.0499	1.97	11	H	78.4
OFU-04-06-03 ^d	Ofu	0.0004	0.0005	0.0090473	0.057761	0.131245	0.115793	1.11700	2.58747	0.70443	0.70443	92	0.0560	2.67	15	H	83.8
OFU-04-06-02 ^d	Ofu	0.0007	0.0006	0.0126725	0.082453	0.187441	0.166696	1.61548	2.58588	0.70469	0.70469	184	0.0542	0.96	7	H	76.5
AVON3-71-11											0.70550		0.0700				
(whole rock):																	
71-11a ^d	Disc1	0.0035	0.0035	0.0250240	0.083017	0.152405	0.138888	1.27387	2.58654	0.70653	0.70653	83	0.0691	1.22	16	G	83.0
71-11a ^c	Disc1	0.0019	0.0021	0.0204900	0.125897	0.216562	0.204083	1.85257	2.58857	0.70692	0.70692	109	0.0720	0.92	15	G	83.0
71-11#1 ^d	Disc3	0.0048	0.0048	0.0316250	0.103649	0.160366	0.150752	1.31592	2.58772	0.70683	0.70680	144	0.0846	5.70	8	G	81.4
AVON3-68-3											0.70539		0.0688				
(whole rock):																	
68-3#6mi1 ^d	Disc1	0.0020	0.0021	0.0186133	0.117638	0.165627	0.163878	1.40909	2.58798	0.70625	0.70624	75	0.0884	3.01	20	G	87.9
68-3#6mi2	Disc1	0.0038	0.0040	0.0305189	0.209211	0.258789	0.264567	2.18215	2.58653	0.70577	0.70575	87	0.1027	1.92	12	C	87.9
68-3#6mi2 ^c	Disc1	0.0037	0.0041	0.0371899	0.294848	0.389761	0.392493	3.31142	2.58653	0.70577	0.70574	93	0.0954	1.73	9	C	87.9
68-3Ami	Disc3	0.0041	0.0042	0.0302365	0.092078	0.197293	0.173102	1.64414	2.58754	0.70482	0.70480	144	0.0600	6.45	10	C	90.1
AVON3-63-2											0.70540		0.0679				
(whole rock):																	
63-2mi	Disc3	0.0049	0.0051	0.0641890	0.514757	0.759082	0.741869	6.46111	2.58815	0.70599	0.70596	58	0.0856	2.68	31	C	–
63-2mi ^c	Disc3	0.0047	0.0056	0.0601701	0.544474	0.708353	0.718034	6.03171	2.58815	0.70616	0.70613	69	0.0969	1.22	36	C	–
63-2ami	Disc3	0.0044	0.0045	0.0283814	0.086324	0.138106	0.128251	1.13104	2.58815	0.70522	0.70520	181	0.0818	4.84	11	C	87.1
63-2bmi1	Disc3	0.0044	0.0045	0.0334163	0.133112	0.234231	0.215648	1.95929	2.58815	0.70528	0.70525	55	0.0728	3.15	23	C	86.6
AVON3-74-1											0.70469		0.0484				
(whole rock):																	
74-1mi	Year1	0.0015	0.0012	0.0174643	0.076749	0.224099	0.189719	1.91969	2.58895	0.70483	0.70477	157	0.0426	1.38	9 ^c	C	85.1
S11 (whole rock):											0.70620		0.0597				
S11mi	Disc3	0.0048	0.0048	0.0330920	0.078499	0.189324	0.161268	1.56507	2.58564	0.70520	0.70518	125	0.0539	6.13	11	C	76.5
AVON3-78-3											0.70889		0.1108				
(whole rock):																	
78-3 mi	Year1	0.0014	0.0012	0.0184433	0.207247	0.241204	0.254752	2.06790	2.58966	0.70814	0.70807	61	0.1068	3.51	18 ^c	C	84.1

All samples, except for OFU-04-06 and S11, are dredge samples from the AVON3 dredging cruise. Melt inclusion type refers to whether it was homogenized (H), glassy (G) or crystalline (C). Host olivine forsterite contents are given in the last column. Internal precision (Int. prec.) is standard error (2σ) and is in ppm ($^{87}\text{Sr}/^{86}\text{Sr}$) or % (Rb/Sr). Melt inclusion $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are corrected for the isobaric interference from Rb by use of the bracketing method (see text for details). All melt inclusion analyses were performed on 01/27/04, 01/10/05, 01/11/05, 08/09/05 and 08/10/06 and corrected for the isobaric Rb interference using the Samoan glass standard analyses from those 5 days (see Supplementary data). Melt inclusion Sr-isotope and Rb/Sr data from a particular sample are listed immediately below the equivalent whole-rock data.

^a Sr-isotopes are corrected for Kr and Rb interferences and fractionation-corrected.

^b After correction for Rb and Sr interferences and fractionation, melt inclusions are corrected for 987 standard solution runs for each analytical session.

^c Cycle length for melt inclusions from disc “Year1” are 16 s integrations during analysis. Cycles for all other measurements are 8 s integration.

^d Has major and/or trace element data in Table 2.

^e Replicate analysis of a melt inclusion is listed immediately below first analysis. Six melt inclusions were large enough to permit replicate analyses. Melt inclusion sample Year1_71-2 was replicated over a 1-year period, and was renamed Disc3_71-2C for the replicate analysis. All other replicate analyses were made during the same analytical session.

(TIMS), is measured by laser ablation, Kr-corrected, and the $^{85}\text{Rb}/^{87}\text{Rb}$ ratio is adjusted until the known TIMS $^{87}\text{Sr}/^{86}\text{Sr}$ value of the glass is achieved. We adopted the strategy of using the required $^{85}\text{Rb}/^{87}\text{Rb}$ of the Samoan basalt glass standards to bracket the $^{85}\text{Rb}/^{87}\text{Rb}$ of the basalt glass unknowns. In order to estimate the overall accuracy associated with this technique, we apply contiguous bracketing of the glass standard runs, and we are able to reproduce the known TIMS values to within an average of ± 320 ppm (2σ standard deviation). However, due to uncertainty associated with the $^{85}\text{Rb}/^{87}\text{Rb}$ ratio (2.5875 ± 0.00275 , 2σ), the final, corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio exhibits an error magnification that is directly proportional to the Rb/Sr ratio of the sample. Samples with low Rb/Sr will exhibit less error from the Rb correction (145 ppm, Rb/Sr=0.04) than samples with high Rb/Sr (505 ppm, Rb/Sr=0.14) (see Supplementary data). However, over the range of Rb/Sr in the Samoan basalt glass standards (0.045–0.126), we find no relationship between the internal (in-run) precision of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (which average 45 ppm, 2σ standard deviation) and Rb/Sr during analyses of basalt glasses by laser ablation. Similarly, there does not appear to be a relationship between Kr/Sr and the internal precision or reproducibility (external precision) of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Samoan glass standards over the range of ratios that we have observed during melt inclusion analysis ($^{82}\text{Kr}/^{88}\text{Sr}$ from 0.00013 to 0.004). Finally, the reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ measurement does not appear to be related to Sr intensity over the range of Sr intensities observed in lasered Samoan glasses, a range that encompasses the melt inclusion analyses.

Six melt inclusions were large enough for replicate analysis (one melt inclusion, 71-2C, was replicated over a one-year period), and five of their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were reproducible within the quoted precision. However, the replicate analysis of melt inclusion 71-11a was different by 550 ppm (see Table 1), while error resulting from the Rb correction is only 260 ppm (2σ) on Samoan glass standards with similar Rb/Sr ratios. The internal precision of the replicate analysis of this melt inclusion was ~ 100 ppm (2σ). Data from this melt inclusion indicates that larger-than-usual $^{85}\text{Rb}/^{87}\text{Rb}$ variations over time can occasionally generate uncertainties (above the 2σ level) in $^{87}\text{Sr}/^{86}\text{Sr}$ that are somewhat larger than error predicted by the data from Samoan glass standards.

An upper limit for the $^{87}\text{Sr}/^{86}\text{Sr}$ measurement precision on Samoan melt inclusions with low Rb/Sr can be inferred from the near-uniform ratios obtained on melt inclusions from the high $^3\text{He}/^4\text{He}$ Ofu basalt. The Rb/Sr values were among the lowest during analy-

sis of Ofu melt inclusions, and the tight clustering of the Ofu melt inclusions may be partially explained by decreased error of $^{87}\text{Sr}/^{86}\text{Sr}$ measurement for these samples compared to other, higher Rb/Sr Samoan glasses and melt inclusions from Vailulu'u and Malu-malu. If we assume that the Ofu melt inclusions are isotopically homogeneous, then the external precision on these 7 melt inclusions is ± 335 ppm (2σ). Some of the apparent variability may be a result of error from the Rb correction, which is ± 190 ppm (2σ) at Rb/Sr ratios of 0.053, and may not reflect true variability. Additionally, internal precision varied from 60 to 226 ppm (2σ standard error) on the seven Ofu melt inclusions.

Masses 85 and 88 represent pure Rb and Sr, respectively, so that fairly precise measurement of Rb/Sr ratios can be generated. After correcting for mass fractionation ($\approx 1.5\%$ /amu), Rb/Sr ratios on Samoan basalt glasses measured by laser ablation are reproducible to 17% (2σ , compared to ratios obtained by XRF/ICP techniques on the same samples), and precise (1.7%, 2σ) during multiple runs on the same glass (see Supplementary data).

Major element compositions of glassy and homogenized melt inclusions were obtained with a JEOL-733 automated electron microprobe at the Massachusetts Institute of Technology using an electron beam with current of 10 nA and accelerating potential of 15 kV focused to a spot of 1–2 μm in diameter for olivine analyses, and defocused to 10 μm for glass analyses. Trace element contents were determined with a Cameca IMS 3f ion microprobe following the techniques described in [27,28]. A small beam (5 μm diameter spot), combined with a high-energy filtering technique (80–100 eV window), was used to determine trace element concentrations. Precision for Sr, La, Zr, Y is estimated to be $\pm 15\%$, and ± 20 –30% for Ba, Nb and Rb. Homogenization of olivine-hosted melt inclusions was performed in a furnace at 1187–1220 C (depending on olivine composition) at 1 atm pressure for 5 min in a graphite capsule.

To correct for the effects of crystallization of olivine in the glassy and homogenized melt inclusions, we add equilibrium olivine to the melt inclusions in 0.1% increments until equilibrium with mantle olivine (Fo_{90}) is achieved, assuming olivine-melt partitioning of Fe and Mg from [29]. Instead of correcting the melt inclusions to be in equilibrium with the host olivine, this correction scheme is chosen so that we can compare them to similarly corrected Samoan whole-rock lavas (after discarding data from the most evolved— $\text{MgO} < 6.5$ wt.%—whole-rock samples).

3. Results

3.1. Sr-isotope variability in melt inclusions

Sr-isotopes were measured in melt inclusions from nine geochemically well-characterized basalt samples [4,25] from five islands and seamounts located along the Samoan hotspot track. Olivines (Fo_{76-91}) with large ellipsoidal melt inclusions (50–250 μm diameter) were separated from the basalt samples for melt inclusion exposure and isotopic analysis. Most of the melt inclusions were crystalline and usually contained dendritic clinopyroxene in a glassy matrix, with spinel and rare sulfide globules; some ($\approx 5\%$) of the melt inclusions were glassy. The high $^3\text{He}/^4\text{He}$ basalt sample OFU-04-06 was unique in that amphibole and apatite were common melt inclusion phases, and carbonate was also observed.

Olivines (Fo_{82-85}) hosting melt inclusions were separated from Malumalu seamount dredge sample 78-1, a picrite with the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7089) of any OIB [4]. Melt inclusion-rich olivines were also recovered from dredge sample 71-2 (Fo_{84-91}) from Vailulu'u, a seamount that displays intermediate enrichment relative to the other Samoan islands and seamounts (bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from 0.7052 to 0.7067, $n=20$). From Ofu Island, olivines (Fo_{76-84}) were recovered from ankaramite dike sample OFU-04-06, which exhibits the highest $^3\text{He}/^4\text{He}$ measured in a Samoan basalt [25]. Lavas from Ofu are the most isotopically homogeneous of the volcanoes in the Samoan chain ($^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70444 to 0.70480, $n=12$). Finally, a smaller number of olivines were separated for melt inclusion analysis from Vailulu'u dredge samples 71-11 (Fo_{81-83}), 63-2 (Fo_{86-87}) and 68-3 (Fo_{87-90}), Malumalu dredge sample 78-3 (Fo_{84}), Ta'u Island dredge sample 74-1 (Fo_{85}), and Savai'i subaerial post-erosional sample S11 (Fo_{76}).

The Sr-isotope data from melt inclusions in just three Samoan whole-rock samples (OFU-04-06, 78-1 and 71-2) define a broad array that encompasses the entire spectrum of Sr-isotope variability (0.70434–0.70926) recorded in Samoan basalts (Fig. 1 and Table 1). Eleven melt inclusions from 78-1 display $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70686–0.70926, and encompass over 30% of the isotope variability observed in the OIB mantle. Vailulu'u melt inclusions from dredge samples 71-2 ($^{87}\text{Sr}/^{86}\text{Sr}=0.70459\text{--}0.70602$, $n=12$ melt inclusions) and 68-3 ($^{87}\text{Sr}/^{86}\text{Sr}=0.70480\text{--}0.70624$, $n=3$) exhibit a smaller range of Sr-isotope values than 78-1. However, the magnitude of the Sr-isotope heterogeneity in the melt inclusions from these two samples is approxi-

Fig. 1. $^{87}\text{Sr}/^{86}\text{Sr}$ (upper panel) and Rb/Sr (lower panel) in melt inclusions from nine basalt samples compared to the total variation in each island/seamount (shown by boxes). References for whole-rock data can be found in [4]. The nine whole rocks from which the melt inclusions were separated are represented by larger symbols. No melt inclusions are more isotopically depleted than the most depleted lava measured in the island chain ($^{87}\text{Sr}/^{86}\text{Sr} > 0.7044$). The range for EPR N-MORB [22] (averaged by segment) plots significantly below the Samoan whole rocks and melt inclusions. Replicate analyses on the same melt inclusion are averaged. The Rb/Sr for Savai'i whole-rock sample SAV1-25 is not included because of alteration. Internal precision (2σ , standard error) for $^{87}\text{Sr}/^{86}\text{Sr}$ is approximately the size of the data symbols. $^{87}\text{Sr}/^{86}\text{Sr}$ error bars represent error propagated from the Rb correction, as determined on Samoan glass standards, and dominates the error associated with $^{87}\text{Sr}/^{86}\text{Sr}$ measurement by LA-ICP-MS; maximum and minimum (500 and 150 ppm) errors are shown for reference. Error bars for Rb/Sr are $\pm 17\%$ (2σ , standard deviation), and are based on the reproducibility of Rb/Sr measurement on Samoan glass standards; internal precision for Rb/Sr averages an order of magnitude better. Samples are listed in order of increasing whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$, from left to right.

mately equal to the variability observed in Vailulu'u seamount lavas, although the melt inclusions sample a more depleted component than observed in whole rocks from this seamount. Among the Vailulu'u samples, only sample 71-11 ($^{87}\text{Sr}/^{86}\text{Sr}=0.70653\text{--}0.70692$, $n=2$)

hosts inclusions that sample compositions similar to the most enriched isotopic compositions observed in Vailulu'u volcano. Like sample 71-11, isotopic analyses of melt inclusions from sample 63-2 ($^{87}\text{Sr}/^{86}\text{Sr}=0.70520\text{--}0.70613$, $n=3$) lie completely within the isotopic range found in the whole rocks from Vailulu'u seamount. OFU-04-06 melt inclusions exhibit the least isotopic variability ($^{87}\text{Sr}/^{86}\text{Sr}=0.70434\text{--}0.70469$, $n=7$) among the samples with isotopic analyses on more than two different inclusions, and this variability is similar to the variability sampled by whole-rock lavas from the island. There is only a single melt inclusion analysis from each of basalt samples 78-3 (0.70807), 74-1 (0.70477) and S11 (0.70518); the Sr-isotope ratios lie within the range observed in the respective host volcanoes.

Although melt inclusions show more depleted isotopic compositions than the island or seamount from which they were recovered, they are not observed to sample compositions more depleted than whole rocks from the Samoan hotspot ($^{87}\text{Sr}/^{86}\text{Sr}\geq 0.7044$). Therefore, the least radiogenic Sr-isotope ratios in Samoan basalts and melt inclusions are significantly more enriched than the depleted upper mantle sampled by MORB along the EPR (East Pacific Rise; 0.70228–0.70287, N-MORB segment averages from [22]); the old oceanic crust upon which the Samoan island chain is constructed is probably isotopically similar to these modern EPR basalts.

Rb/Sr ratios measured by LA-ICP MS on the same set of melt inclusions tell a story similar to that of the isotopes. Melt inclusions in sample 78-1 exhibit the largest variation in Rb/Sr ratios (0.0593–0.1421), and the variability is similar to that observed in the whole rocks measured from Malumalu seamount. The Rb/Sr ratios in OFU-04-06 melt inclusions show some heterogeneity (Rb/Sr from 0.0476 to 0.0595, $n=7$), but this variability is smaller than the variability sampled by whole-rock lavas from the island. Vailulu'u melt inclusions from dredge samples 71-2 (Rb/Sr from 0.0469 to 0.1028, $n=12$ melt inclusions) and 68-3 (Rb/Sr from 0.060 to 0.1027, $n=3$) exhibit a range of Rb/Sr values that falls between 78-1 and OFU-04-06. Unlike the isotopes, however, the magnitude of the Rb/Sr heterogeneity in the melt inclusions from samples 71-2 and 68-3 is greater than the variability observed in Vailulu'u seamount lavas, and, within error of measurement, do not sample a component with lower Rb/Sr than observed in whole rocks from this seamount.

The present dataset suggests that the isotopic variability exhibited by the melt inclusions in a basalt sample may be a function of the whole-rock isotopic

composition. In Fig. 2, the Sr-isotope variability of melt inclusions in three basalt samples—those with the largest number of melt inclusion analyses—is plotted against the bulk $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the respective whole rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$ variability, determined by the difference between the highest and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$

Fig. 2. Upper panel: Melt inclusion isotopic variability (in ppm) as a function of whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the three Samoan lavas with the greatest number of melt inclusion analyses. Melt inclusion isotopic variability increases with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ (and decreasing $^3\text{He}/^4\text{He}$, not shown) in the three Samoan basalts. Variability is determined by the difference between the most isotopically extreme melt inclusions in a basalt sample. The maximum and minimum values for this variability are a result of the uncertainty introduced by the Rb correction, which is directly related to the Rb/Sr of the melt inclusion. For example, the maximum variability in basalt sample 78-1 is determined by the difference between the highest (0.7092 plus 391 ppm uncertainty) and lowest plausible $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7072 minus 393 ppm uncertainty). The minimum variability is determined by the difference between the lowest plausible $^{87}\text{Sr}/^{86}\text{Sr}$ in the most enriched melt inclusion (i.e., 0.7089, or 0.7092 minus 389 ppm uncertainty) and the highest plausible $^{87}\text{Sr}/^{86}\text{Sr}$ in the most depleted melt inclusion (0.7074, or 0.7072 plus 393 ppm uncertainty). Lower panel: Melt inclusion Rb/Sr variability (absolute) as a function of whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Maximum and minimum variability is determined the same way, but assumes an uncertainty for Rb/Sr of 17%. The magnitude of variability due to internal precision is approximated by the size of the data symbols in both panels.

ratios from melt inclusions in a given basalt sample, exhibits a maximum and a minimum due to the uncertainty introduced by the Rb correction. Although the number of data points is limited, the data are consistent with melt inclusion isotopic diversity increasing with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ (increasing EM2 component) and decreasing $^3\text{He}/^4\text{He}$ (not shown). The range of variability for Malumalu sample 78-1 is larger than, but overlaps with, the range of values from Vailulu'u sample 71-2. The melt inclusions from the high $^3\text{He}/^4\text{He}$ Ofu basalt exhibit the smallest range of probable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and they do not overlap with the range from samples 71-2 and 78-1. A similar observation can be made for the variability of Rb/Sr ratios in the melt inclusions, where Rb/Sr tends toward greater melt inclusion variability in samples 78-1 and 71-2; the Ofu sample has the smallest range of variability, and overlaps slightly with the lowest probable variability in sample 71-2. It is notable that OFU-04-06 exhibits the highest $^3\text{He}/^4\text{He}$ ratio (and low $^{87}\text{Sr}/^{86}\text{Sr}$) found in Samoa, an observation that may be linked to the small

degree of isotopic and trace element variability in its melt inclusions.

3.2. Major and trace element characteristics of melt inclusions

Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the melt inclusions define a broad array that encompasses the entire spectrum of Sr-isotope and Rb/Sr variability recorded in Samoan basalts (Fig. 3). Curiously, the melt inclusions from Malumalu do not form an array by themselves, but plot over a broad region. The Rb/Sr and Sr-isotope data array form a crude mantle isochron of 1.1 Ga.

Major and trace elements were measured on melt inclusions from Vailulu'u, Malumalu and Ofu basalts, and they reveal a large range of compositions (Table 2). Although the trace element compositions of Vailulu'u melt inclusions are similar to whole-rock analyses from this seamount, melt inclusions from EM2 endmember basalt 78-1 record a greater degree of trace element variability than all of the whole rocks measured from Malumalu. One

Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Rb/Sr ratios for Samoan whole rocks and melt inclusions, determined by laser ablation. The shaded regions represent the extent of melt inclusion variability for the volcanoes (Vailulu'u, Malumalu and Ofu). The open region encompasses the least evolved ($\text{MgO} \geq 6.5$ wt.%) whole-rock measurements from these three volcanoes and Ta'u, thus encompassing islands and seamounts only on the eastern half of the Samoan hotspot track (where $\sim 98\%$ of the analyzed melt inclusions were recovered). Whole-rock data from Ofu is unpublished, and for the other volcanoes is from [4]. MORB range is limited to EPR N-MORB (M) segment averages [22]. High $^3\text{He}/^4\text{He}$ basalts from Hawaii (H) [37], Iceland (I) [38] and Baffin Island (B) [39] provide an approximation for FOZO (higher $^3\text{He}/^4\text{He}$ ratios exist for Hawaiian basalts [40], but $^{87}\text{Sr}/^{86}\text{Sr}$ data are not available for these samples; Rb/Sr data for high $^3\text{He}/^4\text{He}$ samples from Baffin Island are found in [41]). Error bars on symbols are internal precision of measurement (2σ , mean deviation). Error bars on periphery of figure denote external precision of measurements, as determined by Samoan glass standards with compositions similar to the melt inclusions: Rb/Sr error is 17% (2σ , standard deviation) and $^{87}\text{Sr}/^{86}\text{Sr}$ error is based on error associated with the Rb correction (2σ , standard deviation). Replicate analyses of the same melt inclusion are shown. The melt inclusion data form a crude mantle isochron age of ~ 1.1 Ga.

Table 2

Melt inclusion major and trace element data (uncorrected for olivine fractionation), and host olivine composition

Sample #	Disc #	Grain #	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Mg #	OlFo	Rb	Sr	Y	Zr	Nb	Ba	La	⁸⁷ Sr/ ⁸⁶ Sr ^a	Type
78-1	Disc1	#7	45.64	3.77	12.97	14.11	0.14	6.85	9.53	3.46	2.16	0.46	99.19	49.0	84.6	181	1176	83.6	979	—	—	—	0.70926	H
78-1	Disc1	#9	46.57	2.99	13.06	10.75	0.16	8.02	13.09	2.94	1.57	0.44	99.74	59.6	84.4	49	443	33.0	245	—	—	45.6	0.70732	H
78-1	Disc1	#10–11	44.98	3.22	12.84	11.18	0.14	9.26	11.29	2.62	1.76	0.39	98.10	62.1	84.0	75	507	28.1	269	—	—	—	—	H
78-1	Disc1	#12	46.37	3.76	13.09	11.51	0.17	8.03	11.38	2.93	1.91	0.40	99.65	58.0	84.4	59	545	33.2	339	73.1	390	—	—	H
78-1	Disc2	#5	45.16	3.42	12.62	11.09	0.17	9.15	12.42	2.46	1.42	0.42	98.68	62.0	84.3	130	1127	75.5	568	132.9	796	96.1	—	H
78-1	Disc2	#6	47.22	3.45	13.60	11.80	0.23	7.10	10.17	3.13	2.10	0.42	99.38	54.4	83.6	115	926	54.1	543	122.4	666	93.8	0.70843	H
78-1	Disc2	#7	47.20	2.92	13.65	9.94	0.14	7.83	11.36	2.73	2.00	0.40	98.49	60.9	83.9	—	—	—	—	—	—	—	—	H
78-1	Disc2	#8	45.57	3.20	12.26	11.20	0.17	9.26	11.33	2.71	1.33	0.47	97.88	62.1	83.6	71	679	40.6	360	76.0	409	57.7	—	H
78-1	Disc2	#9	46.81	3.46	14.03	11.81	0.16	7.34	10.54	2.93	1.91	0.43	99.59	55.2	82.8	76	655	38.7	400	84.8	482	72.3	0.70870	H
78-1	Disc2	#10	46.32	3.46	13.16	11.01	0.15	7.65	11.60	4.80	1.27	0.46	100.01	57.9	83.6	33	631	37.3	346	73.4	450	65.1	0.70842	H
78-1	Disc2	#11Le	46.32	3.24	12.74	11.04	0.14	8.18	12.72	3.18	1.33	0.39	99.67	59.5	83.6	55	598	36.7	281	56.1	401	45.5	—	H
78-1	Disc2	#11RtS	—	—	—	—	—	—	—	—	—	—	—	—	83.2	194	1694	100.5	871	193.5	1258	173.6	—	H
78-1	Disc2	#11RtL	44.61	3.77	12.99	11.76	0.19	6.23	13.20	2.70	1.57	0.44	97.85	51.2	83.2	299	2480	158.7	1310	293.5	1887	246.6	—	H
78-1	Disc2	#3	46.09	3.23	12.50	10.68	0.15	8.85	11.47	2.59	1.59	0.43	97.91	62.1	84.1	135	1038	62.5	579	126.8	719	100.6	—	H
78-1	Disc2	#4	46.45	2.99	12.17	10.32	0.15	9.22	12.92	2.37	1.37	0.40	98.80	63.9	83.9	104	901	55.1	465	110.9	686	78.9	—	H
78-1	Disc3	#4	46.07	3.81	13.22	10.47	0.12	6.00	12.52	2.93	1.80	0.42	97.81	53.1	85.2	69	555	26.4	297	64.8	370	55.4	0.70866	G
71-2	Disc1	g#3–4	48.50	2.66	12.55	9.41	0.14	7.38	14.63	2.33	0.84	0.35	99.13	60.8	87.4	26	384	23.0	185	30.4	124	22.4	—	G
71-2	Disc1	i	48.13	2.57	12.54	9.21	0.14	8.07	13.85	2.48	0.78	0.27	98.40	63.4	90.7	—	—	—	—	—	—	—	0.70602	G
71-2	Disc3	#3	46.12	3.48	13.06	10.94	0.15	5.81	14.09	2.55	1.29	0.32	98.23	51.3	84.3	50	517	29.5	237	52.7	347	40.9	—	G
71-2	Disc3	#5	46.71	3.10	12.72	9.66	0.15	7.90	13.10	2.45	1.24	0.32	97.72	61.8	91.0	45	504	27.1	243	58.8	314	35.3	0.70534	G
71-2	Disc3	#6	46.46	3.23	12.31	10.52	0.17	7.54	13.64	2.64	1.14	0.36	98.50	58.7	85.7	50	579	33.3	281	60.1	342	49.9	0.70599	G
71-2	Disc3	C	48.87	3.33	13.16	8.77	0.15	7.63	12.81	2.68	0.83	0.39	98.94	63.3	88.8	27	437	22.2	232	42.6	177	33.9	0.70482	G
71-11	Disc3	#1	49.01	3.13	12.53	11.05	0.18	6.15	12.01	2.85	0.94	0.40	98.51	52.4	81.4	34	419	27.1	232	41.4	205	35.6	0.70680	G
71-11	Disc1	a	49.28	2.82	12.70	10.94	0.14	6.89	11.63	2.60	1.01	0.37	98.73	55.5	83.0	36	409	30.3	223	40.9	214	33.0	0.70672	G
68-3	Disc1	#6mil	48.77	2.88	14.30	8.75	0.13	4.68	14.74	2.64	1.35	0.37	98.98	51.4	87.9	54	533	27.0	260	62.5	378	46.3	0.70624	G
OFU-04-06	Ofu	13	44.25	3.31	12.60	10.10	0.11	7.99	13.38	3.40	0.94	0.50	96.75	61.4	79.8	52	856	41.6	464	76.8	343	106.2	0.70457	H
OFU-04-06	Ofu	14	46.33	3.07	14.03	8.64	0.07	8.03	11.89	3.52	1.08	0.53	97.24	54.9	80.4	61	613	33.3	352	55.6	311	77.8	—	H
OFU-04-06	Ofu	15	46.47	2.81	13.67	10.58	0.14	7.20	10.64	3.96	1.09	0.33	96.96	60.5	77.3	60	700	30.0	374	54.8	303	82.1	0.70443	H
OFU-04-06	Ofu	16	46.74	3.13	14.12	7.00	0.09	8.26	13.11	3.76	1.19	0.45	97.97	49.5	81.9	68	760	38.6	393	72.5	363	91.1	—	H
OFU-04-06	Ofu	18	50.44	1.16	14.17	7.56	0.07	7.33	11.22	4.69	1.38	0.39	98.67	51.4	79.3	63	926	33.8	460	84.1	399	113.9	—	H
OFU-04-06	Ofu	19	47.15	2.14	11.15	17.06	0.21	13.83	2.72	1.56	1.71	0.46	98.00	75.2	76.6	—	—	—	—	—	—	—	—	H
OFU-04-06	Ofu	20	47.36	2.90	14.50	9.00	0.13	7.59	10.84	4.02	1.06	0.39	97.84	55.1	78.6	81	909	39.0	438	70.3	402	32.5	—	H
OFU-04-06	Ofu	24rep	46.35	3.58	13.47	8.58	0.09	8.11	13.70	3.23	0.72	0.29	98.13	55.8	83.0	—	—	—	—	—	—	—	—	H
OFU-04-06	Ofu	25	45.74	3.16	13.55	11.98	0.12	7.71	11.15	3.54	0.89	0.42	98.33	63.6	77.2	59	659	38.1	383	48.7	243	—	0.70454	H
OFU-04-06	Ofu	26	46.14	2.51	12.70	10.60	0.10	8.04	13.61	3.01	0.74	0.34	97.93	62.3	76.5	45	573	37.7	338	42.3	191	—	0.70443	H

OFU-04-06	Ofu	27	44.62	3.36	13.38	10.12	0.10	7.99	12.36	3.35	0.91	0.49	96.82	60.0	79.5	55	807	40.2	457	75.8	321	111.4	—	H
OFU-04-06	Ofu	28	47.60	2.70	13.87	9.87	0.08	7.49	10.92	4.18	0.94	0.33	98.13	58.5	78.4	58	744	34.6	382	71.1	322	94.3	0.70434	H
OFU-04-06	Ofu	30	47.23	3.03	13.82	7.23	0.09	7.78	12.39	3.74	1.15	0.24	96.79	50.9	82.3	63	634	32.8	324	54.0	283	76.6	—	H
OFU-04-06	Ofu	31	42.22	2.01	13.18	14.43	0.12	7.24	12.41	4.17	1.14	0.43	97.95	68.4	80.3	87	1006	46.6	515	79.4	445	136.2	—	H
OFU-04-06	Ofu	33	41.65	2.83	13.21	16.38	0.17	6.96	10.68	3.77	1.06	0.34	97.17	71.1	77.7	66	961	39.1	479	81.9	391	105.9	—	H
OFU-04-06	Ofu	2	46.18	3.00	13.70	9.93	0.13	7.53	11.26	3.70	0.99	0.32	96.80	58.9	76.5	50	800	35.5	409	81.5	326	80.9	0.70469	H
OFU-04-06	Ofu	3	45.75	3.12	13.20	7.91	0.10	8.20	13.67	3.01	0.83	0.37	96.24	54.3	83.8	41	714	36.8	398	72.2	301	72.4	0.70443	H
OFU-04-06	Ofu	4	45.71	3.05	13.40	10.95	0.06	7.62	10.88	3.93	0.93	0.33	96.89	61.8	77.2	56	772	33.6	420	73.2	326	70.2	—	H
OFU-04-06	Ofu	5	47.03	3.01	14.37	8.75	0.12	7.66	11.77	3.70	1.21	0.19	97.92	54.7	81.4	79	661	31.6	333	63.5	393	78.9	—	H
OFU-04-06	Ofu	8	45.83	3.21	13.50	10.96	0.13	7.74	11.19	4.06	0.98	0.36	98.04	61.6	77.7	63	861	40.0	462	81.2	363	102.5	—	H
OFU-04-06	Ofu	9	44.84	3.37	13.52	12.21	0.15	6.89	10.62	4.25	1.04	0.32	97.31	64.1	77.4	77	1006	42.7	528	98.4	444	104.7	—	H
OFU-04-06	Ofu	22	38.04	4.65	10.75	12.83	0.18	9.84	17.18	1.15	0.12	0.59	95.55	70.3	80.9	18	1161	72.4	821	121.9	255	38.9	—	H
OFU-04-06	Ofu	21	45.30	4.63	14.07	10.83	0.20	6.89	9.58	4.35	1.57	0.74	98.40	60.4	78.1	67	779	34.8	417	51.7	271	51.4	—	H
OFU-04-06	Ofu	23	45.58	5.87	12.35	8.58	0.12	8.17	13.00	3.71	1.32	0.84	99.47	57.9	80.6	85	1042	48.6	551	78.9	374	38.4	—	H
OFU-04-06	Ofu	7(fir)	—	—	—	—	—	—	—	—	—	—	—	—	—	110	894	21.2	289	112.8	588	97.6	—	H
OFU-04-06	Ofu	7(sec)	—	—	—	—	—	—	—	—	—	—	—	—	—	65	809	37.5	428	74.1	365	104.7	—	H

Rb/Sr ratios by LA-ICP-MS are considered to be more accurate than those obtained by ion probe. Any discrepancy between the Rb/Sr ratios measured by the two methods is probably due to the difficulty of measuring Rb by ion probe techniques. Samples 78-1, 71-2, 71-11 and 68-3 are from the Samoan AVON3 dredging cruise, and their sample names are preceded by the prefix "AVON3."

Major element data are in wt.%, and trace elements are in ppm. Forsterite contents of the host olivines (Ol Fo) are also given. Glassy (G) or Homogenized (H).

^a See data in Table 1 for Sr-isotope data.

melt inclusion from sample 78-1 displays high Sr and Ba concentrations (2500 and 1900 ppm, respectively) that are 6 times more enriched than any whole-rock lavas examined from Malumalu. This ultra-enriched composition is significantly more enriched than observed in any Samoan basalts, and is derived from either an extremely enriched source or from very small degrees of melting.

Melt inclusions from OFU-04-06 also exhibit some unusual major and trace element compositions. One Ofu melt inclusion exhibits unusually low K₂O concentrations. Additionally, the OFU-04-06 melt inclusions exhibit a large range in SiO₂, including one sample with unusually low SiO₂ (38.0%) and high CaO (17.2%). These uncommon major element compositions may be due to the combination of unusual phases present in the OFU-04-06 melt inclusions prior to homogenization in the lab. Low glass totals in the OFU-04-06 inclusions are likely due to high volatile contents in the homogenized glasses, a hypothesis consistent with the volatile-rich phases in melt inclusions from this sample.

In addition to Rb/Sr ratios, several other major and trace element parameters correlate with ⁸⁷Sr/⁸⁶Sr in the melt inclusions. Melt inclusions from Ofu, Vailulu'u and Malumalu exhibit negative Ba anomalies that also are observed in Samoan shield-stage lavas [4] (Fig. 4). An approximation for this Ba anomaly is (Ba/Nb)_N (normalized to PUM, primitive upper mantle [30]), a ratio which correlates with ⁸⁷Sr/⁸⁶Sr in whole rocks and melt inclusions (Fig. 5). The (Ba/Nb)_N values are lowest (largest Ba-anomaly) in the basalts and melt inclusions with low ⁸⁷Sr/⁸⁶Sr, and highest in the basalts and melt inclusions with elevated ⁸⁷Sr/⁸⁶Sr ratios. It is notable that basalts and melt inclusions associated with elevated ³He/⁴He ratios, and not the high ⁸⁷Sr/⁸⁶Sr EM2 end-member basalts, have the largest Ba anomalies. The mechanism that generates this anomaly is unknown [4], and the anomaly also exists in MORB and HIMU basalts, but not in basalts with EM1 characteristics.

The negative K₂O anomaly in the Samoan melt inclusions (Fig. 4) is commonly observed in OIBs. Curiously, however, PUM-normalized K exhibits little variability regardless of the degree of enrichment of the other trace elements (with the exception of a single Ofu melt inclusion). Despite the limited variability, olivine fractionation-corrected K₂O concentrations exhibit a relationship with ⁸⁷Sr/⁸⁶Sr in the melt inclusions (Fig. 5).

Nb/Zr also correlates with ⁸⁷Sr/⁸⁶Sr in Samoan basalts and melt inclusions (Fig. 5). The lowest Nb/Zr ratios are associated with unradiogenic ⁸⁷Sr/⁸⁶Sr values. Nb/Zr ratios correlate with Pb-isotopes [4] and inversely with ³He/

Fig. 4. PUM-normalized trace element patterns of Samoan basalts and melt inclusions; melt inclusion data is from ion probe analysis, except for K and Ti, which were measured by electron probe. Vailulu'u melt inclusions are from three samples: 71-2 (grey lines), 68-3 (dashed line), 71-11 (solid black lines). Malumalu and Ofu melt inclusions are from samples 78-1 and OFU-04-06, respectively. All melt inclusions (except for one melt inclusion from 78-1 and two from OFU-04-06 that have no major element compositions, see Table 2) are corrected for olivine fractionation to be in equilibrium with mantle olivine of $F_{0.90}$ (see text for correction scheme). The grey field encloses the range of whole-rock patterns from the least evolved basalts (>6.5 wt.% MgO) from Vailulu'u, Ofu and Malumalu; whole-rock compositions have been corrected for olivine addition/fractionation. PUM values from [30].

^4He (not shown) in Samoan basalts. Nb/Zr may serve as a proxy for $^3\text{He}/^4\text{He}$ isotopes in Samoan melt inclusions; therefore, it may be important that the Nb/Zr ratios in several of the Ofu-04-06 melt inclusions exhibit values lower than the ratios observed in whole rocks.

3.3. Melting models of the EM2 source

It is important to place constraints on the trace element variability introduced by melting processes. A plot of Sr versus Ti/Zr shows that the majority of the melt inclusions form an array that extends outside of the whole-rock field to enriched Sr and low Ti/Zr values (Fig. 6). The low Ti/Zr ratios (15–88) observed in the melt inclusions extend to lower values than observed in whole-rock basalts from the eastern Samoa islands and seamounts (63–130). Such low values cannot be produced by crystal fractionation of melts before olivine entrapment, and assimilation of MORB (Ti/Zr=88) also fails to produce low Ti/Zr values [31]. A model of the Samoan EM2 source composition [4] provides a robust estimate for the mantle source sampled by the extreme EM2 basalt sample 78-1, and variable degrees of aggregated modal fractional melts of this source (Sr=20.0 ppm, Ti/Zr=101.9) in the garnet and spinel stability fields can describe much of the melt inclusion array in Fig. 6. Consistent with the model of the EM2 source as a metasomatized harzburgite [4], we adopt a harzburgite source lithology (1% spinel, 3.6% clinopyroxene [cpx], 20.6% orthopyroxene [opx] and 74.8% olivine), with mineral modes from [32] and mineral/melt partition coefficients from [33]. We assume the mineral modes of a similar bulk composition for melting in the garnet stability field (3.8% garnet, 2.7% cpx, 17.7% opx and 75.8% olivine) using the spinel to garnet conversion from [34]. The two melting models follow similar trajectories, but melting in the spinel stability field is required to generate the exceptionally high Sr and low Ti/Zr observed in the ultra-enriched Malumalu melt inclusions. Interestingly, if the EM2 source [4] has a more cpx-rich lithology than the harzburgite in our melting model, it will not produce melts with the Sr concentrations observed in the most enriched melt inclusion at reasonable degrees (>1%) of melting (Fig. 7).

Other geochemical indicators, including Y/Zr ratios, more clearly resolve the relative roles of melting in the garnet and spinel stability fields. Due to the relative compatibility of Y in residual garnet, low Y/Zr ratios are consistent with melting in the presence of garnet. A role for melting in the garnet stability field is suggested in a plot of Y/Zr against Nb/Zr in Fig. 6. This is particularly true for the Ofu melt inclusions, which trend to the lowest Y/Zr ratios

Fig. 5. Nb/Zr, K₂O and Ba/Nb_N versus $^{87}\text{Sr}/^{86}\text{Sr}$. K₂O measured by electron probe, and Nb, Zr and Ba by ion probe. (Ba/Nb)_N (normalized to PUM) is used as a proxy for the pervasive negative Ba anomaly in Samoan shield-stage basalts. The EM2 basalts and melt inclusions are associated with elevated Nb/Zr, K₂O and (Ba/Nb)_N (smaller negative Ba anomalies), and the low $^{87}\text{Sr}/^{86}\text{Sr}$ basalts exhibit lower Nb/Zr, K₂O and (Ba/Nb)_N (larger negative Ba anomalies). All melt inclusions are corrected for olivine fractionation. The grey fields enclose the range of whole-rock patterns from the least evolved basalts (>6.5 wt.% MgO) from Vailulu'u, Ofu and Malumalu (whole-rock compositions have been corrected for olivine addition/fractionation). Symbols are the same as Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ internal precision (2 σ , standard error) is approximately the size of the symbol.

observed in the melt inclusions suite and straddle the garnet melting trend at 5% melt. This is similar to the Ti/Zr versus Sr plot, where the garnet melting curve trends through the Ofu melt inclusion field at ~4% melt. Malumalu and Vailulu'u melt inclusions (and Samoan whole rocks) are offset to higher Y/Zr ratios, perhaps suggesting a larger role for melting in the spinel stability field, an observation that is consistent with the same subset of melt inclusions in the Ti/Zr versus Sr melt model.

No single melting model of the EM2 source perfectly describes the melt inclusion fields for all three volcanoes, but we find that a combination of melting and mixing satisfactorily reproduces the melt inclusion geochemical variability. The relative roles of melting and mixing of different components can be partially deconvolved in a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus 1/Sr (Fig. 8), where two-component mixing trajectories are linear and variable degrees of melting result in horizontal trajectories. The Ofu melt inclusions lie on a horizontal trend, which can be described by various degrees of melting of a single source that exhibits a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~0.7045, and the Malumalu and Vailulu'u melt inclusions form a diagonal array that suggests a role for two-component mixing.

4. Discussion

4.1. A homogeneous source for PHEM basalts

Compelling evidence that the Samoan melt inclusions sample a heterogeneous source comes from Sr-isotope analysis of the melt inclusions from Vailulu'u and Malumalu basalts. However, the uniformly unradiogenic character of the Ofu melt inclusions precludes a significant contribution from an enriched, radiogenic (EM2) component. This suggests that Samoan melts with high $^3\text{He}/^4\text{He}$ sample a homogeneous source and do not mix with melts of an enriched component. By comparison, the melt inclusions from Malumalu and Vailulu'u span a large range of Sr concentrations and isotopic compositions, indicating that both variable degrees of melting and mixing have occurred. An aggregated fractional melt trajectory for the garnet stability field is plotted (Fig. 8) for the EM2 source [4], and the Malumalu and Vailulu'u melt inclusions form a broad array that trends diagonally away from the horizontal Ofu melting trajectory toward low degree (~1%) melts of the EM2 source; the Vailulu'u and Malumalu melt inclusions can be produced by aggregated melts of an Ofu source that then mix with aggregated fractional garnet melts of the EM2 source.

Unlike the EM2 source, the trace element source composition of the high $^3\text{He}/^4\text{He}$, lower $^{87}\text{Sr}/^{86}\text{Sr}$ Ofu source component is less clear. Called PHEM [23], this

Fig. 6. Upper panel: Ti/Zr versus Sr concentration in melt inclusions and whole rocks with melting models. All melt inclusions and whole rocks are corrected for olivine fractionation to be in equilibrium with mantle olivine. Grey field is for whole-rock samples from Vailulu'u, Malumalu and Ofu. Lines with closed boxes represent aggregated fractional melting trends of the EM2 source [4] in the garnet and spinel stability fields, using partition coefficients from [33]. Harzburgite mineral modes are from [32]. All melting is non-modal. Tick marks are every 1% melting, beginning at 0% and increasing to the left. Lower panel: Y/Zr versus Nb/Zr in melt inclusions and whole rock, including melting models in the garnet and spinel stability fields. Tick marks are every 1% and the degree of melting increases to the left. Melting parameters and grey field are the same as upper panel.

component melts to form basalts and melt inclusions from Ofu. However, it is possible to bracket the source composition of this component and estimate the degree of melting captured in the Ofu melt inclusions. Although the Ofu basalts are more isotopically depleted than the EM2 basalts, an isotopically and trace element depleted DMM lherzolite source (7 ppm Sr) [35] fails to produce the high Sr concentrations observed in the Ofu melt inclusions (Fig. 7). This would suggest that the Ofu source is either more refractory or more trace element enriched, or both, than the lherzolitic [35] DMM source. The first option can be explored by invoking a more refractory, harzburgitic DMM source. However, only unreasonably low ($F < 1\%$) degrees of melting can produce the most enriched Sr concentration observed an

Ofu melt inclusion. The second scenario can be tested by invoking the trace element enriched EM2 source, and assigning it a lherzolitic lithology that is similar to DMM. At reasonable degrees of melting ($F = 1.5\%$), such a source can generate melts with sufficiently high Sr contents to match the range observed in Ofu. Finally, a harzburgitic EM2 source, which is both more refractory and trace element enriched than DMM, can generate the most enriched melt inclusions from Malumalu and Ofu between 1% and 2% melting. The harzburgitic EM2 source can serve as a probable upper limit for the trace element enrichment of the PHEM source because we consider it unlikely for the less isotopically enriched PHEM component to exhibit greater trace element enrichment than EM2. However,

Fig. 7. Sr in melt versus degree of melting (F) for various combinations of two lithologies and two trace element source abundances. Two dashed lines represent olivine fractionation-corrected Sr concentrations in the most enriched melt inclusions from Malumalu sample 78-1 (upper line) and Vailulu'u sample 71-2 (lower line). DMM trace element source and lherzolite lithology from [35], converted to equivalent garnet facies lithology using relationship from [34]. EM2 source from [4]. Harzburgite lithology from [32]. Note that only the EM2 source with a harzburgite lithology can produce the highest Sr concentration observed in the melt inclusion from sample 78-1 at $F \geq 1\%$. All melting is non-modal in the garnet stability field. Neither modal melting nor melting in the spinel stability field significantly changes our conclusions at $F \geq 1\%$.

a PHEM source with a lithology (and/or Sr concentrations) intermediate between DMM and EM2 cannot be ruled out. If PHEM has the same Sr content and lithology as the EM2 source, the Vailulu'u and Malumalu melt inclusion arrays can be explained as mixtures of $6.5 \pm 1.5\%$ melts of PHEM and $\sim 1\%$ melts of EM2. However, the degree of melting of the PHEM source that contributes to the Malumalu–Vailulu'u mixing array should be taken as a maximum.

Unlike the Ofu melt inclusions, which sample a pure PHEM source, no melt inclusions sample a pure EM2 melt (as calculated by [4], using ultra-enriched Sr-isotope compositions from Samoan xenoliths [36]). Mixing lines in Fig. 8 between a 1% EM2 melt and $6.5 \pm 1.5\%$ PHEM melts indicate that the subset of Vailulu'u and Malumalu melt inclusions with both $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration data are dominated by a PHEM component, and exhibit less than a $\sim 30\%$ contribution from the EM2 component. However, one Malumalu melt inclusion exhibits a much larger contribution from an EM2 component, as indicated by its high (~ 1865 ppm) Sr content and low (~ 17) Ti/Zr ratio (Fig. 6). The PHEM–EM2 melt mixing lines in Fig. 8 suggest that this melt inclusion contains more than a 70% contribution from the EM2 melt component. The mixing model suggests that a 70% contribution from an EM2 melt would produce an extrapolated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.712 , which is a significantly higher ratio than has been observed in a Samoan basalt, but close to the $^{87}\text{Sr}/$

^{86}Sr of cpx in metasomatized xenoliths from Savai'i in western Samoa. Unfortunately, this ultra-enriched melt inclusion was too small for isotopic analysis.

4.2. Isotopic variability in Samoan melt inclusions: MORB or FOZO?

Correlations between trace elements and Sr isotopes suggest that trace element variability in Samoan basalts and melt inclusions may reflect heterogeneity in the Samoan mantle. Rb/Sr, K_2O , $(\text{Ba}/\text{Nb})_N$ and Nb/Zr ratios correlate with Sr isotopes in Samoan lavas and melt inclusions, suggesting that these trace elements are heterogeneous in the Samoan mantle source. However, a combination of melting processes and variable source lithology may drive the observed correlations, limiting the role for source heterogeneity. For example, the relatively constant K_2O concentrations and negative (PUM-normalized) anomalies in Samoan lavas may be a result of residual phlogopite, which may cause K_2O to behave more compatibly in the Samoan source during melting. However, K_2O correlates with $^{87}\text{Sr}/^{86}\text{Sr}$ in the whole rocks and melt inclusions (Fig. 5), suggesting a role for K_2O heterogeneity in the Samoan source, and that K_2O concentrations in Samoan basalts and melt inclusions may be controlled only partially by melting processes.

Assuming that Rb/Sr variability in Samoan melts reflects source variability, the array formed by the $^{87}\text{Sr}/$

Fig. 8. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/[\text{Sr}]$ for Samoan melt inclusions and basalts. Malumalu and Vailulu'u melt inclusions form a quasi-linear array extending away from the whole-rock basalts from Malumalu, Ofu and Vailulu'u (grey field, same as Fig. 6). Ofu melt inclusions fall off this array, plotting at lower $^{87}\text{Sr}/^{86}\text{Sr}$ at a given Sr concentration. Aggregated non-modal fractional melting trends of the EM2 and PHEM sources in the garnet stability field are shown as horizontal lines (tick marks are every 1% melting, beginning at 0% and increasing to the right). Two mixing lines, both extending diagonally from a 1% EM2 melt to 5% and 8% PHEM melts, are shown (each tick represents 10% mixture, starting at 0% EM2 and increasing to the upper left). Ofu melt inclusions lie on the melting trend for PHEM, and require no mixing with an EM2 component. Malumalu and Vailulu'u melt inclusions can be described by mixing of melts from the EM2 and PHEM sources. Sr concentrations in melt inclusions and whole rocks are corrected for olivine fractionation. PHEM and EM2 source compositions plot outside of the figure as indicated, at $1/\text{Sr}$ values of ~ 0.05 (Sr concentrations of 20.0 ppm). The published source for EM2 [4] is used in this figure. As a limit, PHEM is given the trace element source abundances and lithology of EM2 in the melt model. Symbols same as in Fig. 3.

^{86}Sr and Rb/Sr data can be modeled as binary mixing between a PHEM and an EM2 component, a model originally proposed by Farley et al. [23]. Such a model is consistent with the trace element melting/mixing model proposed above, which suggests that the Ofu melt inclusions sample only a high $^3\text{He}/^4\text{He}$ PHEM mantle reservoir and the Vailulu'u and Malumalu melt inclusions result from mixing melts from both the PHEM and EM2 mantle reservoirs.

Previous work on the Pb-isotopic variability in melt inclusions [17] suggested that the unradiogenic end-member in EM2 basalts from Tahaa may be depleted (MORB or FOZO?), and thus lie at even lower $^{87}\text{Sr}/^{86}\text{Sr}$ values than observed in the high $^3\text{He}/^4\text{He}$ PHEM lavas from Ofu (Fig. 3). In fact, an extrapolation of the Samoa melt inclusion and whole-rock basalt array in Fig. 3 does indeed trend toward one of two depleted components that are significantly less radiogenic than PHEM: MORB [22] or a common high $^3\text{He}/^4\text{He}$ mantle component, called FOZO [24] (Fig. 3). The FOZO component is represented by basalts with the highest $^3\text{He}/^4\text{He}$ from Hawaii [37], Iceland [38] and Baffin Island [39]. Both MORB and FOZO lie on a similar extension of the

Samoa melt inclusion $^{87}\text{Sr}/^{86}\text{Sr}$ –Rb/Sr array, so it is difficult to distinguish which, if either, of these two components is sampled by the Samoan melt inclusions. If the depleted component is MORB, it may be entrained in melt inclusions by shallow anatexis due to preferential cooling and olivine crystallization near magma chamber and conduit walls [7,8,21]. However, the presence of FOZO (or any other high $^3\text{He}/^4\text{He}$ component) in the Samoan melt inclusions would require that the isotopic variability in melt inclusions reflect true source heterogeneity, assuming that a high $^3\text{He}/^4\text{He}$ component does not exist in the oceanic crust or lithosphere.

4.3. The case against MORB

It may be possible to look at other lines of geochemical evidence to discern whether MORB or FOZO play a role in augmenting the isotopic diversity in Samoan melt inclusions. Models suggesting that melt inclusion isotopic variability is caused only by contamination from unradiogenic oceanic crust and lithosphere at shallow levels do not explain how several Samoan melt inclusions have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than their host

bulk rock compositions (see Fig. 1). For example, Samoan whole-rock basalt sample 71-11 hosts several melt inclusions that have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (up to 0.70692) that are significantly more enriched than its host rock (0.70550). The presence of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in melt inclusions that are higher than the bulk rock require that at least some of the isotopic variability present in melt inclusions is derived from the mantle source, because the enriched component in melt inclusion 71-11a is too enriched to be found in the oceanic crust and lithosphere. Therefore, if assimilation of oceanic crust and lithosphere contributes heterogeneity to the Samoan melt inclusions, it cannot be the only means by which isotopic heterogeneity is produced in Samoan melt inclusions, and some contribution from the melt source must be involved as well.

On a different tack, the case for the less radiogenic melt inclusions sampling the depleted oceanic crust and lithosphere by assimilation is limited severely by the observation that, within analytical uncertainty, not a single melt inclusion has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that is lower than the least radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}=0.7044$) whole-rock basalt measured in the Samoan islands (Fig. 1). The Samoan melt inclusions trace out a range of Sr-isotope variability that is confined to the region of Sr-isotope space defined by the Samoan whole-rock data (Fig. 3). On an island-by-island basis, the interpretation is more complicated, as melt inclusions from two Vailulu'u whole-rocks sample a component more depleted than found in whole rocks measured from the seamount. However, the least radiogenic component found in Vailulu'u melt inclusions is also found in lavas from nearby Samoan islands (e.g., Ta'u and Ofu), exhibits elevated $^3\text{He}/^4\text{He}$ ratios, and is thus known to exist in the Samoan plume. Many of the downstream Samoan seamounts also are dominated by $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.7044 and 0.7049 [3]. It seems unnecessary, therefore, to invoke contamination from the oceanic crust and lithosphere to explain the presence of the less radiogenic component when it already exists inside the plume! Although the argument can be made that an insufficient number of melt inclusions have been analyzed to detect a component more depleted than what is found in whole rocks, the number of melt inclusions analyzed for Sr isotopes ($n=41$) is already significant, and is equal to $\sim 30\%$ of the number of published $^{87}\text{Sr}/^{86}\text{Sr}$ whole-rock analyses from the Samoan hotspot.

The high $^3\text{He}/^4\text{He}$, unradiogenic Sr component in Samoan basalts (PHEM) is unique in that it exhibits $^{87}\text{Sr}/^{86}\text{Sr}$ ratios more enriched than in the high $^3\text{He}/^4\text{He}$ Hawaii, Iceland or Baffin Island basalts,

suggesting that the high $^3\text{He}/^4\text{He}$ reservoir in the mantle is at least mildly heterogeneous in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The same line of reasoning that precludes the presence of entrained melts from oceanic lithosphere in the Samoan melt inclusions also minimizes the possibility that a traditional, depleted FOZO-like component ($^{87}\text{Sr}/^{86}\text{Sr}=0.7030$ [24]) serves as the unradiogenic Sr component: If melt inclusion diversity were a result of entrainment of a component (MORB or FOZO) more depleted than found in Samoan basalts, then the melt inclusions would extend to $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than found in whole rocks (0.7044). However, the high $^3\text{He}/^4\text{He}$ Samoan sample OFU-04-06 defines the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ portion of the Samoan whole-rock mixing array (see Fig. 3) and the melt inclusions are identical to the whole rock, suggesting that the least radiogenic Sr composition sampled by the Ofu basalts is the same component found in the melt inclusions. Therefore, we maintain that the unradiogenic Sr component in Samoan melt inclusions is more enriched than MORB or FOZO, and is likely the same PHEM component sampled by the high $^3\text{He}/^4\text{He}$ Samoan basalts, suggesting that a two-component EM2–PHEM mixing model may be the most appropriate for melt inclusions originating in the enriched Samoan mantle. Scatter around such a mixing model (Fig. 8) may be due to minor contributions from other components [4] that may exist in the Samoan mantle.

4.4. Implications for source heterogeneity (or lack thereof)

The results for Sr-isotope measurements in Samoan melt inclusions support an argument for an origin of the isotopic variability in the melt source, not contamination by oceanic crust and lithosphere. We assume that the isotopic variability (or lack thereof) in Samoan melt inclusions is not a product of variable degrees of homogenization in magma conduits and chambers before olivine entrapment, but rather that the isotopic variability in melt inclusions reflects the heterogeneity of the melt source: When the melt source is heterogeneous, melt inclusions capture the range of heterogeneity while the isotopic composition of the bulk rock lava represents an average of the heterogeneity sampled in the melt. By extension, we infer that the high $^3\text{He}/^4\text{He}$ whole-rock sample OFU-04-06 tends to sample a more homogeneous source, as the melt inclusions are nearly isotopically homogeneous and identical to the bulk rock. Perhaps, then, only melting of a pure PHEM source allows the high $^3\text{He}/^4\text{He}$ composition to persist in the

Ofu whole-rock lavas. Vailulu'u and Malumalu melt inclusions are more isotopically heterogeneous, and thus are inferred to sample a heterogeneous source that captures much of the mixing spectrum between the EM2 and PHEM components. The contribution of an EM2 component may explain the diminished $^3\text{He}/^4\text{He}$ composition in the lavas from these two volcanoes. Although $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of the melt inclusions from high $^3\text{He}/^4\text{He}$ basalts from other localities are not yet available, perhaps the high $^3\text{He}/^4\text{He}$ mantle that these basalts sample is homogeneous and devoid of enriched domains. This hypothesis is consistent with the melting–mixing model above (see Fig. 8), which suggests that the isotopically homogeneous melt inclusions from the high $^3\text{He}/^4\text{He}$ basalt from Ofu exhibit no evidence of mixing with an EM2 component.

It is notable that while near-pure PHEM melts are observed in Samoan melt inclusions, pure EM2 melts ($^{87}\text{Sr}/^{86}\text{Sr}=0.7128$ [4,36]) were not unequivocally detected in this study (i.e., by measurement of Sr isotopes). Several melt inclusions with ultra-enriched trace element patterns were observed, but most of the melt inclusions are composed of <30% EM2 component. Perhaps this indicates that, compared to the PHEM component, the EM2 component in the Samoan plume is rare. Alternatively, the EM2 component may not be rare in the Samoan plume, but is more refractory and produces less melt than the PHEM component. In this way, perhaps, EM2 melts are less frequently sampled by melt inclusions. Future work on melt inclusions will help resolve the relative contributions of the enriched and high $^3\text{He}/^4\text{He}$ sources to OIB lavas.

5. Summary

The following conclusions can be drawn from this study:

- 1.) The Sr-isotopic diversity in melt inclusions from Samoan basalts does not extend significantly above or below the range defined by whole rocks from the Samoan hotspot.
- 2.) A few melt inclusions exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ ratios significantly higher than their host whole rock. This is taken as evidence that assimilation of MORB lithosphere cannot be the only mechanism that contributes isotopic diversity to the melt inclusions.
- 3.) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the high $^3\text{He}/^4\text{He}$ basalt is essentially indistinguishable from the Sr-isotope ratios (0.7044) measured in its melt inclusions, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in melt inclusions from

other Samoan basalts do not exhibit ratios lower than 0.7044. This observation is consistent with the hypothesis that a high $^3\text{He}/^4\text{He}$ component, not MORB, is the unradiogenic Sr endmember in Samoan melt inclusions.

- 4.) Melt inclusions from a high $^3\text{He}/^4\text{He}$ Samoan basalt (with less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$) are isotopically more homogeneous than the melt inclusions from basalts with higher $^{87}\text{Sr}/^{86}\text{Sr}$ (more contribution from an EM2 component). This may indicate that the Samoan high $^3\text{He}/^4\text{He}$ basalts sample a source that is more isotopically homogeneous than the source that produces basalts with an EM2 component.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2006.02.040](https://doi.org/10.1016/j.epsl.2006.02.040).

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Supplementary Data (Jackson and Hart, 2006)

Sr isotopes by laser ablation PIMMS: Application to Samoan basaltic melt inclusions

1. Introduction

We have thoroughly, but not exhaustively, investigated the parameters necessary for precise and accurate Sr isotope analysis of basalt glasses by *in situ* laser ablation PIMMS. The lower limit of external precision attained under optimal conditions for the SRM987 Sr solution standard is ± 5 ppm (>25 volt data, 1σ), and is fairly comparable to good TIMS data. For lower intensity data (~ 1 -5 volts), more comparable to our typical laser ablation work, the external solution precision is in the 20-80 ppm range. We have instituted a new method for Kr correction that is based on ^{84}Kr , and a method for Rb correction that utilizes basalt glass standards with significant Rb/Sr ratios and known $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Even in basalts requiring very large Rb corrections, we are able to obtain $^{87}\text{Sr}/^{86}\text{Sr}$ data with ~ 320 ppm external precision and 45 ppm internal (in-run) precision (2σ standard deviation) on a suite of Samoan glasses with known $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

We developed an analytical protocol for the measurement of Sr isotope ratios by Laser Ablation PIMMS for analysis of melt inclusions in olivine phenocrysts in OIBs (ocean island basalts) from the EM2 (Samoa), EM1 (Pitcairn, Christmas) and HIMU (Mangaia) mantle end-members. We acknowledge a significant existing body of work on Sr isotope measurement by laser ablation PIMMS, but will not attempt to review this literature or compare it with the protocols we have installed on the NEPTUNE at the Woods Hole Oceanographic Institution [1-6].

2. Techniques

2.1. Instrumental Description

The data discussed here were obtained with a ThermoFinnigan NEPTUNE multicollector ICP-MS, coupled to a NEW Wave UP213 laser, housed in the Plasma Facility at the Woods Hole Oceanographic Institution. This NEPTUNE was installed in June 2003, replacing an earlier one that had been installed in February 2002, but damaged by the October 2002 fire in the Ion Probe Facility.

The typical operating parameters of the NEPTUNE and laser are given in Table 1 (note that our techniques have evolved over time, and some earlier data may have utilized somewhat different protocols). Currently, we aspirate clean dilute (5%) nitric acid during the lasering, to allow solution standards to be interspersed with laser runs when needed. The arrangement of Faraday cups, and the relevant isotopic masses that are collected, is given in Table 2. Amplifiers are not rotated, as this rotates the Faraday (off-mass) baselines as well. The mean raw Faraday intensities are transferred after all analyses to an offline data reduction program (TweaKr), for the various corrections.

We have opted to run the laser at 100% power and in apertured mode. While we could likely emplace higher energy density in focused mode, this tends to throw off larger chips and particles, particularly from basalt glass samples. We have not made any

investigations of the effects of particle size on mass bias, interferences, and the like. Each analysis takes about 6.5 minutes of lasering, including offpeak baseline integration for 64 seconds and 20 cycles of 16 second integrations (and, more recently, 40 cycles of 8 second integrations). With a 120 μm spot and 200 μm long raster lines (see Table 1), spaced at only 20 μm , the final ablation pit is pyramidal, approximately 300 x 300 μm , and 250 μm deep. Typically, there will be little or no drift of ^{88}Sr intensity with time during ablation of homogeneous basalt glass standards, and the 1σ standard deviation of intensity will fall in the range 5-15%.

2.2. Standards and Canonical Isotope Abundances

For Rb and Sr isotope standards, we have used NIST standards SRM984 and SRM987. The certified values for these standards are listed in Table 3, along with the quoted uncertainties. Note that $^{85}\text{Rb}/^{87}\text{Rb}$ in SRM 984 is only certified to ± 423 ppm, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ to only 380 ppm, and $^{84}\text{Sr}/^{86}\text{Sr}$ to 0.25%. It is likely that the uncertainties in $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ are not independent, but possibly related by some fractionation-dependence. Note also that the certified $^{86}\text{Sr}/^{88}\text{Sr}$ value is 0.1193515, not the consent value of 0.119400 adopted by the community. We have corrected all of the SRM 987 certificate ratios, by exponential law, to be consistent with the consent value of 0.1194. Ironically, this results in a “corrected” $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7101938, which is lower than (but marginally within errors of) the value commonly adopted by the community of 0.710240 (which is itself different from the “uncorrected” certificate value of 0.710339). It will obviously be important for published papers to be very clear as to their usage of SRM 987 standard values. For Kr, we adopt the isotope abundances compiled by Ozima and Podosek (2001).

2.3. Backgrounds and Baselines

The NEPTUNE software allows a choice of baseline protocols. PIMMS users frequently use “on-peak” baselines, after sample wash-out [1, 3-6]; the NEPTUNE also allows a “defocused” beam baseline. Our experience is that baselines can be measurably ($> 50 \mu\text{V}$) elevated across a broad mass region during actual sample analysis and thus different from those measured in a defocused “beam-off” state, or while running gas or acid blanks. We have chosen therefore to adopt the common TIMS procedure of running “off-peak” baselines while sample analysis is underway; while this consumes part of the sample, we see no other way to ensure reliability of baselines. (However, baselines on Samoan basalt standards and basaltic melt inclusions do not change significantly over the course of an analytical session, and we have adopted the practice of applying baselines from larger melt inclusions—run during the same analytical session—to exceptionally small melt inclusions to save precious material). We have chosen to measure baselines at a position 0.70 amu below each mass; this avoids potential baseline interferences from doubly-charged half-mass REE peaks, allows the Faradays that are intentionally set at 83.5 and 85.5 in order to monitor these REE^{+2} to offset 0.2 amu below mass 83 and 85 during baseline measurement, and places the ^{88}Sr cup near the minimum in the valley between ^{87}Sr and ^{88}Sr during baseline measurement. With this protocol, the only baseline that will have a significant tail contribution is ^{87}Sr . With the measured abundance sensitivity at Sr mass of ~ 1 ppm at 1 amu, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio will be elevated by < 12

ppm; this error is small compared to our external precision goal, and will also be normalized, to first order, through the use of the SRM987 standard.

2.4. Kr Correction

As is well known, there are interferences at ^{84}Sr and ^{86}Sr masses from Kr. Conventionally, the Kr is considered to be a contaminant in the Ar plasma gas, and is corrected by measurement of ^{82}Kr or ^{83}Kr . Over the past two years of measurement here, our ^{83}Kr intensity has varied from ~ 0.05 mV to ~ 20 mV, and we believe that not all of it comes in with the argon, nor is all of mass 83 actually Kr. Typically, after changing samples in the laser cell, there is a component of air Kr which slowly decreases as the chamber is purged. Ultimately, the Kr intensity with He flowing from the cell into the machine will decrease substantially below that in aspirated solutions (because the He has less Kr than the argon). It appears to us that there is a component of atmospheric Kr dissolved in aspirated solutions and this contributes to the Kr background. This could be possibly moderated by hermetically isolating the solutions from the atmosphere. Air entrainment by the plasma at the torch is also probable, but has proven difficult to constrain.

We have typically measured both ^{82}Kr and ^{83}Kr during all Sr analyses. Deviations of up to a factor of two from the canonical $^{83}\text{Kr}/^{82}\text{Kr}$ ratio of ~ 1 are very common in laser runs, with values most often above one, but also frequently below one (Fig. 1). Even solution runs on the 987 standard will frequently show 10-20% deviations from a ratio of 1, typically with the ratios being too low (interferences on mass 82). Clearly there exist isobaric interferences that seriously hamper efforts to use either of these masses to correct for Kr. We have adopted an alternative scheme which basically uses the most abundant Kr isotope at mass 84 ($\sim 57\%$) to make the Kr correction on mass 86. This mass has a Sr “interference” on it, but for ^{88}Sr intensities in the 1-2 volt range, the Kr makes up 35-75% of the mass 84 peak (i.e. the Kr and Sr are approximately equal in intensity). By “subtracting” Kr until the $^{84}\text{Sr}/^{88}\text{Sr}$ ratio equals the canonical value of 0.00675476 (while iterating the mass-bias correction), this allows a robust correction to be made on mass 86 (there is a large error demagnification in this process, due to the fact that $^{86}\text{Kr}/^{84}\text{Kr}$ is ~ 0.30 , while the $^{86}\text{Sr}/^{84}\text{Sr}$ ratio is ~ 17.7). Obviously, this technique relies on the absence of any other significant isobaric interferences at mass 84; in any event, these are likely to be less fatal than those at mass 83, because of the $^{84}\text{Kr}/^{83}\text{Kr}$ ratio of ~ 5 . One indication that this calculation method is helpful is the observation that the external precision of samples and standards run at low-intensity (1-2 volts on mass 88) is typically improved by 30-50%, compared to the same data corrected with ^{83}Kr . Further discussion of isobaric interference issues may be found in section II F, below.

We are able to correct for Kr interferences so that elevated Kr/Sr ratios do not noticeably diminish the precision or accuracy of glass analysis while using our protocol, provided that the ^{88}Sr intensity is > 1 V and $^{82}\text{Kr}/^{88}\text{Sr}$ is < 0.004 (Table 4). At exceptionally high Kr/Sr ratios, there may be a tendency for measurement precision to degrade. Therefore, analyses of unknowns that exhibit high Kr/Sr ratios ($^{82}\text{Kr}/^{88}\text{Sr} > 0.004$) are discarded.

Uncertainty in the isotopic ratios of Kr used in our correction scheme does not significantly contribute to diminishing the accuracy of $^{87}\text{Sr}/^{86}\text{Sr}$ analyses by laser ablation. At elevated Kr/Sr ($^{82}\text{Kr}/^{88}\text{Sr} = 0.004$) —where such uncertainties will play the

largest role in affecting the final Kr-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio—a 1% uncertainty in any or all of the Kr-isotope ratios will change the final corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio by <15 ppm. Additionally, allowing the Kr-isotope ratios to fractionate by up to 2% (before or during entry into the plasma) changes the $^{87}\text{Sr}/^{86}\text{Sr}$ by <15 ppm.

2.5. Rb Correction

The analysis of basaltic melt inclusions typically involves samples in which 20-50% of intensity on mass 87 is due to Rb, and large Rb corrections are required. Our goal was to devise a protocol where the Rb-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are accurate to within a few hundred ppm. We adopted the strategy of using natural basalt glasses (Table 5) with precisely known $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (obtained by TIMS) to bracket the basalt glass unknowns; for each “standard” glass, the $^{85}\text{Rb}/^{87}\text{Rb}$ ratio required to give the TIMS $^{87}\text{Sr}/^{86}\text{Sr}$ is calculated, and these bracketing $^{85}\text{Rb}/^{87}\text{Rb}$ ratios are then used for the Rb corrections in the unknown glasses. This method depends only on the Rb mass bias being relatively invariant on short time scales (20 minutes), and not being a function of the particular major element composition of the various glasses analyzed.

To assess these issues, we performed laser ablation analyses of a suite of 14 Samoan basalt glasses of known $^{87}\text{Sr}/^{86}\text{Sr}$, with significant variability in major and trace element composition. The results of nine one-day analysis campaigns are shown in Fig. 2; interspersed with these laser ablation analyses during the first two days were a series of runs on mixed 984-987 Rb-Sr solutions. While the total variability of the “Required $^{85}\text{Rb}/^{87}\text{Rb}$ ” (basically the variability of the Rb mass bias factor) is substantial (2317 ppm, excluding the 987-984 Rb-Sr solution runs), the variation with time is relatively smooth, such that the bracketing technique will be fairly effective (note that the error on ^{87}Sr due to the Rb effect is de-magnified by a factor of ~2.59 due to the $^{85}\text{Rb}/^{87}\text{Rb}$ ratio).

Several things may be noted. First, the “empirically” determined Rb ratio in lasered basalts has an average value of 2.58745, which is some 2100 ppm lower than the canonical value certified for the SRM984 Rb standard (the stated uncertainty in SRM984 is ± 770 ppm). Whether this reflects the existence of natural isotope variations in Rb, or simply an underestimate of the SRM certified value is unclear. If the former, then it will perhaps be important to use basalt glass standards that are petrogenetically related the unknowns. Secondly, there is a clear tendency for the Rb-Sr solution runs to lie at the high side of the data series, averaging 2.5900 (1200 ppm lower than the canonical value for the SRM984 Rb standard). This would suggest a slight difference in Rb mass bias for solution runs versus laser ablation runs (and this would not be surprising, given the much larger plasma loading from the laser runs).

To assess the overall accuracy of this correction scheme, we have “corrected” each run in two ways: first, using the contiguous bracketing runs, and secondly, correcting each run with the global average “required” $^{85}\text{Rb}/^{87}\text{Rb}$ ratio of 2.58745. The resulting “corrected” $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are then compared with the known values (note that the internal precision of the solution runs averaged about ± 10 ppm (1σ , standard error); that of the laser runs averaged ± 17 ppm, with 88 intensities ranging from 1-12 volts). For the “bracketing technique”, the mean deviation (measured against TIMS) for the nine analytical sessions is 127 ppm (320 ppm, 2σ standard deviation, assuming a Gaussian distribution); for the “global average” technique, the mean deviation is 155 ppm (Fig. 3). We adopt the first scheme to correct unknowns and when discussing the accuracy of

standard glass (and melt inclusion) runs; this technique has the advantage of capturing the downward drift of the $^{85}\text{Rb}/^{87}\text{Rb}$ required values over time (see Fig. 2). While obviously not as precise as TIMS analyses, this level of reproducibility is excellent for an *in situ* technique, and will allow us to embark on a realistic program of melt-inclusion analysis.

Due to the uncertainty of the $^{85}\text{Rb}/^{87}\text{Rb}$ required value, there will be an error magnification on the corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of basaltic unknowns as Rb/Sr increases. In order to model this effect, we selected several glass standard runs with different Rb/Sr ratios and similar, low Kr/Sr ratios, and varied the $^{85}\text{Rb}/^{87}\text{Rb}$ ratio by 2 standard deviations about the mean global value of 2.58745 (± 0.00278 , 2σ standard deviation). The propagated error increases linearly to 630 ppm when Rb/Sr is 0.14, and the accuracy appears to scale with the Rb/Sr such that the uncertainty in $^{85}\text{Rb}/^{87}\text{Rb}$ magnifies the error on the final $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 4). However, the “bracketing method” for the Rb correction reduces the uncertainty in the $^{85}\text{Rb}/^{87}\text{Rb}$ required value by $\sim 20\%$, so that the propagated error from the reduced uncertainty translates to an improvement in the accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ (i.e., to 505 ppm when Rb/Sr is 0.14). The internal precision for $^{87}\text{Sr}/^{86}\text{Sr}$ measurements on lasered glasses is generally an order of magnitude better than the accuracy (this is also true for the Rb/Sr measurements), and does not appear to worsen with increasing Rb/Sr ratios. However, the internal precision of the $^{87}\text{Sr}/^{86}\text{Sr}$, but not the accuracy, does vary with Sr intensities (Fig. 5), and, to a lesser extent, the number and length (8 or 16 second integrations) of cycles of analysis. The precision on the melt inclusion analyses also varies as a function of Sr intensity and the number and length of cycles. However, because the accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ of Samoan glasses is not related to Sr intensity over the range of 1-12 Volts on mass 88 (Table 4), somewhat lower Sr intensities during the melt inclusion runs (1-6.5 Volts) should not affect the overall accuracy of $^{87}\text{Sr}/^{86}\text{Sr}$.

2.6. Other Interferences

We have directly measured possible isobaric mass interferences resulting from Ca dimers and argides, FeO_2 , doubly-charged Er and Yb and KrH. The Ca dimers and argides invoke errors of less than <10 ppm, for Ca/Sr ratios typical of alkali basalts; there is no straightforward way to monitor or correct for these. Similarly, in a typical basalt laser run (with 500 ppm Sr), the total propagated error in $^{87}\text{Sr}/^{86}\text{Sr}$ from FeO_2 will then be less than 40 ppm (and could be nil). Additionally, the REE^{++} invoke errors of <30 ppm for typical Sr/REE ratios in alkali basalts; these can in principal be corrected for by monitoring the 83.5 and 85.5 half-mass peaks due to $^{167}\text{Er}^{++}$ and $^{171}\text{Yb}^{++}$. Finally, there seems to be some evidence for the formation of KrH in the plasma, with Kr/KrH exhibiting ratios from 35-70. Kr hydrides create isobaric interferences on masses 83, 84, 85 and 87, and they may play an important role when Kr/Sr ratios are elevated. In practice, however, it appears that there are frequently other unexplained interferences at these masses, as well as at the Kr and Rb masses, so that correction for these isobaric interferences is not always successful. These problems not only limit the attainable precision of laser ablation analyses, but can limit the precision of straightforward Sr solution analyses as well, even of the SRM987 standard. A continuing investigation of these issues (and a fuller discussion of interferences from Ca dimers, argides, FeO_2 , KrH and doubly charged Er and Yb) is underway (Hart *et al.*, in prep).

2.7. Measurement of Rb/Sr by LA-ICP-MS

Masses 85 and 88 represent pure Rb and Sr, respectively, so that fairly precise measurement of Rb/Sr ratios can be generated. After correcting for mass fractionation during each run, Rb/Sr ratios on Samoan basalt glasses measured by laser ablation are accurate to 7% (1 mean deviation, compared to ratios obtained by XRF/ICP techniques on the same glasses), and precise (0.67%, 1 mean deviation) during multiple runs on a suite of Samoan glasses (Fig. 6). We note that this technique does not appear to work when running a “dry” plasma; Rb and Sr are strongly fractionated from each other, so that the measured Rb/Sr ratios are up to 80% higher than in the standard glass (see last 4 analyses in Table 4).

2.8. Replicability

We have not yet made a comprehensive study of reproducibility of sample analyses. We have done an analysis of a group of 50 runs on the SRM987 standard, spread over a 17 month time period, using solutions varying in concentration from 10 ppb to 600 ppb. All errors discussed here will be given at the 1σ level. Considering first the 200 and 600 ppb solutions, the average internal precision for these was 7 ppm (for ^{88}Sr intensities varying from 8-28 volts). The average external precision, calculated from the variations within a single day’s analysis session, was 12 ppm (and the number of standards run during each of these sessions varied from 2-6). While the overall ratio of external to internal precision was ~ 1.8 , there was not a significant correlation between external and internal precision on a session-to-session basis (i.e. the internal precision on individual runs is not a good guide to the expected external precision). For the daily means of 11 sessions over the 17 month time period, the average $^{87}\text{Sr}/^{86}\text{Sr}$ was 0.710255, with a 1σ standard deviation of a single analysis of 15 ppm. We should note that this time period involved a number of different baseline protocols and cup configurations, so the statistics may not be representative of our current procedures. There is one obvious conclusion, however, and that is that the precision on a daily basis is similar to the long-term precision; in other words, the variability in standard runs has almost as much “daily” scatter as it does “yearly” scatter.

Within this data set, there is a fair correlation between Sr intensity and the precision of the data; external precision for a given session is ± 5 ppm for >25 volt data, ± 7 -20 ppm for 9-15 volt data and ± 50 -80 ppm for 0.3-1 volt data. Overall, the 1σ external precision in ppm, as a function of ^{88}Sr intensity in volts, may be empirically expressed as: $\sim [80/(\text{volts})^{0.8}]$.

3. Summary

The Finnigan NEPTUNE multi-collector ICP-MS has proven to be an excellent instrument for developing robust Sr isotope analysis protocols. Among its advantages are the stability of the Faraday-amplifier system, the ability to run with intensities up to 50 volts, and the stability of the mass bias for Sr and Rb. While the external precision of solution analyses are not yet comparable to the best TIMS techniques, the *in situ* laser ablation technique appears to be a reliable and very promising tool for the study of small scale-length isotopic heterogeneities, even in samples with a significant Rb component.

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Figure Captions

Fig. 1. Variation of intensity ratio of mass 82 to mass 83 over time. Series of Samoan basalt glasses analyzed by laser ablation (colored symbols) and mixed Sr-Rb standard solutions (SRM987-SRM984, black diamonds). The certificate value for $^{82}\text{Kr}/^{83}\text{Kr}$ is 1.004. We observe no relationship between mass 82/mass 83 and the precision or accuracy of $^{87}\text{Sr}/^{86}\text{Sr}$ measurement by LA-MC-ICPMS.

Fig. 2. $^{85}\text{Rb}/^{87}\text{Rb}$ ratio required to give correct $^{87}\text{Sr}/^{86}\text{Sr}$ of a series of Samoan basalt glasses (analyzed by TIMS, open diamonds) and mixed Sr-Rb standard solutions (SRM987-SRM984, filled diamonds). The certificate value for $^{85}\text{Rb}/^{87}\text{Rb}$ in SRM984 is 2.593 ± 0.002 ; all of the “calculated” Rb ratios are lower than the certificate value, and outside quoted error limits. Runs using a dry plasma not shown.

Fig. 3. Reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ for 12 Samoan basalt glass standards (with known $^{87}\text{Sr}/^{86}\text{Sr}$ by TIMS) by LA-MC-ICPMS. Two data trends represent reproducibility (external precision) using the “global average” and the “bracketing” correction schemes for the isobaric interference of Rb on mass 87. The bracketing method gives better overall external precision, and is adopted as the correction scheme in the manuscript. Mixed NBS987 and NBS984 solution runs not included in the figure. The downward drift of $^{85}\text{Rb}/^{87}\text{Rb}$ (see Fig. 2) is noted in the downward drift of error using the “global average” Rb correction scheme. Error bars on symbols are internal (in-run) precision (2 mean deviations). Dashed lines mark external precision of ± 320 ppm (2σ , standard deviation). Larger scatter in later runs is due to higher Rb/Sr ratios of the glass standards analyzed. Better external precision in early runs is due to smaller variation in $^{85}\text{Rb}/^{87}\text{Rb}$ over time. The glass standard runs at the beginning and the end of each analytical session are not correctible using the bracketing technique and are not plotted. However, all glass standards are correctible using the “global average” Rb correction scheme, so more data points are plotted for this latter correction scheme.

Fig. 4. Rb/Sr vs. propagated error on $^{87}\text{Sr}/^{86}\text{Sr}$ measurement due to uncertainty of the $^{85}\text{Rb}/^{87}\text{Rb}$ required value. The average $^{85}\text{Rb}/^{87}\text{Rb}$ required values (used for correcting the ^{87}Rb isobaric interference on ^{87}Sr) during all laser runs on Samoan glass standards is $2.58745 (\pm 0.00278, 2\sigma)$, and this uncertainty generates larger errors on the final $^{87}\text{Sr}/^{86}\text{Sr}$ at higher Rb/Sr ratios. The upper model line shows the error (2σ , standard deviation) on final $^{87}\text{Sr}/^{86}\text{Sr}$ ratio when using the “global average” technique for the Rb correction (see text for description). Symbols on line represent error propagation on (from the uncertainty on the $^{85}\text{Rb}/^{87}\text{Rb}$) using actual basalt analyses by laser ablation. Alternatively, error using the “bracketing” method for the Rb correction is 20% lower, and is described by the lower line. The Rb correction contributes the vast majority of the error on the final $^{87}\text{Sr}/^{86}\text{Sr}$ in our protocol for measuring basal glasses by LA-MC-ICPMS. Therefore, we consider the lower model curve to be a good approximation of the reproducibility of our method.

Fig. 5. Relationship between intensity on mass 88 and internal precision during laser ablation analysis of Samoan glass standards. Various Neptune and laser operating conditions and variations in basalt and plasma chemistry, including Rb/Sr and Kr/Sr, show little or no relationship with measurement precision. The curve models the relationship between intensity and internal precision (1 mean deviation), and is described by the following relationship: $\text{Precision} = 45 * (\sqrt{\text{Intensity}}) / \text{Intensity}$.

Fig. 6. Samoan glass Rb/Sr measured by LA-MC-ICPMS Neptune plotted against Rb/Sr measured by standard techniques (XRF or ICP) on powders of the same glasses. Error bars (2σ standard deviation from the mean of measured values) are shown on samples with at least 9 laser analyses. All other glasses had one or two analyses. One-to-one line is solid, and weighted least squares regression (including equation) is dashed.

Table 1. Typical NEPTUNE and Laser Operating Parameters

RF Power	1200 W
Argon cooling gas, flow rate	15L/min
Ar auxiliary gas, flow rate	0.8 L/min
He sample gas, flow rate	0.5 L/min
Interface cones	X-cones
Mass analyzer pressure	5×10^{-9} mbar
Resolution mode	Low (400)
Abundance sensitivity	~ 1 ppm at -1 amu, mass 88 (RPQ off)
Detection system	Faraday cups (9)
Signal analysis set-up	8 sec or 16 sec integration/cycle, 40 or 20 cycles
Background-baseline protocol	1 min integration pre-analysis, -0.7 amu all Faradays
Nebuliser and uptake rate	Elemental Scientific, Inc., PFA 20-50 microliters per minute
Spray chamber	Elemental Scientific, Inc., Stable Introduction System (SIS)
Sensitivity, solution Sr	75 V ^{88}Sr per ppm Sr in 5% HNO_3
Sensitivity, laser Sr	~ 1 volt ^{88}Sr per 100 ppm Sr in basalt at 1 mj
Laser type	New Wave UP213, quad Nd YAG 213 nm
Carrier gas	Helium
Beam optics	Apertured mode
Spot size	120 μm (60 μm or less in high-Sr carbonates)
Raster pattern	200 x 200 μm , 20 μm line spacing, 4 $\mu\text{m}/\text{sec}$
Pulse rate	20 Hz
Power setting	100% (lower for high-Sr carbonates)
Power delivered	~ 1.0-1.3 mj
Pre-ablation	same raster and spot size, 5 Hz, 45% power, 30 $\mu\text{m}/\text{sec}$

**Table 2. Faraday Cup Configuration
Laser Ablation Sr Isotope Analysis**

<u>Cup</u>	<u>Mass</u>
H4	88
H3	87
H2	86
H1	85
C	84
L1	83
L2	82.5
L3	82
L4	81.5

Centered for Sr amu; C ~ 83.913

Table 3. Adopted Isotopic Abundances.

<u>Krypton</u>	<u>Isotopic Abundance</u>
78	0.003469
80	0.02257
82	0.11523
83	0.11477
84	0.56998
86	0.17398

From Ozima and Podosek, 2001

<u>Strontium SRM987</u>	<u>Isotopic Abundance**</u>	<u>Isotopic Abundance*</u>
84	0.005578	0.005574
86	0.098600	0.098566
87	0.070029	0.070015
88	0.825793	0.825845

	<u>Isotopic Ratios**</u>	<u>Isotopic Ratios*</u>		
84/86	0.056573	0.056549	±2529	ppm
87/86	0.710194	0.710339	±367	ppm
88/86	8.375209	8.37861	±388	ppm
84/88	0.006755	0.006749	±2529	ppm
86/88	0.119400	0.119352	±388	ppm

*NIST Certificate Values for SRM987 with quoted uncertainties.

**Renormalized to 0.1194 using exponential law; this value has been used by community consensus for decades. The corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ value adopted by most of the community is 0.71024.

<u>Rubidium SRM984</u>	
85	0.72168
87	0.27832
85/87*	2.593 ±771 ppm

*NIST Certificate Values for SRM984, with quoted uncertainties.

Table 4. Corrected and normalized $^{87}\text{Sr}/^{86}\text{Sr}$ glass standard data, including Rb/Sr ratios and raw exported Neptune data (in Volts) on masses 82 to 88

Date	Glass	Mass 82	Mass 83	Mass 84	Mass 85	Mass 86	Mass 87	Mass 88	$^{85}\text{Rb}/^{87}\text{Rb}$	Mass	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Rb/Sr	Rb/Sr	Rb/Sr	Rb/Sr	mass	# of
	Name ^a	Meas'd	Meas'd	Meas'd	Meas'd	Meas'd	Meas'd	Meas'd	Required ^b	Bias ^k	Laser ^c	Laser ^d	Laser ^m	I. Prec. ^e	E. Prec. ^f	E. Prec. ^l	TIMS ^g	Laser ^d	I. Prec. ^e	E. Prec. ^f	XRF ^g	82/88 ^h	Cycles ⁱ
01/26/04	75-10	0.0019	0.0015	0.070160	0.383076	1.161550	0.981164	9.99332	2.58799	1.45	0.70451	0.70450	--	10	41	--	0.704533	0.041	1.18	8.4	0.045	0.00019	20
01/26/04	75-10	0.0019	0.0015	0.068130	0.410905	1.130253	0.970173	9.72817	2.58762	1.47	0.70452	0.70452	0.70454	11	19	12	0.704533	0.045	0.42	0.9	0.045	0.00020	20
01/26/04	75-10	0.0019	0.0015	0.056972	0.316560	0.928578	0.788522	7.99055	2.58761	1.48	0.70452	0.70452	0.70456	10	16	39	0.704533	0.042	0.97	5.4	0.045	0.00023	20
01/26/04	75-10	0.0018	0.0014	0.038589	0.210680	0.591571	0.505435	5.08531	2.58867	1.49	0.70447	0.70446	0.70450	11	97	41	0.704533	0.044	1.00	1.1	0.045	0.00035	20
01/26/04	75-10	0.0019	0.0015	0.059566	0.310559	0.978671	0.821938	8.42300	2.58865	1.48	0.70448	0.70447	0.70456	9	85	34	0.704533	0.039	3.32	12.0	0.045	0.00022	20
01/26/04	76-13	0.0017	0.0014	0.055907	0.544459	0.915110	0.871425	7.87805	2.58963	1.50	0.70620	0.70619	0.70633	13	285	89	0.706395	0.074	0.30	4.5	0.077	0.00022	20
01/26/04	76-8	0.0017	0.0014	0.054455	0.526363	0.889211	0.845639	7.65417	2.58922	1.49	0.70621	0.70621	0.70639	11	231	22	0.706374	0.073	0.16	9.8	0.081	0.00023	20
01/26/04	63-13	0.0017	0.0013	0.045648	0.441395	0.731734	0.698360	6.29660	2.58914	1.50	0.70536	0.70536	0.70547	11	226	71	0.705520	0.075	0.90	4.7	0.071	0.00028	20
01/26/04	68-3	0.0018	0.0013	0.045375	0.373755	0.727534	0.668448	6.26096	2.58796	1.50	0.70535	0.70534	0.70542	15	62	51	0.705388	0.064	0.60	7.3	0.069	0.00029	20
01/26/04	72-2	0.0019	0.0013	0.048745	0.436044	0.789158	0.737371	6.79224	2.58771	1.50	0.70537	0.70537	0.70538	19	37	16	0.705395	0.069	0.37	15.1	0.060	0.00028	20
01/26/04	73-12	0.0019	0.0013	0.045637	0.450865	0.733196	0.704204	6.30990	2.58719	1.50	0.70668	0.70667	0.70670	14	28	63	0.706653	0.076	0.58	0.1	0.076	0.00030	18
01/26/04	71-2	0.0019	0.0013	0.045247	0.412129	0.726657	0.683560	6.25381	2.58762	1.50	0.70593	0.70592	0.70597	14	27	37	0.705943	0.070	0.22	6.8	0.075	0.00030	20
01/26/04	73-1	0.0018	0.0013	0.050270	0.533292	0.818134	0.797957	7.04356	2.58866	1.51	0.70660	0.70660	0.70666	10	175	86	0.706720	0.081	0.49	0.3	0.081	0.00026	20
01/26/04	70-1	0.0016	0.0010	0.035357	0.270199	0.577103	0.519443	4.96111	2.58846	1.43	0.70530	0.70530	0.70540	14	107	41	0.705371	0.058	0.70	2.1	0.060	0.00033	20
01/26/04	71-11	0.0016	0.0010	0.036493	0.316405	0.590123	0.547012	5.07213	2.58908	1.43	0.70526	0.70526	0.70537	12	194	27	0.705394	0.067	0.27	4.7	0.070	0.00031	20
01/26/04	71-22	0.0017	0.0013	0.041431	0.362145	0.673708	0.625087	5.79313	2.58923	1.44	0.70533	0.70532	--	14	211	--	0.705473	0.067	0.55	6.1	0.071	0.00029	20
01/27/04	73-1	0.0015	0.0010	0.042357	0.501491	0.715500	0.713457	6.18177	2.58963	1.65	0.70655	0.70648	--	14	336	--	0.706720	0.086	0.54	7.0	0.081	0.00024	20
01/27/04	76-13	0.0012	0.0009	0.041502	0.427055	0.703095	0.674792	6.07676	2.58938	1.67	0.70628	0.70621	0.70641	14	259	25	0.706395	0.075	0.45	3.4	0.077	0.00020	17
01/27/04	63-13	0.0011	0.0009	0.035692	0.355703	0.599686	0.571649	5.18396	2.58951	1.69	0.70539	0.70533	0.70553	17	270	8	0.705520	0.073	1.43	1.8	0.071	0.00021	20
01/27/04	78-1	0.0011	0.0008	0.041195	0.639397	0.702572	0.761301	6.07662	2.58977	1.70	0.70862	0.70856	0.70875	16	462	185	0.708886	0.112	1.26	11.1	0.126	0.00018	20
01/27/04	75-10	0.0011	0.0008	0.042356	0.280778	0.725189	0.631261	6.27295	2.58813	1.70	0.70455	0.70449	0.70463	12	61	137	0.704533	0.047	0.41	6.1	0.045	0.00017	20
01/27/04	76-13	0.0016	0.0013	0.055752	0.552520	0.923794	0.881225	7.95726	2.58977	1.51	0.70624	0.70618	0.70632	12	304	111	0.706395	0.074	0.27	4.1	0.077	0.00020	10
01/27/04	76-13	0.0016	0.0013	0.055497	0.554683	0.920418	0.879848	7.93062	2.58968	1.53	0.70625	0.70619	0.70641	10	295	17	0.706395	0.075	0.26	3.5	0.077	0.00020	20
01/27/04	76-13	0.0016	0.0013	0.058108	0.578687	0.970494	0.925562	8.36646	2.58986	1.55	0.70624	0.70617	0.70638	11	315	24	0.706395	0.074	0.41	0.8	0.077	0.00019	20
01/27/04	76-13	0.0015	0.0013	0.049800	0.506317	0.817493	0.786891	7.04391	2.58966	1.54	0.70625	0.70618	--	12	301	--	0.706395	0.077	0.42	4.6	0.077	0.00022	20
02/13/04	71-11	0.0020	0.0020	0.052127	0.412318	0.785318	0.723659	6.73813	2.58794	1.41	0.70542	0.70535	--	13	62	--	0.705394	0.065	0.21	6.5	0.070	0.00030	20
02/13/04	78-8	0.0020	0.0019	0.049567	0.579772	0.740226	0.759702	6.35140	2.58835	1.42	0.70757	0.70750	--	13	159	--	0.707614	0.098	0.40	0.5	0.097	0.00032	20
03/26/04	70-1	0.0019	0.0016	0.046911	0.327674	0.704302	0.633370	6.06027	2.58680	1.56	0.70545	0.70541	--	17	60	--	0.705371	0.058	0.27	3.2	0.060	0.00032	20
12/09/04	75-10	0.0027	0.0026	0.062513	0.321199	0.902189	0.770682	7.75525	2.58656	1.56	0.70465	0.70458	--	9	64	--	0.704533	0.044	0.34	1.4	0.045	0.00035	49
12/09/04	75-10	0.0025	0.0025	0.062778	0.327432	0.917974	0.785039	7.90096	2.58672	1.61	0.70464	0.70457	0.70459	10	52	82	0.704533	0.044	0.17	1.5	0.045	0.00032	48
12/09/04	76-13	0.0025	0.0024	0.063843	0.557662	0.950939	0.902924	8.19690	2.58901	1.67	0.70632	0.70625	0.70629	10	203	144	0.706395	0.072	0.13	6.5	0.077	0.00030	49

12/09/04 76-13	0.0024	0.0024	0.062189	0.541662	0.926303	0.879131	7.98773	2.58901	1.69	0.70632	0.70625	0.70624	9	203	215	0.706395	0.072	0.13	6.9	0.077	0.00030	48
12/09/04 75-10	0.0021	0.0022	0.041088	0.190853	0.563339	0.478042	4.85665	2.58560	1.77	0.70469	0.70463	0.70466	16	133	175	0.704533	0.042	1.64	7.0	0.045	0.00043	50
12/09/04 75-10	0.0020	0.0019	0.044719	0.210583	0.648179	0.547229	5.59980	2.58695	1.82	0.70462	0.70456	--	12	32	--	0.704533	0.040	2.09	11.2	0.045	0.00035	50
01/10/05 76-13	0.0029	0.0032	0.062592	0.558316	0.908212	0.873053	7.83316	2.58638	1.73	0.70650	0.70649	--	12	136	--	0.706395	0.076	0.17	2.2	0.077	0.00037	37
01/10/05 76-13	0.0028	0.0031	0.062148	0.561306	0.908499	0.874702	7.83946	2.58683	1.74	0.70645	0.70645	0.70634	11	76	76	0.706395	0.076	0.19	1.8	0.077	0.00036	38
01/10/05 71-2	0.0033	0.0035	0.045848	0.326355	0.560609	0.529545	4.81303	2.58615	1.70	0.70606	0.70605	0.70601	15	158	95	0.705943	0.072	0.24	4.7	0.075	0.00069	38
01/10/05 71-2	0.0035	0.0038	0.053988	0.403808	0.691899	0.654374	5.94536	2.58697	1.69	0.70599	0.70598	0.70585	12	54	132	0.705943	0.072	0.30	4.5	0.075	0.00059	40
01/10/05 76-13	0.0036	0.0044	0.065799	0.643348	0.910299	0.907215	7.83305	2.58571	1.66	0.70658	0.70658	0.70655	13	258	223	0.706395	0.087	0.36	12.9	0.077	0.00046	40
01/10/05 71-2	0.0033	0.0034	0.031707	0.179591	0.292804	0.278502	2.49353	2.58737	1.73	0.70595	0.70595	0.70589	19	5	81	0.705943	0.076	0.51	1.2	0.075	0.00133	38
01/10/05 71-2	0.0019	0.0019	0.019831	0.129680	0.205503	0.197576	1.75832	2.58781	1.78	0.70591	0.70590	0.70600	26	56	75	0.705943	0.078	0.34	3.4	0.075	0.00106	40
01/10/05 71-2	0.0019	0.0020	0.018789	0.111868	0.176592	0.169506	1.50584	2.58933	1.77	0.70576	0.70575	0.70575	43	268	278	0.705943	0.079	0.68	4.2	0.075	0.00129	27
01/10/05 76-13	0.0021	0.0027	0.040442	0.401984	0.569223	0.567925	4.90895	2.58686	1.76	0.70646	0.70645	0.70665	19	83	360	0.706395	0.087	0.38	12.2	0.077	0.00043	40
01/10/05 76-13	0.0021	0.0026	0.027671	0.212827	0.335122	0.323659	2.87663	2.58910	1.71	0.70624	0.70623	0.70619	47	233	290	0.706395	0.078	0.98	1.5	0.077	0.00073	30
01/10/05 76-13	0.0019	0.0025	0.034968	0.346399	0.485332	0.485705	4.18601	2.58712	1.78	0.70643	0.70643	0.70663	19	44	338	0.706395	0.088	0.30	13.3	0.077	0.00046	40
01/10/05 71-2	0.0018	0.0018	0.016824	0.097919	0.154975	0.148658	1.32174	2.58951	1.82	0.70574	0.70574	--	43	291	--	0.705943	0.078	0.84	3.8	0.075	0.00133	31
01/11/05 71-2	0.0046	0.0051	0.069247	0.570788	0.881891	0.852357	7.52080	2.58694	1.29	0.70599	0.70596	--	18	26	--	0.705943	0.082	0.66	8.1	0.075	0.00061	40
01/11/05 71-2	0.0045	0.0051	0.058418	0.470999	0.717218	0.695719	6.11468	2.58698	1.33	0.70601	0.70599	0.70592	17	60	36	0.705943	0.083	0.58	9.6	0.075	0.00073	40
01/11/05 71-2	0.0040	0.0048	0.061762	0.582067	0.830511	0.822118	7.10423	2.58651	1.38	0.70607	0.70604	0.70597	16	135	39	0.705943	0.088	0.63	16.3	0.075	0.00056	40
01/11/05 76-13	0.0031	0.0035	0.042900	0.404831	0.547640	0.550584	4.68347	2.58655	1.44	0.70652	0.70649	0.70636	19	135	53	0.706395	0.092	0.65	19.6	0.077	0.00066	40
01/11/05 76-13	0.0034	0.0041	0.054000	0.586498	0.753766	0.770557	6.45857	2.58594	1.43	0.70659	0.70657	0.70643	16	245	48	0.706395	0.097	0.66	25.8	0.077	0.00052	40
01/11/05 76-13	0.0035	0.0044	0.053429	0.584683	0.737877	0.758293	6.31971	2.58591	1.42	0.70660	0.70658	0.70648	16	255	126	0.706395	0.099	0.47	28.2	0.077	0.00055	40
01/11/05 71-2	0.0046	0.0049	0.064039	0.471377	0.775869	0.736914	6.60756	2.58735	1.29	0.70597	0.70595	0.70584	17	7	149	0.705943	0.077	0.54	1.6	0.075	0.00070	40
01/11/05 76-13	0.0049	0.0053	0.064899	0.528307	0.775994	0.759615	6.60372	2.58653	1.27	0.70651	0.70649	0.70650	16	128	148	0.706395	0.086	0.60	11.3	0.077	0.00074	40
01/11/05 71-2	0.0048	0.0050	0.063217	0.452777	0.746571	0.708570	6.35639	2.58772	1.31	0.70594	0.70591	0.70589	20	43	79	0.705943	0.076	0.49	1.4	0.075	0.00075	40
01/11/05 71-2	0.0050	0.0052	0.059835	0.419486	0.671236	0.641146	5.70452	2.58771	1.29	0.70594	0.70591	0.70585	17	42	131	0.705943	0.079	0.47	4.7	0.075	0.00087	40
01/11/05 76-13	0.0052	0.0066	0.099696	1.041701	1.410914	1.417626	12.0573	2.58577	1.27	0.70661	0.70658	0.70649	10	260	135	0.706395	0.093	0.23	20.2	0.077	0.00043	40
01/11/05 76-13	0.0050	0.0065	0.096919	1.069271	1.373301	1.402463	11.7439	2.58552	1.31	0.70664	0.70662	0.70656	11	315	227	0.706395	0.098	0.46	26.6	0.077	0.00043	40
01/11/05 71-2	0.0048	0.0050	0.053745	0.351423	0.566159	0.539079	4.80269	2.58798	1.29	0.70592	0.70589	0.70584	12	78	142	0.705943	0.079	0.39	4.2	0.075	0.00101	40
01/11/05 71-2	0.0042	0.0044	0.045297	0.297450	0.470912	0.450860	4.00124	2.58832	1.40	0.70588	0.70585	0.70590	26	126	55	0.705943	0.080	0.71	5.5	0.075	0.00106	26
01/11/05 71-2	0.0042	0.0045	0.058865	0.471070	0.730507	0.706057	6.24085	2.58785	1.42	0.70593	0.70590	0.70596	15	63	22	0.705943	0.081	0.58	7.0	0.075	0.00067	40
01/11/05 71-2	0.0039	0.0044	0.054667	0.450610	0.678735	0.661178	5.79870	2.58770	1.42	0.70594	0.70591	0.70594	14	43	11	0.705943	0.083	0.24	10.2	0.075	0.00067	40
01/11/05 71-2	0.0048	0.0055	0.079954	0.671602	1.063082	1.022383	9.08473	2.58739	1.35	0.70597	0.70594	0.70601	15	1	94	0.705943	0.079	0.35	5.1	0.075	0.00053	40
01/11/05 71-2	0.0047	0.0050	0.052864	0.347356	0.566080	0.537973	4.80994	2.58846	1.35	0.70587	0.70584	--	26	141	--	0.705943	0.077	0.89	2.6	0.075	0.00098	40
08/09/05 71-2	0.0014	0.0011	0.022728	0.258610	0.388432	0.379989	3.33312	2.58724	1.28	0.70596	0.70596	--	19	23	--	0.705943	0.083	1.38	10.5	0.075	0.00041	37

08/09/05 71-2	0.0010	0.0012	0.039667	0.410998	0.676025	0.646988	5.81840	2.58823	1.44	0.70587	0.70587	0.70593	21	108	20	0.705943	0.076	0.77	0.1	0.075	0.00017	40
08/09/05 75-10	0.0010	0.0009	0.041922	0.267759	0.717313	0.618485	6.17226	2.58758	1.43	0.70453	0.70452	0.70460	13	15	96	0.704533	0.046	1.00	3.8	0.045	0.00016	40
08/09/05 71-2	0.0009	0.0009	0.034364	0.350906	0.581416	0.555389	5.00466	2.58932	1.46	0.70577	0.70577	0.70574	16	249	288	0.705943	0.075	0.42	0.7	0.075	0.00019	40
08/09/05 75-10	0.0010	0.0012	0.044398	0.305593	0.761972	0.665350	6.55471	2.58663	1.41	0.70458	0.70458	0.70468	14	67	209	0.704533	0.050	0.81	11.6	0.045	0.00015	40
08/09/05 76-13	0.0009	0.0011	0.040285	0.445631	0.686601	0.668344	5.90585	2.58878	1.41	0.70626	0.70626	0.70619	18	192	291	0.706395	0.081	0.51	4.5	0.077	0.00016	40
08/09/05 76-13	0.0011	0.0021	0.058298	0.720332	1.014084	1.011925	8.72086	2.58676	1.38	0.70647	0.70646	0.70663	16	97	331	0.706395	0.088	0.79	14.5	0.077	0.00013	40
08/09/05 71-2	0.0005	0.0005	0.017692	0.167519	0.288194	0.271203	2.45862	2.58909	1.03	0.70580	0.70580	0.70570	22	210	347	0.705943	0.074	0.79	2.2	0.075	0.00020	40
08/09/05 75-10	0.0006	0.0008	0.029739	0.191258	0.502920	0.433086	4.29411	2.58584	1.03	0.70463	0.70462	--	18	127	--	0.704533	0.048	1.71	7.8	0.045	0.00015	40
08/10/05 71-2	0.0008	0.0008	0.030262	0.298953	0.507454	0.483010	4.38372	2.58702	1.65	0.70598	0.70598	--	16	48	--	0.705943	0.072	0.63	4.0	0.075	0.00018	40
08/10/05 75-10	0.0008	0.0010	0.038555	0.249734	0.660744	0.572473	5.70962	2.58474	1.65	0.70469	0.70469	0.70462	17	217	123	0.704533	0.046	0.83	3.9	0.045	0.00015	40
08/10/05 76-13	0.0010	0.0017	0.046609	0.547945	0.808282	0.798610	6.98314	2.58548	1.63	0.70659	0.70659	0.70646	17	280	92	0.706395	0.083	0.77	8.0	0.077	0.00014	40
08/10/05 71-2	0.0008	0.0009	0.031222	0.316861	0.530073	0.506826	4.58580	2.58748	1.72	0.70594	0.70594	0.70574	22	10	290	0.705943	0.073	0.28	2.9	0.075	0.00018	40
08/10/05 75-10	0.0008	0.0009	0.038968	0.201179	0.669617	0.559369	5.78558	2.58498	1.64	0.70464	0.70464	0.70466	12	157	177	0.704533	0.037	4.72	17.4	0.045	0.00013	40
08/10/05 71-2	0.0007	0.0006	0.018731	0.177420	0.298953	0.284978	2.58205	2.58792	1.70	0.70590	0.70590	0.70570	26	67	346	0.705943	0.073	0.65	3.4	0.075	0.00029	38
08/10/05 76-13	0.0010	0.0021	0.053202	0.659724	0.930221	0.931071	8.04115	2.58547	1.65	0.70660	0.70660	--	20	295	--	0.706395	0.087	0.60	12.8	0.077	0.00013	40
08/11/05 71-2	0.0008	0.0008	0.028474	0.280326	0.481040	0.457445	4.16744	2.58755	1.80	0.70593	0.70593	--	19	19	--	0.705943	0.071	0.54	5.7	0.075	0.00019	40
08/11/05 71-2	0.0008	0.0009	0.025628	0.249742	0.428075	0.407073	3.70673	2.58701	1.78	0.70598	0.70598	0.70597	21	49	43	0.705943	0.071	0.58	5.5	0.075	0.00021	40
08/11/05 71-2	0.0008	0.0009	0.027774	0.267394	0.463111	0.439103	4.00773	2.58715	1.75	0.70596	0.70596	0.70592	20	31	33	0.705943	0.071	1.25	6.4	0.075	0.00021	33
08/11/05 71-2	0.0006	0.0008	0.025284	0.255547	0.433576	0.413754	3.75980	2.58677	1.83	0.70600	0.70600	0.70597	23	80	36	0.705943	0.072	0.48	4.8	0.075	0.00016	40
08/11/05 71-2	0.0007	0.0008	0.026528	0.274040	0.455528	0.436904	3.94988	2.58697	1.83	0.70598	0.70598	0.70597	26	56	42	0.705943	0.073	1.15	2.9	0.075	0.00017	28
08/11/05 71-2	0.0007	0.0006	0.022004	0.216339	0.367855	0.350677	3.18822	2.58782	1.83	0.70590	0.70591	0.70588	19	53	93	0.705943	0.072	0.40	5.0	0.075	0.00021	40
08/11/05 71-2	0.0007	0.0008	0.024642	0.251123	0.417276	0.400127	3.61669	2.58720	1.82	0.70596	0.70596	0.70597	19	25	40	0.705943	0.073	0.51	2.8	0.075	0.00019	40
08/11/05 71-2	0.0007	0.0008	0.025226	0.258615	0.427220	0.410275	3.70300	2.58721	1.82	0.70596	0.70596	0.70598	21	25	54	0.705943	0.074	0.34	2.2	0.075	0.00019	40
08/11/05 71-2	0.0007	0.0007	0.023358	0.232289	0.395225	0.376807	3.42680	2.58804	1.84	0.70589	0.70589	--	17	81	--	0.705943	0.072	0.31	5.1	0.075	0.00019	40
01/16/06 78-1	0.0062	0.0061	0.070911	0.689532	0.762508	0.818940	6.52057	2.58430	1.69	0.70947	0.70932	--	13	610	--	0.708886	0.112	0.65	10.6	0.126	0.00096	45
01/16/06 78-1	0.0059	0.0058	0.050415	0.365045	0.405995	0.432392	3.43846	2.58490	1.72	0.70939	0.70924	0.70891	22	494	36	0.708886	0.113	1.03	10.3	0.126	0.00172	45
01/16/06 78-1 ⁱ	0.0058	0.0057	0.089039	1.008890	1.140008	1.219198	9.79527	2.58586	1.68	0.70925	0.70909	0.70881	16	294	106	0.708886	0.109	0.72	12.9	0.126	0.00060	45
01/16/06 78-1 ⁱ	0.0056	0.0055	0.062132	0.584565	0.661023	0.704447	5.65166	2.58572	1.70	0.70927	0.70911	0.70878	26	323	146	0.708886	0.110	0.90	12.6	0.126	0.00098	39
01/16/06 78-1 ⁱ	0.0053	0.0053	0.042605	0.276774	0.311453	0.329490	2.62646	2.58406	1.71	0.70951	0.70935	0.70913	21	654	340	0.708886	0.112	0.32	11.0	0.126	0.00201	45
01/16/06 78-1 ⁱ	0.0050	0.0050	0.033419	0.140970	0.164176	0.169158	1.35428	2.58587	1.72	0.70925	0.70910	0.70873	33	296	214	0.708886	0.110	0.58	12.1	0.126	0.00371	45
01/16/06 78-1 ⁱ	0.0050	0.0050	0.036845	0.206490	0.230955	0.243559	1.93289	2.58548	1.70	0.70931	0.70916	0.70910	35	382	306	0.708886	0.113	0.85	9.7	0.126	0.00259	27
01/16/06 78-1 ⁱ	0.0085	0.0085	0.049816	0.121730	0.146879	0.145002	1.15711	2.58816	1.77	0.70894	0.70878	0.70854	52	148	489	0.708886	0.111	0.56	11.3	0.126	0.00732	45
01/16/06 71-2 ^j	0.0155	0.0157	0.091273	0.139273	0.263105	0.227057	2.06673	2.58584	1.76	0.70624	0.70608	0.70605	28	197	147	0.705943	0.071	0.37	5.4	0.075	0.00752	45
01/16/06 71-2 ^j	0.0183	0.0185	0.123513	0.333251	0.611060	0.551464	5.04318	2.58586	1.72	0.70623	0.70608	--	13	190	--	0.705943	0.070	0.37	7.2	0.075	0.00364	45

01/16/06 78-1 ^j	0.0105	0.0098	0.071513	0.683739	0.460786	0.592918	3.84615	2.58924	1.48	0.70862	0.70846	--	37	602	--	0.708886	0.190	0.19	51.3	0.126	0.00273	41
01/16/06 78-1 ^j	0.0111	0.0104	0.090872	1.314651	0.775036	1.069266	6.54519	2.58742	1.44	0.70904	0.70888	--	24	8	--	0.708886	0.215	0.82	71.1	0.126	0.00169	45
01/16/06 71-2 ^j	0.0119	0.0112	0.086823	0.653507	0.631526	0.700407	5.29883	2.58759	1.45	0.70607	0.70591	--	27	43	--	0.705943	0.132	0.55	74.8	0.075	0.00225	45
01/16/06 71-2 ^j	0.0126	0.0119	0.093511	0.738091	0.694135	0.778190	5.82947	2.58734	1.45	0.70611	0.70595	--	20	14	--	0.705943	0.135	0.38	79.4	0.075	0.00217	45

Analyses are listed in chronological order. Cycles are 16 second integrations of measurement during analysis until 3/26/04. Cycles are 8 second integrations thereafter.

^a All samples are dredge samples from the AVON3 dredging cruise (Workman *et al.*, 2004) [7]

^b ⁸⁵Rb/⁸⁷Rb required values are obtained after correcting for Kr and Rb interferences, fractionation correction, and normalization to NBS 987 solution run: during each analytical session. The average ⁸⁵Rb/⁸⁷Rb required value is 2.58745, which is used to obtain the Rb correction using the "global average" technique

^c Sr-isotopes are corrected for Kr and Rb interferences and fractionation corrected

^d After correction for Rb and Sr interferences and fractionation, glass standard runs are corrected for 987 standard solution runs for each analytical session

^e Internal (in-run) precision (I. Prec.) is quoted as 1 σ standard error, and is calculated offline using the Tweakr program. In the above dataset, the average internal precision is 17 ppm for ⁸⁷Sr/⁸⁶Sr, and 0.67% for Rb/Sr.

^f External precision (E. Prec.) is calculated assuming that the TIMS ⁸⁷Sr/⁸⁶Sr (ppm) and XRF Rb/Sr (%) values obtained on bulk powders are correct. The average external precision of ⁸⁷Sr/⁸⁶Sr measurements on the above glass standards is 155 ppm mean deviation (1 σ), which translates to 388 ppm standard deviation (2 σ) if a Gaussian distribution is assumed. The average external precision on Rb/Sr measurements on glass standards is 6.7% (mean deviation, 1 σ), which translates to a standard deviation of 16.7% (2 σ). Uses global average ⁸⁵Rb/⁸⁷Rb value (2.58745) for isobaric Rb interference.

^g ⁸⁷Sr/⁸⁶Sr and Rb/Sr values obtained by conventional methods (XRF or ICP) are reported in Workman *et al.*, 2004 [7].

^h Raw voltages on mass 82 divided by mass 88. This is a proxy for Kr/Sr during analysis

ⁱ Samples are run at less than 100% laser power (between 45-90% power)

^j Unlike all other Samoan glass standard and melt inclusion analyses, these four analyses were performed with a "dry" plasma (i.e., no aspiration of the 5% nitric solution during laser analysis).

These dry runs are not used in calculations or in the figures, and were performed for comparative purposes only. We find that the Rb is strongly fractionated from Sr, and that the ⁸⁵Rb/⁸⁷Rb required and mass bias tend to be lower than similar runs made with a wet plasma during the same analytical session.

^k The amount of mass bias correction required to obtain the canonical value for ⁸⁶Sr/⁸⁸Sr. Units are %/amu.

^l External precision is calculated assuming that the TIMS ⁸⁷Sr/⁸⁶Sr is correct. External precision is calculated using the "bracketing" technique for the correction of the isobaric interference from Rb on mass 87. The external precision is somewhat improved (127 ppm, 1 mean deviation) compared to the global average technique for the Rb correction (155 ppm) when comparing the same set of glass analyses.

Bracketing is a useful technique for individual, 1-day analytical sessions only, as ⁸⁵Rb/⁸⁷Rb values can change significantly between analytical sessions. Therefore,

the first and last runs of the Samoan glass standards of each analytical session cannot be corrected with the bracketing technique. Runs with a dry plasma are not examined.

^m Same as previous column, but ⁸⁷Sr/⁸⁶Sr values calculated by correcting for the Rb interference using the "bracketing method", our preferred correction scheme and the one adopted in the manuscript for correcting unknowns.

Table 5. Compositions of Samoan glasses ("standards") used in determining $^{85}\text{Rb}/^{87}\text{Rb}$ required values in this study.

Glass Name	76-8	78-1	78-8	76-13	75-10	63-13	70-1	71-11	71-22	72-2	73-1	73-12	71-2	68-3
Volcano	Malumalu	Malumalu	Malumalu	Malumalu	Ta'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u	Vailulu'u
$^{86}\text{Sr}/^{87}\text{Sr}$	0.706374	0.708886	0.707614	0.706395	0.704533	0.705520	0.705371	0.705394	0.705473	0.705395	0.706720	0.706653	0.705943	0.705388
SiO ₂	47.04	45.54	47.33	46.35	47.10	47.16	47.57	47.57	45.21	45.53	47.14	47.10	43.85	47.84
Al ₂ O ₃	13.69	8.94	14.19	13.55	16.29	14.76	13.63	13.71	8.13	14.10	13.97	12.07	6.37	11.86
TiO ₂	3.88	1.96	3.29	3.86	4.02	3.01	2.91	2.75	1.68	3.31	2.80	2.46	1.44	2.55
FeO*	11.93	11.89	11.45	12.78	12.56	11.59	11.44	10.64	10.77	12.13	11.26	10.25	10.80	10.51
MnO	0.18	0.17	0.17	0.20	0.20	0.18	0.18	0.18	0.17	0.19	0.18	0.18	0.17	0.17
CaO	11.86	8.23	11.47	11.80	9.11	12.37	13.05	12.72	9.99	11.88	12.93	12.80	8.07	12.75
MgO	6.27	19.68	6.93	6.42	5.16	6.57	7.56	8.60	21.79	8.56	7.52	11.70	27.44	10.68
K ₂ O	1.92	1.41	2.05	1.94	1.46	1.28	0.98	1.15	0.67	1.40	1.37	1.15	0.59	0.99
Na ₂ O	2.75	1.92	2.74	2.61	3.47	2.72	2.35	2.35	1.39	2.54	2.50	2.02	1.11	2.36
P ₂ O ₅	0.49	0.27	0.40	0.49	0.63	0.37	0.34	0.33	0.20	0.37	0.34	0.28	0.17	0.29
Pre-total	99.27	100.27	99.74	99.12	99.58	99.01	98.81	98.74	98.71	98.39	99.10	99.13	98.50	99.49
Ni	65	616	97	71	5	59	57	135	778	110	79	220	1080	285
Cr	137	1289	106	130	15	110	98	316	1687	227	202	768	2141	822
V	356	194	342	384	282	339	338	324	212	367	325	295	177	300
Ga	22	14	21	26	26	20	21	19	14	23	14	17	9	20
Cu	72	49	79	95	21	58	82	91	156	79	70	59	138	82
Zn	121	102	104	125	140	95	92	92	78	102	86	77	77	89
Cs	0.51	0.39	0.60	0.5	0.39	0.28	0.31	0.34	0.21	0.39	0.38	0.31	0.19	0.30
Rb	44.3	41.8	51.4	42.8	27.6	33.6	25.0	30.4	19.0	29.3	38.1	30.4	16.9	26.6
Ba	355	255	372	341	264	279	203	247	149	287	347	282	128	218
Th	6.4	6.0	6.3	5.3	4.9	5.2	4.2	4.4	2.6	5.0	6.1	4.9	2.3	4.0
U	1.30	1.05	1.36	1.29	1.10	1.07	0.93	0.95	0.56	1.11	1.15	0.87	0.49	0.87
Nb	56.7	39.0	59.0	57.5	51.3	45.1	37.1	40.5	24.7	47.5	46.7	38.2	20.7	36.4
Ta	3.9	2.6	3.8	3.8	3.6	3.1	2.5	2.8	1.6	3.2	3.1	2.5	1.4	2.5
La	48.4	39.4	52.0	48.6	43.1	37.4	31.0	32.9	20.2	38.3	44.2	36.1	17.1	29.3
Ce	95.9	73.0	98.8	96.3	90.5	74.4	65.0	65.6	40.4	76.3	83.6	68.8	34.4	58.7
Pb	4.2	4.2	4.6	5.2	3.3	2.8	2.2	2.3	1.6	2.5	4.8	6.2	1.3	2.5
Pr	11.2	7.9	11.5	11.8	11.1	8.7	7.6	7.9	4.7	9.1	9.4	7.8	4.0	6.9
Nd	46.3	31.0	44.2	47.2	48.0	35.4	31.5	31.6	19.0	37.2	36.0	30.2	16.5	28.5
Sr	544	333	529	554	617	470	420	434	267	492	473	398	224	387
Zr	276	183	256	281	327	218	198	186	117	221	212	177	98	168
Hf	7.2	4.7	6.4	7.1	8.3	5.8	5.4	5.2	3.1	5.9	5.8	4.9	2.6	4.4
Sm	10.5	6.5	9.1	10.2	11.6	7.8	7.5	7.3	4.4	8.4	7.8	6.7	3.7	6.5
Eu	3.2	1.9	2.5	2.9	3.8	2.5	2.3	2.3	1.4	2.6	2.4	2.1	1.1	2.0
Gd	9.5	5.8	8.0	9.1	10.7	7.1	6.8	6.4	3.9	7.3	6.8	6.0	3.2	5.8
Tb	1.4	0.8	1.1	1.3	1.6	1.1	1.0	1.0	0.6	1.1	1.1	0.9	0.5	0.9
Dy	7.4	4.4	5.8	6.6	8.8	5.9	5.7	5.4	3.3	6.0	5.6	5.0	2.7	4.8
Ho	1.3	0.8	1.0	1.2	1.6	1.1	1.0	1.0	0.6	1.1	1.0	0.9	0.5	0.9
Y	32.2	19.6	30.5	33.1	40.2	27.5	26.4	25.9	15.6	29.3	27.3	23.5	12.6	22.5
Er	3.0	1.8	2.5	2.8	3.8	2.7	2.5	2.4	1.4	2.7	2.5	2.2	1.2	2.1
Tm	0.38	0.23	0.34	0.37	0.50	0.35	0.33	0.32	0.19	0.35	0.33	0.28	0.16	0.28
Yb	2.05	1.24	1.97	2.13	2.80	2.02	1.87	1.83	1.11	2.02	1.90	1.64	0.87	1.63
Lu	0.29	0.19	0.29	0.31	0.40	0.30	0.27	0.27	0.16	0.29	0.28	0.23	0.13	0.24
Sc	31.0	25.2	28.5	25.0	20.5	33.4	41.9	39.2	36.0	38.0	39.1	42.7	29.8	40.9

Most glass data can be found in [7]. Major element data normalized to 100%. All glass standards names have the prefix "AVON3"

Fig. 1

Fig. 2

Fig.3

Supp Data Fig. 4

Fig. 5

Fig. 6