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## Sulfur isotope characterization of primordial and recycled sources feeding the Samoan mantle plume

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23 and an Ultra-Low Velocity Zone (ULVZ) that is thought to contribute, in addition to recycled  
24 components, the recently discovered early-formed (primordial) components with  
25 negative  $\mu^{182}\text{W}$  and high  $^3\text{He}/^4\text{He}$ . Recent work measuring sulfur isotopes in ocean island  
26 basalts has established that recycled oceanic and continental crust host unique S-isotope  
27 compositions that can be identified at various hotspot localities. Here we document  
28 previously unknown relationships between  $\Delta^{33}\text{S}$  and radiogenic tungsten, helium and  
29 lead isotopes from 7 Samoan basalts (from the islands of Ofu, Vailulu'u and Malumalu) that  
30 suggest mixing between several endmembers. One, a HIMU influence that has slight  
31 positive  $\Delta^{33}\text{S}$  and positive  $\delta^{34}\text{S}$ ; another, related to EM II that has near zero  $\Delta^{33}\text{S}$  and  
32 positive  $\delta^{34}\text{S}$  ; a third, which is primordial with negative  $\mu^{182}\text{W}$ , high  $^3\text{He}/^4\text{He}$ , that  
33 has  $\Delta^{33}\text{S}=0$  and negative  $\delta^{34}\text{S}$ . From this, we conclude that the indistinguishable  $\Delta^{33}\text{S}$  of the  
34 primordial endmember from that of the convective mantle indicates that sulfur isotopes  
35 were homogenized early in Earth's history. The Vailulu'u sample with HIMU characteristics,  
36 carries a small but resolvable  $\Delta^{33}\text{S}$  that allows, but does not require mass-independent  
37 Archean  $\Delta^{33}\text{S}$  to shift the  $\Delta^{33}\text{S}$ . The observed correlations involving  $\Delta^{33}\text{S}$  supports  
38 arguments linking Pb, He, and W geochemistry to a deep mantle process and places  
39 constraints on questions related to the sources of mantle geochemical heterogeneity.

40

41

## 42 **1. Introduction**

43 Basalts erupted at ocean islands (OIBs) are thought to sample both the deep and  
44 convective mantle, and provide insight into the diversity of mantle reservoirs. Long-lived  
45 radiogenic isotope compositions of strontium (Sr), neodymium (Nd), and lead (Pb) from  
46 OIBs reveal compositional heterogeneity of the mantle and have formed the basis for  
47 identifying distinct mantle reservoirs produced by melt removal and incorporation of  
48 recycled components over time (Zindler and Hart 1986). The process of core formation and  
49 further planetary differentiation allowed for the production of an early formed reservoir  
50 (from here forward in this paper, we refer to this as a *primordial* reservoir). Components of  
51 this reservoir are observed in modern mantle plume basalts such as Samoa, and are  
52 manifested as isotopic anomalies in the short lived radiogenic isotope composition of  
53 tungsten (W) (Mundl-Petermeier et al., 2019; Mundl et al., 2017; Rizo et al., 2016; also see  
54 Kruijer and Kleine, 2018) and noble gas signatures of helium (He), neon (Ne), xenon (Xe),  
55 and argon (Ar) (e.g. Kurz et al., 2009; Mukhopadhyay, 2012). The isotopic observations that  
56 identify primordial components in mantle plume systems have suggested links to Large  
57 Low Shear Velocity Provinces (LLSVPs) and Ultra Low Velocity Zones (ULVZs) in the deep  
58 mantle (Williams et al., 2019).

59 Here, we present new bulk rock quadruple sulfur isotope data on (n=7) basalts from  
60 three Samoan volcanoes--Ofu, Vailulu'u and Malumalu (figure 1)--to explore whether sulfur  
61 isotopes provide insight into the primordial signatures described above. So far sulfur  
62 isotopes have been used to track recycling of exogenic sulfur into plume systems (Cabral et  
63 al., 2013; Delavault et al., 2016; Labidi et al., 2015), to identify an isotopic imprint of  
64 planetary differentiation (Labidi et al., 2013), and to trace magmatic processes such as

65 degassing (Beaudry et al., 2018). The observation of mass-independent ( $\Delta^{33}\text{S} \neq 0$ ) and  
66 mass-dependent ( $\Delta^{33}\text{S} = 0$ , variable  $\delta^{34}\text{S}$ ) signatures of sulfur in mantle samples highlights  
67 its potential value for study in other mantle systems. The samples studied here yield a  
68 relationship between  $\mu^{182}\text{W}$  and  $^3\text{He}/^4\text{He}$  that illustrate a contribution from a primordial  
69 component (negative  $\mu^{182}\text{W}$  anomalies associated with high  $^3\text{He}/^4\text{He}$ ) and a non-primordial  
70 component. This offers an opportunity to place constraints on the primordial sulfur isotope  
71 composition of the mantle and to offer insight into the source of non-primordial W and He  
72 isotope compositions.

73

74

## 75 **2. Geologic Context/Background**

76

### 77 *2.1 Samoan radiogenic isotopic geochemistry*

78

79 Samoa is historically seen as sampling the archetypical Enriched Mantle-II (EMII)  
80 mantle source (e.g. Zindler and Hart, 1986). More recent work on radiogenic isotope  
81 signatures of lead (Pb) argues that the various Samoan volcanoes receive contributions  
82 from multiple mantle endmember sources (Jackson et al. 2014a) including a depleted  
83 component, recycled components, and a primordial component, and these are sampled in  
84 the Vai, Malu, and Upo volcanic lineaments. Radiogenic isotopic compositions of strontium  
85 (Sr), neodymium (Nd), and lead (Pb) for samples from Samoa reveal signatures of recycled,  
86 subducted oceanic and continental crust in endmembers such as: the Enriched Mantle 1  
87 (EMI) component in rejuvenated Samoan lavas, the Enriched Mantle 2 (EMII) component at

88 Malumalu seamount and Savai'i submarine lavas, and the dilute HIMU (high  $\mu = ^{238}\text{U}/^{204}\text{Pb}$ )  
89 component at Ta'u island and Vailulu'u seamount (Jackson et al., 2014; Workman et al.,  
90 2004). The EMI endmember is characterized by relatively low  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$   
91 at high  $^{87}\text{Sr}/^{86}\text{Sr}$ , and high  $^{208}\text{Pb}/^{204}\text{Pb}$  at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ . The EMII source is  
92 characterized by the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  at a given  $^{206}\text{Pb}/^{204}\text{Pb}$  and its origin  
93 is argued to reflect the subduction and recycling of continental sediments (Jackson et al.,  
94 2007a; Workman et al., 2008). The HIMU endmember is thought to reflect recycled oceanic  
95 crust after it experienced Pb loss during subduction, hence leading to ingrowth of  
96 radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  (e.g. Kelley et al., 2005 and references within) .

97         Studies of ocean island basalts, including Samoa, also suggest various ocean islands  
98 host primordial mantle components. Evidence for this comes from high  $^3\text{He}/^4\text{He}$  ratios in  
99 Hawaii (e.g. Kurz et al., 1983, Valbracht et al., 1997 and references within), Samoa (Jackson  
100 et al., 2009, 2007b), Iceland (e.g. Macpherson et al., 2005 and references within), Galapagos  
101 (Graham et al., 1993; Kurz et al., 2009), and Baffin Island (Starkey et al., 2009; Stuart et al.,  
102 2003). Additional evidence for early-formed "primordial" mantle domains is observed  
103 through the association of primitive Ar and Ne, and ancient Xe isotope signatures in mantle  
104 plumes with high  $^3\text{He}/^4\text{He}$  (e.g. Kurz et al., 2009; Mukhopadhyay, 2012), negative  $\mu^{182}\text{W}$   
105 compositions associated with high  $^3\text{He}/^4\text{He}$  in Samoa and Hawaii (Mundl et al., 2017), and  
106 positive  $\mu^{182}\text{W}$  in Baffin island and Ontong Java Plateau (Rizo et al., 2016; also see Kruijjer  
107 and Kleine, 2018).

108             *2.2 Unique seismic structures beneath Samoa*

109 In addition to the isotopic heterogeneity observed in the mantle, seismic evidence  
110 for compositional heterogeneity in the deep mantle has been mounting. Recent studies  
111 confirm that at the largest scales, the pair of Large low Shear Velocity Province (LLSVPs)  
112 appear to be associated with both low shear wavespeed and high density, a telltale  
113 signature of compositional heterogeneity (Lau et al., 2017; Moulik and Ekström, 2016). At  
114 smaller scales, Ultra Low Velocity Zones (ULVZs), whose properties have been interpreted  
115 to represent either partial melt (Williams and Garnero, 1996) or very high iron enrichment  
116 (Wicks et al., 2010), have now been detected beneath Samoa (Thorne et al., 2013), Hawaii  
117 (Cottaar and Romanowicz, 2012), and Iceland (Yuan and Romanowicz, 2017). High  
118 resolution global tomographic models constructed using full waveform inversion have  
119 been interpreted to require the presence of compositional heterogeneity within plume  
120 conduits themselves (French and Romanowicz, 2015). Importantly, efforts in mantle  
121 geochemistry have begun to associate mantle reservoirs that host primordial components,  
122 such as that sampled by Samoa, to Large Low shear Velocity Provinces (e.g. Williams et al.,  
123 2019) and Ultra Low Velocity Zones (e.g. Mundl et al., 2017) that reside at the base of the  
124 mantle. These observations continue to contribute evidence that mantle plumes are  
125 sampling reservoirs that are both deep and compositionally distinct from the ambient  
126 mantle.

127

### 128 **3. Methods**

129 Splits (1 to 3 gram aliquots) of the same fine crushed powder from Mundl et al.  
130 (2017) were placed into Teflon reactors for acid digestion as described by Labidi et al.

131 (2012). These samples are a different type from those studied by Labidi et al. (2015) in that  
132 the samples are not glasses but, are rather the same powder from the interiors of the  
133 sampled flows used by Mundl. et al (2017). Prior to digestion, the setup was degassed with  
134  $N_2$  for  $\sim 15$  minutes. After degassing, the samples were acidified and digested in heated  
135 ( $70$ - $80^\circ C$ )  $3.2M$   $CrCl_2$ ,  $12M$   $HCl$ , and  $29M$   $HF$  in the amounts of  $10$  ml,  $5$  ml, and  $5ml$   
136 respectively. The amount of solution was doubled for larger samples ( $>2$  grams of powder).  
137 Sulfides were released as  $H_2S$  that is then bubbled (pulsed bubbling of  $\sim 3$ - $5$  bubbles every  
138  $\sim 1$ - $2$  seconds) through a water trap and lastly trapped as  $Ag_2S$  in an acidic  $AgNO_3$  trap  
139 solution. The captured  $Ag_2S$  subsequently transferred to a  $1.5$  ml Eppendorf centrifuge tube  
140 where it was then rinsed, agitated with a vortex machine for  $10$  seconds, and centrifuged  
141 with Milli-Q water. The supernatant was pipetted off and the rinsing procedure was  
142 repeated  $6$  times. After rinsing, the  $Ag_2S$  was dried at  $70^\circ C$ . The dried  $Ag_2S$  was then  
143 weighed to determine sulfur concentration and the  $Ag_2S$  ( $0.3mg$  to  $5$  mg) reacted with  $3$ - $5$   
144 times excess  $F_2$  in heated ( $\sim 250^\circ C$ ) nickel reaction tubes for at least  $8$  hours. Note, some  
145 samples yielded greater than  $5$  mg of  $Ag_2S$  (up to  $15$  mg). For these samples,  $3$ - $5mg$  splits  
146 were taken and used for isotopic analyses. The resulting  $SF_6$  was transferred to a liquid  
147 nitrogen cooled trap and the residual  $F_2$  was passivated by a reaction with  $\sim 110^\circ C$   $KBr$   
148 salt. After passivation, the liquid nitrogen trap was replaced by an ethanol slush ( $\sim -108^\circ C$   
149 to  $-115^\circ C$ ) in an effort to separate  $HF$  from the remaining  $SF_6$ . Once separated, the  $SF_6$  was  
150 transferred to a liquid nitrogen cooled injection loop of a gas chromatograph (GC). Next, the  
151  $SF_6$  was simultaneously thawed and injected into the gas chromatograph with flowing  
152 helium at a rate of  $20$  mL/min. The gas chromatograph allows for a final  $SF_6$  purification  
153 using a  $1/8$ -inch diameter,  $20$ -foot long Haysep-Q™ GC column. The  $SF_6$  was monitored

154 while passing through the (GC) and captured from the helium flow in liquid nitrogen cooled  
155 spiral metal tubes. Lastly, the captured purified SF<sub>6</sub> was measured manometrically to  
156 determine procedural yields and preserved in individual sample fingers of glass manifolds.  
157 Yields determined from fluorination range from 70% to 106%. The glass manifold was then  
158 attached to an additional liquid nitrogen cooled manifold that is used to introduce SF<sub>6</sub> into  
159 the sample bellows of a Thermo Finnigan MAT 253 dual-inlet mass spectrometer.

### 160 *3.1 Mass Spectrometry*

161 Sulfur has four stable isotopes (<sup>32</sup>S (95.2%), <sup>33</sup>S (0.75%), <sup>34</sup>S (4.25%), and <sup>36</sup>S  
162 (0.02%)), and isotopic variations of sulfur isotopes were determined using mass  
163 spectrometry of purified SF<sub>6</sub>. The purified SF<sub>6</sub> was measured by monitoring SF<sub>5</sub><sup>+</sup> ion beams  
164 at m/z of 127, 128, 129, and 131. Data are reported in per mil using the following notation:

$$165 \quad \delta^{33}\text{S} = [((^{33}\text{S}/^{32}\text{S})_{\text{sample}} / (^{33}\text{S}/^{32}\text{S})_{\text{CDT}}) - 1]$$

$$166 \quad \delta^{34}\text{S} = [((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{CDT}}) - 1]$$

$$167 \quad \delta^{36}\text{S} = [((^{36}\text{S}/^{32}\text{S})_{\text{sample}} / (^{36}\text{S}/^{32}\text{S})_{\text{CDT}}) - 1]$$

168

$$169 \quad \Delta^{33}\text{S} = [((^{33}\text{S}/^{32}\text{S})_{\text{sample}} / (^{33}\text{S}/^{32}\text{S})_{\text{CDT}}) - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{CDT}})^{0.515}]$$

$$170 \quad \Delta^{36}\text{S} = [((^{36}\text{S}/^{32}\text{S})_{\text{sample}} / (^{36}\text{S}/^{32}\text{S})_{\text{CDT}}) - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{CDT}})^{1.9}]$$

171 All analyses were normalized to analyses of a large, single reservoir of SF<sub>6</sub> gas produced by  
172 fluorination of IAEA-S1 undertaken in the same session as the sample analyses. This  
173 normalization was conducted during each analytical session to account for changes in the

174 composition of different aliquots of mass spectrometer reference gas. We developed this  
175 approach for studies of meteorite samples and found that the approach yields more  
176 accurate and reproducible  $\Delta^{33}\text{S}$  (Antonelli et al., 2014). The data are then normalized to the  
177 value measured for Canyon Diablo Troilite (CDT) using the same approach and calibration  
178 in Antonelli et al. (2014) and Dottin et al. (2018). This places IAEA-S1 at a value of  $\delta^{33}\text{S} = -$   
179  $0.091\text{‰}$ ,  $\delta^{34}\text{S} = -0.401\text{‰}$ ,  $\delta^{36}\text{S} = -1.558\text{‰}$ ,  $\Delta^{33}\text{S} = 0.116\text{‰}$ ,  $\Delta^{36}\text{S} = -0.796\text{‰}$ .

180 Estimates of uncertainty can be assigned on the basis of measured long-term  
181 reproducibility of independent fluorinations of a variety of reference materials. These  
182 uncertainties include contributions from mass spectrometry and chemical preparation and,  
183 for  $\Delta^{33}\text{S}$ , vary depending on the mass spectrometry counting times. For  $\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}$  the  
184 long-term reproducibility on reference materials is  $\pm 0.3\text{‰}$  and  $\pm 0.3\text{‰}$  ( $2\sigma$ ). For  $\Delta^{33}\text{S}$ , the  
185 long-term reproducibility is  $\pm 0.008\text{‰}$ , and  $\pm 0.016\text{‰}$  ( $2\sigma$ ), for mass spectrometry analyses  
186 made using 9 and 3 analytical cycles, respectively.

187 The reproducibility reported in Table 1 of 2 (SE) represents the in-run precision  
188 from mass spectrometry and renormalization determined by Monte Carlo error  
189 propagation. The reproducibility (SE) for  $\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}$  is smaller than seen from the long-  
190 term reproducibility on IAEA-S1 due to factors associated with the chemical procedures in  
191 preparing the  $\text{SF}_6$  ( $\delta^{34}\text{S}$ ) and interferences ( $\Delta^{36}\text{S}$ ). The reproducibility (SE) is comparable to  
192 that seen for  $\Delta^{33}\text{S}$  on the basis of long-term reproducibility on IAEA-S1. This suggests  
193 greatest contributor to reproducibility for  $\Delta^{33}\text{S}$  comes from mass spectrometry. Estimates  
194 of precision (total uncertainty) are assumed to be the larger of the long-term  
195 reproducibility of reference materials and the propagated, normalized mass spectrometry

196 data. These are presented in Table 1. For figures we plot estimated uncertainty. We use a  
197 Bayesian approach (details given in supplementary information) to assess match between  
198 data and models for relationships between sulfur isotope data and other geochemical  
199 systems.

200

#### 201 **4. Results**

202 Data from 7 Samoan basalts are presented in table 1 and figure 2. Sulfur  
203 concentrations of the bulk rock phase represent a lower limit, as a small amount of S could  
204 be lost in the sample preparation (rinsing and weighing procedure). Concentrations range  
205 from 30 ppm to 800 ppm S and isotopic compositions extend from +1.08 to +4.23‰ ( $\pm$   
206 0.3), -0.004 to +0.027‰ ( $\pm$  0.008), and -0.29 to +0.22‰ ( $\pm$  0.3) in  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$   
207 respectively. With the exception of sample Ofu-04-15 ( $\delta^{34}\text{S}$ = +4.23‰), the  $\delta^{34}\text{S}$  data are  
208 within the range of compositions previously reported (+0.11‰ to +2.79‰, Labidi et al.,  
209 2015). The  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  are all within the previously reported range, +0.001‰ to  
210 +0.022‰, and -0.063‰ to +0.271‰, for  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  respectively<sup>1</sup>. The compositions we  
211 observe are within the range of bulk sulfur isotope compositions reported for the global  
212 dataset of glasses from ocean island and mid ocean ridge basalts where values range from  
213  $\sim$  -3‰ to +3‰ in  $\delta^{34}\text{S}$  and -0.01‰ to +0.01‰ in  $\Delta^{33}\text{S}$  (Labidi et al., 2015, 2014, 2013).  
214 However, the observed compositions are not as extreme as the isotopic data obtained on  
215 individual sulfides via secondary ion mass spectrometry (SIMS), at localities such as the

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<sup>1</sup> The compositions reported here are not shifted to the CDT scale in  $\delta^{34}\text{S}$  and the UMD-CDT scale for  $\Delta^{33}\text{S}$ . This shift in normalization yields a -0.1 ‰ shift in  $\delta^{34}\text{S}$  and a +0.01 ‰ shift in  $\Delta^{33}\text{S}$  which would convert to +0.01 to +2.69, +0.011 to +0.032, and -0.063 to +0.271 for in  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$  respectively.

216 Canary Islands that reveal large negative  $\delta^{34}\text{S}$  variations (up to  $-8.2\text{‰}$ ) assigned to  
217 degassing with strictly mass dependent  $\Delta^{33}\text{S}$  (Beaudry et al., 2018) and Mangaia and  
218 Pitcairn that show large negative  $\delta^{34}\text{S}$  variations ( $-17.25\text{‰}$  to  $-2.25\text{‰}$ ) associated with  
219 sub-permil  $\Delta^{33}\text{S}$  variations (0 to  $-0.85\text{‰}$ ) (Cabral et al., 2013; Delavault et al., 2016). These  
220 SIMS measurements resolve isotopic difference on a granular scale, which is different from  
221 bulk measurements presented here, and have larger uncertainties.

222 Our data reveal relationships between  $\Delta^{33}\text{S}$  and radiogenic isotopic compositions of  
223 W, Pb, and He. The data do not, however, preserve a relationship between  $\delta^{34}\text{S}$  and  
224 radiogenic isotopic compositions of W, Pb, and He. In order to assess the significance of  
225 these relationships, we employed a Bayesian model selection approach to quantify the  
226 relative probability that the underlying relationship is represented by a line (M1) versus a  
227 constant value (i.e. line with zero slope; M2). We explicitly marginalize out the extra  
228 tunable parameter (slope of the line) present in M1, and assume that the errors in both  
229 composition estimates are normally distributed and uncorrelated. We find that the  
230 radiogenic W, Pb, and He vs.  $\Delta^{33}\text{S}$  data strongly prefer M1 over M2 ( $> 99\%$  chance of being  
231 true).

## 232 **5. Discussion**

### 233 *5.1 Preservation of mantle sulfur in interiors of pillow basalts?*

234 We report sulfur concentrations in the interior of pillow basalts erupted at Ofu,  
235 Vailulu'u and Malumalu that range from 30 to 800 ppm. These are lower than  
236 concentrations seen in glasses erupted at these islands (600 to 2000 ppm S, Labidi et al.  
237 2015). Typically, samples of glass, erupted at ocean depths greater than 1000 meters have

238 the greatest chance of preserving the sulfur concentrations and isotopic compositions of  
239 the erupted melt (Moore and Fabbi, 1971). The bulk rock samples from Vailulu'u and  
240 Malumalu are from submarine eruptions (they were collected at water depths of  $\geq 92$  bars)  
241 and preserve slightly higher sulfur concentrations, but are at the low end (600-800 ppm) of  
242 the S concentrations reported for samples of glass from the same localities by Workman et  
243 al. (2006) and Labidi et al. (2015) and in some cases (see table 1, supplementary figure 2)  
244 reveal even lower concentrations ( $\sim 200$  ppm) than the lowest value ( $\sim 600$  ppm) reported  
245 by Labidi et al., (2015). Bulk rock samples with the lowest S concentrations (30 and 60 ppm  
246 S) are subaerial lavas from Ofu. Sulfur loss can also be associated with isotopic shifts in  
247  $\delta^{34}\text{S}$ , but not  $\Delta^{33}\text{S}$  or  $\Delta^{36}\text{S}$ .

248 The sulfur isotope compositions of Samoan basalts (from this study and Labidi et al.,  
249 2015) are  $^{34}\text{S}$ -enriched relative to the composition of mantle sulfur proposed by Labidi et  
250 al. (2013, 2014) of  $-1 \pm 0.5\%$ . These  $^{34}\text{S}$ -enrichments could be caused by recycling of  $^{34}\text{S}$ -  
251 bearing subducted components (Labidi et al. 2015), or by syn-eruptive or post-eruptive  
252 sulfur loss. While sulfur loss could be accounted for by episodes of sulfide segregation, as  
253 seen in some Samoan melts (Labidi et al. 2015), we argue that the lowest sulfur  
254 concentrations observed here illustrate sulfur loss through an event(s) of sulfur degassing  
255 and that the loss of sulfur ( $^{32}\text{S}$ ) could account for the increasing  $^{34}\text{S}$ -enriched characteristic  
256 of the Ofu samples ( $\delta^{34}\text{S} = +1.8\%$  and  $+4.3\%$ ). A similar shift in  $\delta^{34}\text{S}$  from degassing cannot  
257 be ruled out for the samples from Vailulu'u and Malumalu, however, some of these samples  
258 still overlap the range of sulfur isotopic compositions seen for Samoan glasses by Labidi et  
259 al. (2015) (Figure 2).

260 Sulfur loss through degassing can occur as an equilibrium fractionation, a kinetic  
261 fractionation, or a combination of both. At the Quartz-Fayalite-Magnetite reaction buffer,  
262 SO<sub>2</sub> dominates the gas phase (Burgisser et al., 2015; Gaillard and Scaillet, 2009), and  
263 degassing is expected for melts erupting at less than 100 bars pressure (~1000 m depth )  
264 (Gaillard and Scaillet, 2009). At 1200 degrees C, sulfur dioxide is <sup>34</sup>S-enriched by ~1.5 to  
265 3‰ relative to the dissolved sulfide in the melt (e.g. Mandeville et al., 2009), and  
266 equilibrium degassing of sulfur dioxide drives the melt to more negative δ<sup>34</sup>S compositions.  
267 If instead the S were degassed as H<sub>2</sub>S, S loss would result in a negligible fractionation of <sup>34</sup>S  
268 (Mandeville et al., 2009) but H<sub>2</sub>S loss is not supported by degassing models of melts with  
269 these compositions and oxygen fugacities (Burgisser et al., 2015). The alternative, kinetic  
270 degassing, results upon rapid loss of S and generates a <sup>34</sup>S heavy residual melt, rather than  
271 depletion, driving the melt towards positive δ<sup>34</sup>S (e.g. de Moor et al., 2013 and references  
272 within). Note, positive δ<sup>34</sup>S can be achieved during decompression degassing in highly  
273 oxidizing conditions (> QFM +3, Fiege et al., 2014). Degassing almost certainly occurred,  
274 however our data do not allow for a single process with a singular fractionation to be  
275 identified (supplementary figure 1). This limits our ability to project back to the δ<sup>34</sup>S of an  
276 initial magma. We note that oxidative weathering of the crystalline interiors may have  
277 induced the loss of reduced S. Studies of isotope effects associated with low temperature  
278 oxidation by Heidele et al. (2013) show no change in the δ<sup>34</sup>S of the residual sulfides from  
279 oxidation, but, reveal a fractionation for the product sulfate which they attribute to  
280 formation of more than one product. Thus, in the event of oxidative weathering, it is  
281 expected that the δ<sup>34</sup>S of sulfide would still reflect that of its parental melt.

## 282 *5.2 Recycled sulfur in Samoa*

283           The submarine erupted samples we analyzed from Vailulu'u and Malumalu have  
284 higher S concentrations than the analyzed Ofu samples and we suggest (see above) that  
285 sulfur degassing may have only minimally modified the isotopic composition. These  
286 samples have  $\delta^{34}\text{S}$  compositions (+1.23 to +2.30‰) that fall within the range of values  
287 previously reported on glassy Samoan basalts by Labidi et al., (2015) and exhibit similar  
288 radiogenic isotope compositions for Pb, Sr, and He (Figure 3). Even though the sulfur  
289 concentrations are generally lower than that observed by Labidi et al., (2015)  
290 (supplementary figure 2), the geochemical similarity between the samples suggests they  
291 are part of the same population. Thus, we defer to the study by Labidi et al. (2015) for  
292 insight into the  $\delta^{34}\text{S}$  of the primary magma, where they identified a mixing array between a  
293 lower  $^{87}\text{Sr}/^{86}\text{Sr}$  mantle domain with negative  $\delta^{34}\text{S}$ , and an EMII endmember with positive  
294  $\delta^{34}\text{S}$ .

295           The relationship between  $\Delta^{33}\text{S}$  and other geochemical systems such as tungsten,  
296 helium and lead isotopes reflects mixing of mantle reservoirs sampled by the Samoa mantle  
297 plume, including a recycled component with dilute HIMU characteristics (Jackson et al.,  
298 2014), an EMII sulfur component that has been documented by Labidi et al. (2015) and a  
299 primordial endmember defined by negative  $\mu^{182}\text{W}$  and high  $^3\text{He}/^4\text{He}$  (Mundl et al., 2017).  
300 Below, we explore in greater detail various scenarios for interpreting the relationships  
301 between sulfur and other geochemical systems. We start by discussing the connection with  
302 the recycled component and then discuss the connection with the primordial endmember  
303 in the context of its suggested origin and placement this endmember.

304 Our data from Vailulu'u and Malumalu occupy the same field for  $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$   
305 (figure 4) and also the same field for  $\delta^{34}\text{S}$  vs  $\Delta^{33}\text{S}$  (figure 2) as defined for volcanic glasses  
306 of the Samoan volcanic chain reported by Labidi et al. (2015). Labidi et al. (2015) argue  
307 that these relationships between  $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  reflect mixing between an EMII mantle  
308 endmember with positive  $\delta^{34}\text{S}$  ( $+10 \pm 3\%$ ) and radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  and a mantle domain  
309 with negative  $\delta^{34}\text{S}_{\text{V-CDT}}$  ( $-0.89 \pm 0.11$  ( $1\sigma$ )) and less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$ . Minor scatter in  
310 the  $\Delta^{33}\text{S}$  of the combined data allows for other components with different  $\Delta^{33}\text{S}$ , such as  
311 HIMU, as underplating of HIMU-enriched material to the crust below Samoa has been  
312 proposed as the outcome of the earlier passage of the Cook-Austral plumes (Workman et  
313 al., 2004); however, the HIMU component may also be indigenous to the Samoan plume  
314 (Jackson et al., 2014). Jackson et al. (2014) argue that the Vailulu'u lavas reveal  
315 characteristics suggestive of a dilute HIMU signature. The slightly elevated  $\Delta^{33}\text{S}$  in Vailulu'u  
316 lavas is interpreted to reflect a dilute contribution from a HIMU component that possess  
317 variable anomalous  $\Delta^{33}\text{S}$ . A similar observation is observed in lavas from Vailulu'u in Labidi  
318 et al. (2015). Given the data from Malumalu (EM2) and Vailulu'u (dilute HIMU) occupy  
319 different fields for  $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  and a slightly different field for  $\delta^{34}\text{S}$  vs  $\Delta^{33}\text{S}$  (figure 2),  
320 the case may be that the sources of sulfur are indeed different for the Vai and Malu volcanic  
321 lineament. The high  $^{87}\text{Sr}/^{86}\text{Sr}$  in EM2 Malumalu lavas (and possibly the Vailulu'u lavas,  
322 which also have moderately elevated  $^{87}\text{Sr}/^{86}\text{Sr}$ ), combined with observed  $\delta^{34}\text{S}$  vs  $\Delta^{33}\text{S}$ ,  
323 allows for a potential mixture of both Proterozoic and Archean sediments (Labidi et al.,  
324 2015). In this type of mixture, the small magnitude  $\Delta^{33}\text{S}$  signature could also be contributed  
325 by Proterozoic sediments (See Johnston (2011) for data compilations showing such  
326 characteristics for early to middle Proterozoic sediments). Such small-magnitude positive

327 and negative shifts of  $\Delta^{33}\text{S}$  are a natural outcome of biological and biogeochemical cycling  
328 (Ono et al., 2006) and are seen in sulfide and sulfate from a wide range of sedimentary and  
329 hydrothermal systems (Johnston, 2011).

### 330 *5.3 Sulfur from the primordial mantle*

331 The plume component with which this recycled endmember is mixed hosts a  
332 heterogeneous radiogenic Pb isotopic composition. The data from Samoa define four arrays  
333 in  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{204}\text{Pb}/^{204}\text{Pb}$  that all converge on a small range of values (19.0-19.3 in  
334  $^{206}\text{Pb}/^{204}\text{Pb}$ , 39.0-39.4 in  $^{208}\text{Pb}/^{204}\text{Pb}$ ) (Jackson et al., 2014) that are associated with the  
335 high  $^3\text{He}/^4\text{He}$  ratios of the “common component” (20-33.8  $R_A$ ). Samples from Samoa with  
336 high  $^3\text{He}/^4\text{He}$  also preserve negative  $\mu^{182}\text{W}$  compositions (Mundl et al., 2017). Such  $^{182}\text{W}$   
337 deficits require a separate evolution from mantle-hosted  $^{182}\text{Hf}$ , which went extinct within  
338 the first 60 million years of solar system history.  $^{182}\text{W}$  deficits are thus signatures formed  
339 early in Earth’s accretionary history that were immediately isolated from mantle  
340 convection and mixing (Mundl et al., 2017).

341 The observed relationships between S with He and W (figure 3) suggests the  
342 contribution of sulfur from an undegassed, early-formed mantle reservoir. Our data  
343 establish that materials linked to the deep primordial component have  $\Delta^{33}\text{S} \approx 0\text{‰}$ , similar  
344 to the average MORB value of  $0.008 \pm 0.006\text{‰}$  ( $n=80$ , 1 s.d., Labidi and Cartigny 2016). A  
345 homogeneous mantle  $\Delta^{33}\text{S}$  with variable  $\mu^{182}\text{W}$  supports a process that homogenized  $\Delta^{33}\text{S}$   
346 prior to the ingrowth of  $\mu^{182}\text{W}$  signatures in different reservoirs. In Samoan lavas, the  
347 recycled components bring materials with  $\Delta^{33}\text{S} \neq 0\text{‰}$  associated with the recycled  
348 component with HIMU characteristics (Jackson et al., 2014) and the observed relationship

349 is apparent because this component has a different  $\Delta^{33}\text{S}$  than the endmember with  
350 negative  $\mu^{182}\text{W}$ . It was shown that the convective mantle is defined by  $\Delta^{33}\text{S}$  and  $\mu^{182}\text{W}$  both  
351 equal to zero (e.g. Labidi et al., 2014; Willbold et al., 2011). We therefore expect future  
352 analyses will fill in a three-component mixing field for  $\Delta^{33}\text{S}$  and  $\mu^{182}\text{W}$  (though, hints of this  
353 field may already be present in figure 5); endmember 1 is a primordial component,  
354 endmember 2 is a recycled component, endmember 3 is the convecting mantle.

355         To allow for an early segregated metal-rich reservoir with a  $^{182}\text{W}$  deficit, Mundl et al.  
356 (2017) suggest a connection to deep mantle reservoirs such as the seismically-defined  
357 Large Low Shear Velocity Province (LLSVP) or Ultra Low Velocity Zone (ULVZ) beneath  
358 Samoa which have been suggested to host Fe-rich metals (e.g. Zhang et al., 2016) and/or  
359 may have interacted with the core (Rizo et al., 2019). Work by Frost et al. (2004) suggests  
360 the formation of such metal could have occurred via an  $\text{Fe}^{2+}$  disproportionation pathway  
361 driven by formation of bridgmanite early in Earth's history. This process has the potential  
362 to yield a reservoir of deep mantle metal with moderate W abundances and low HSEs  
363 (Mundl et al., 2017). Zhang et al. (2016) point out that S will concentrate in this metal  
364 phase, which in turn will mute the expression of the equilibrium metal/silicate  
365 fractionation ( $>1\%$ : Labidi et al., 2016) and yield an isotopic composition similar to that of  
366 the mantle in which it formed (negative  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S} = 0\%$ ). This composition is  
367 consistent with the composition of sulfur we infer for the endmember with negative  $\mu^{182}\text{W}$ .

368         An alternative proposed mechanism for producing negative  $\mu^{182}\text{W}$  variations  
369 involve high-pressure episodes of core formation that are recorded and preserved in the  
370 deep mantle (Jackson et al. 2018). At high pressure, sulfur remains a siderophile element

371 (Suer et al. 2017) but the isotopic effect remains unconstrained. There is a potential for  
372 changes in the mass dependent fractionation of  $^{34}\text{S}/^{32}\text{S}$  (see discussion in Labidi et al.  
373 2016), but we consider it unlikely that the  $\Delta^{33}\text{S}$  would be affected in the formation of the  
374 deep mantle reservoir.

375         Mundl et al., (2017) discount the possibility that physical core metal entrainment  
376 was the source of primordial (negative)  $\mu^{182}\text{W}$  because HSEs are not sufficiently enriched  
377 in Samoan lavas and are uncorrelated with negative  $\mu^{182}\text{W}$ . In consideration of the mantle  
378 nature of sulfur in samples with increasingly negative  $\mu^{182}\text{W}$  from Vailulu'u and Malumalu<sup>2</sup>,  
379 the data suggest the primordial component likely has negative  $\delta^{34}\text{S}$ , which would be  
380 inconsistent with the core being the source of the sulfur that was later diluted with  
381 recycled sediments. Labidi et al. (2013) and Labidi and Cartigny (2016) argue that the  $\delta^{34}\text{S}$   
382 of the bulk Earth, if chondritic, must be between -0.27 and +0.04‰. In this case, the mantle  
383 and core bracket this value with the mantle having strongly negative  $\delta^{34}\text{S}$  ( $-0.89 \pm 0.11\%$   
384 ( $1\sigma$ )) while the core is slightly  $^{34}\text{S}$ -enriched. Further support for the Mundl et al. (2017)  
385 suggestion that the  $\mu^{182}\text{W}$  anomalies did not originate from entrainment of core material,  
386 may be provided by the lack of significant curvature in the  $\Delta^{33}\text{S} - \mu^{182}\text{W}$  array (Figure 5)  
387 and the prevalence of near zero or slightly positive  $\Delta^{33}\text{S}$  for early solar system materials  
388 (Antonelli et al., 2014). Significant curvature would be expected if the mantle mixed with  
389 core material to generate the  $\Delta^{33}\text{S} - \mu^{182}\text{W}$  array (Figure 5) observed here, due to different  
390 W/S ratios in the mantle and core. The lack of curvature also implies the W/S  
391 concentration ratio is not much different in the mixing endmembers and, unless the

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<sup>2</sup> We set aside the data for two samples from Ofu because of the likelihood of late shifts of  $\delta^{34}\text{S}$  from extreme degassing owing to shallow eruption of the Ofu lavas.

392 primordial reservoir has negative  $\Delta^{33}\text{S}$ , the negative  $\mu^{182}\text{W}$  endmember may not be  
393 significantly more negative (e.g. if it was a direct core contribution) than the most negative  
394 values that have been measured thus far.

395 More recent work by Mundl et al. (2019) introduce an argument for anomalous  
396  $\mu^{182}\text{W}$  that involves a chemical and isotopic equilibration process for W between a basal  
397 silicate layer and the core. Mundl et al. (2019) argue that the best candidate reservoirs are  
398 seismically imaged ULVZs. An equilibration process that that generates a reservoir with  
399  $\mu^{182}\text{W}$  of  $\sim -17$  for a  $\Delta^{33}\text{S} \sim 0$  would explain our data (Mundl et al., 2020). The resulting  
400 reservoir would mix with a recycled endmember with  $\Delta^{33}\text{S} \neq 0$  to produce the arrays that  
401 are seen. Using simple mixing calculations, the data are well fit with this model assuming  
402 the amount of tungsten mixed into the basal silicate reservoir yields a  $\mu^{182}\text{W}$  of  $\sim -17$ .

## 403 **6. Conclusions**

404 The Samoan islands are the type locality for the EM (II) reservoir but also receive dilute  
405 contributions from EM (I), HIMU, and DMM related components. Furthermore, Samoa sits  
406 above a seismically imaged LLSVP and ULVZ that is thought to be the source of material  
407 that exhibit primordial isotope compositions, seen as high  $^3\text{He}/^4\text{He}$  and negative  $\mu^{182}\text{W}$ . We  
408 have characterized the nature of sulfur in primordial and recycled mantle sources using  
409 multiple sulfur isotopes of bulk rock Samoan basalts by focusing on Samoan islands with  
410 high  $^3\text{He}/^4\text{He}$  and negative  $\mu^{182}\text{W}$ . Relationships between  $\Delta^{33}\text{S}$  and other geochemical  
411 systems such as radiogenic tungsten, helium and lead isotopes is observed and suggests  
412 mixing between a component with HIMU characteristics (slight positive  $\Delta^{33}\text{S}$  and  
413 positive  $\delta^{34}\text{S}$ ) with a primordial endmember (negative  $\mu^{182}\text{W}$ , high  $^3\text{He}/^4\text{He}$ ,  $\Delta^{33}\text{S}=0$  and

414 negative  $\delta^{34}\text{S}$ ). The antiquity of the primordial endmember is indicated by  $^{182}\text{W}$  deficits that  
415 require a separate evolution from mantle-hosted  $^{182}\text{Hf}$  within the first 60 million years of  
416 solar system history. The similar indistinguishable  $\Delta^{33}\text{S}$  from that of the convective mantle  
417 indicates that sulfur isotopes were thus homogenized early in Earth's history. The small  
418 but resolvable  $\Delta^{33}\text{S}$  in the recycled endmember reflects sulfur that is contributed by a  
419 Samoan plume component with HIMU characteristics (with a possible mixture of  
420 Proterozoic sulfur from continental crust sediments). Although a contribution from mass-  
421 independent Archean  $\Delta^{33}\text{S}$  could be associated with HIMU, it is not required to explain the  
422  $\Delta^{33}\text{S}$  variation because younger (Proterozoic) contributions may also have small positive  
423 and negative deviations from  $\Delta^{33}\text{S}=0$ . The correlations between sulfur, Pb, He, and W are  
424 most easily reconciled with a deep mantle process linked to a dense, undegassed basal  
425 reservoir such as a ULVZ. Although our data do not support a reservoir with  $\mu^{182}\text{W}=-220$   
426 and  $\Delta^{33}\text{S} = 0$ , the relationship between sulfur and tungsten could reflect W isotope  
427 equilibration through a core-mantle equilibration process, where a diluted core W isotope  
428 composition having less negative  $\mu^{182}\text{W}$  is incorporated into the plume that also hosts  
429 recycled sediments having  $\Delta^{33}\text{S} \neq 0$ . Ultimately, our work identifies relationships between  
430 sulfur and radiogenic Pb, He, and W that provide a means of continuing to unravel the  
431 complexities of geochemical heterogeneity of the mantle. With this work, we further the  
432 understanding of how the subduction and recycling of oceanic and continental crust can  
433 influence geochemical signatures observed at ocean islands and how well dispersed the  
434 various reservoirs are in the mantle.

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