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2 **Sulfur isotope evidence for a geochemical zonation of the Samoan mantle plume**

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12 **Key Points:**

- 13 • Basalts from Samoan volcanoes preserve heterogeneous sulfur isotope signatures.
- 14 • We observe unique S-isotope compositions associated with distinct groups of Samoan
15 volcanoes.
- 16 • Sulfur isotope variability is associated with multiple distinct recycled components.

17

18

19 Abstract

20 Basalts from the Samoan volcanoes sample contributions from all of the classical mantle
21 endmembers, including extreme EM II and high $^3\text{He}/^4\text{He}$ components, as well as dilute
22 contributions from the HIMU, EM I, and DM components. Here, we present multiple sulfur
23 isotope data on sulfide extracted from subaerial and submarine whole rocks (N= 18) associated
24 with several Samoan volcanoes—Malumalu, Malutut, Upolu, Savai'i, and Tutuila—that sample
25 the full range of geochemical heterogeneity at Samoa and upon exhaustive compilation of S -
26 isotope data for Samoan lavas, allow for an assessment of the S-isotope compositions associated
27 with the different mantle components sampled by the Samoan hotspot. We observe variable S
28 concentrations (10-1000 ppm) and $\delta^{34}\text{S}$ values ($-0.29\text{‰} \pm 0.30$ to $+4.84\text{‰} \pm 0.30$, 2σ). The
29 observed variable S concentrations are likely due to sulfide segregation and degassing processes.
30 The range in $\delta^{34}\text{S}$ reflects mixing between the mantle origin and recycled components, and
31 isotope fractionations associated with degassing. The majority of samples reveal $\Delta^{33}\text{S}$ within
32 uncertainty of $\Delta^{33}\text{S}=0 \text{‰} \pm 0.008$. Important exceptions to this observation include: (1) a
33 negative $\Delta^{33}\text{S}$ ($-0.018\text{‰} \pm 0.008$, 2σ) from a rejuvenated basalt on Upolu island (associated with
34 a diluted EM I component) and (2) previously documented small (but resolvable) $\Delta^{33}\text{S}$ values
35 (up to $+0.027 \pm 0.016$) associated with the Vai Trend (associated with a diluted HIMU
36 component). The variability we observed in $\Delta^{33}\text{S}$ is interpreted to reflect contributions of sulfur
37 of different origins and likely multiple crustal protoliths. $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ relationships suggest all
38 recycled S is of post-Archean origin.

39 Plain Language Summary

40 Samoa is a group of volcanoes as islands and seamounts that reside in the south Pacific Ocean.
41 This group of volcanoes are unique in that they erupt material from the deep mantle that was
42 once at the surface, suggesting large scale crustal recycling was at play. Furthermore, distinct
43 groupings of volcanoes and seamounts appear to erupt distinct recycled components. However,
44 the nature and relative age of these components are not well understood. We use sulfur isotopes
45 to gain insights into the materials erupted at Samoa. We provide evidence that the mantle plume
46 beneath Samoa is geochemically zoned, as S isotopes are distinct at different groups of islands.
47 We also argue that the identified recycled materials are best linked to Proterozoic sulfur and in
48 some cases may represent recycled S reservoirs that are distributed among multiple Pacific
49 Ocean island basalts.

50 1 Introduction

51 Ocean island basalts (OIB) are volcanic rocks associated with hotspots erupted at
52 intraplate locations in the world's ocean basins. Through the geochemical characterization of
53 OIB and mid-ocean ridge basalts (MORB) with long lived-radiogenic isotopes of strontium (Sr),
54 neodymium (Nd), and lead (Pb), the mantle can be characterized into four chemically distinct
55 geochemical components: Depleted MORB Mantle (DMM), Enriched Mantle 1 (EM I),
56 Enriched Mantle 2 (EM II), and HIMU (high $\mu = ^{238}\text{U}/^{204}\text{Pb}$) (Zindler and Hart, 1986). These

57 components represent mantle depleted by melt extraction (DMM), and components that formed
58 from recycling of continental materials (EM) and oceanic crust (HIMU) (e.g. Hart and Hofmann,
59 1982; Hofmann and Hart, 1982; Jackson et al., 2007a; Workman et al., 2008; Hofmann, 1997;
60 Zindler and Hart, 1986).

61 The Samoan islands and seamounts, collectively called Samoa, are located in the south
62 Pacific Ocean, positioned just north of the northern terminus of the Tonga trench. Samoa is the
63 type locality for the EM II mantle signature, which hosts the highest $^{87}\text{Sr}/^{86}\text{Sr}$ in global OIB—
64 interpreted to reflect ancient recycled terrigenous sediment of submarine origin (Adams et al.,
65 2021; Adams et al., 2021; Workman et al., 2008) or recycled continental crustal materials (e.g.
66 Jackson et al., 2007a). A complication is that various islands within Samoa exhibit
67 geochemically distinct trends in $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ space. This indicates the presence
68 of dilute contributions from other mantle endmembers including HIMU (recycled oceanic crust)
69 and DM (Depleted Mantle) (Jackson et al., 2014). Some of the islands at Samoa have also
70 experienced rejuvenated volcanism (volcanism after a period of quiescence), erupting
71 geochemically distinct material with dilute EM I type compositions (Jackson et al., 2014).

72 In addition to hosting recycled components, Samoa also exhibits a contribution from a
73 deep primordial component. This primordial material was initially identified by high $^3\text{He}/^4\text{He}$
74 (Farley et al., 1992; Jackson et al., 2007b) and later shown to be associated with negative $\mu^{182}\text{W}$
75 (Mundl et al., 2017; Mundl-Petermeier et al., 2020), linking the reservoir to possible chemical
76 equilibration between the core and the deep mantle. In Pb isotope space, the various geochemical
77 trends identified in Samoan lavas converge on Pb isotope compositions associated with a high
78 $^3\text{He}/^4\text{He}$ (Jackson et al., 2014) component, termed FOZO (Focus Zone; Hart et al., 1992), PHEM
79 (Primitive Helium Mantle; Farley et al. 1992) or C (Common; Hanan and Graham, 1996). The

80 convergence on this component provides evidence for mixing between primordial mantle and
81 multiple recycled components in the Samoan plume.

82 Sulfur isotope compositions of OIB can provide unique constraints on the origin of
83 mantle components and have been used to trace and identify various sources of sulfur that have
84 been recycled into the mantle. The ability to identify recycled sulfur protoliths is rooted in the
85 clear dichotomy in $\Delta^{33}\text{S}$ measurements among Archean vs. Post-Archean sediments, where
86 Archean sediments readily host large $\Delta^{33}\text{S}$ variations vs. post Archean materials with typically
87 $\Delta^{33}\text{S} = 0\text{‰}$ (e.g., Johnston, 2011), as well as clear differences in the $\delta^{34}\text{S}$ composition of various
88 crustal components (e.g. Lower Ocean Crust = +3 ‰ in $\delta^{34}\text{S}$, (e.g. Alt, 1995)). At Mangaia, the
89 type locality for the HIMU mantle reservoir, work by Cabral et al. (2013) identified anomalous S
90 isotope compositions in the form of negative $\delta^{34}\text{S}$ and negative $\Delta^{33}\text{S}$ that are argued to reflect the
91 recycling of Archean S stored in oceanic crust. Dottin et al. (2020a) suggested that Mangaia
92 basalts also preserve slightly positive $\Delta^{33}\text{S}$ that is linked to recycled post-Archean sulfur. At
93 Pitcairn, an EM I locality, Delavault et al. (2016) observed negative $\delta^{34}\text{S}$ and negative $\Delta^{33}\text{S}$ in
94 individual sulfide grains and argued that the compositions originate from recycled Archean S.
95 Note, that recycled Archean S is not widely observed, as other localities showing EM I (e.g.
96 Discovery, Labidi et al., 2013) and mild HIMU compositions (e.g. Canary Islands, Beaudry et
97 al., 2018) do not exhibit anomalous $\Delta^{33}\text{S}$. Basalts with EM II signatures at Samoa were
98 previously shown to host positive $\delta^{34}\text{S}$ but $\Delta^{33}\text{S}$ that averages within uncertainty of the origin
99 ($\Delta^{33}\text{S} = 0$) (Labidi et al., 2015), which is argued to reflect the recycling of sediments of
100 Proterozoic age. Recent work by Dottin et al. (2020b) identified slightly positive $\Delta^{33}\text{S}$ at
101 Vailulu'u, associated with a dilute HIMU contribution, and demonstrate that the magnitude of
102 the $\Delta^{33}\text{S}$ signature is consistent with a post-Archean recycled component (Dottin et al. 2020b).

103 Furthermore, the $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ relationship among basalts analyzed in Labidi et al. (2015)
104 and Dottin et al. (2020b) also hint at a post-Archean age for the recycled S. The depleted mantle
105 (DM) has been characterized for multiple S isotopes and consistently show a negative $\delta^{34}\text{S}$
106 composition ($\sim -1\text{‰}$) and $\Delta^{33}\text{S} = 0.008 \pm 0.006\text{‰}$ relative to CDT (Labidi et al., 2013, 2014). The
107 negative $\delta^{34}\text{S}$ is argued to be a relic of core-formation (Labidi et al. 2013, 2014). With multiple
108 localities for the HIMU, EM I, EM II and DM endmembers characterized for S-isotopes, we can
109 evaluate whether similar S-isotope signatures are entrained into the Samoan mantle plume, and
110 further, whether the compositions are associated with values observed at endmember type
111 localities such as the HIMU signature at Mangaia. Similarity in S isotope compositions among
112 Samoan basalts and other OIB would imply that particular recycled components are globally
113 distributed. Alternatively, differences in S isotope composition among mantle endmembers
114 would provide insight into the level of heterogeneity of S among the various flavors of mantle.
115 Here, we present new bulk rock quadruple sulfur isotope analyses of sulfide in basalts ($N = 18$)
116 from a number of different localities along the Samoan hotspot track, including Malumalu
117 seamount, Malutut seamount, Savai'i island, Tutuila, and Upolu island (figure 1). In this work
118 we exhaustively compile existing S isotope data for the Samoan lavas and employ the new and
119 published data to explore whether there are distinct S-isotope compositions revealed by basalts
120 from the various geochemical trends. Although sulfates are known to occur in Samoan melts
121 (Labidi et al., 2015), we focus solely on the reduced sulfur species with the goal of tracking
122 potential $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ variations, which we hypothesize may be linked to distinct recycled
123 sources. We note that sulfates in Samoan basalts have been shown to share the same $\Delta^{33}\text{S}$
124 composition with the host sulfides (Labidi et al. 2015). In this study we have analyzed sulfide-
125 hosted S in whole rock samples. This is because, unlike pristine glass, the sulfate hosted in the

126 whole rock material may have been modified by the composition of seawater. Here, we take
127 advantage of the S-isotope literature previously published on OIBs for reduced sulfur in basalts,
128 and aim to draw potential connections among the various recycled protoliths delivered to mantle
129 plumes.

130 1.1 Geologic Background

131

132 Work by Jackson et al. (2014) show that the islands of Samoa can be grouped into three
133 geochemically-defined volcanic trends that are analogous to the Loa and Kea volcanic trends in
134 Hawaii (Abouchami et al., 2005; Weis et al., 2011): the Vai trend, the Malu trend, and the Upo
135 trend (figure 2); each of these three geographic trends exhibit geochemical fingerprints in shield-
136 stage lavas that are resolvable from each other. Additionally, three of the Samoan islands
137 (Savai'i, Upolu, and Tutuila) host a thin veneer of rejuvenated volcanism with a geochemical
138 signature (major elements, trace elements and isotopic compositions) distinct from the shield
139 stage lavas (Konter and Jackson, 2012; Reinhard et al., 2019). The Vai trend is captured by the
140 youngest chain of volcanic islands in Samoa and displays high $^{206}\text{Pb}/^{204}\text{Pb}$ that is attributed to
141 influence from a shallow-level, dilute HIMU component (Workman et al., 2004), but the HIMU
142 component may be embedded in the plume (Jackson et al., 2014). The Malu trend, captured by
143 the second youngest group of islands, reflects influence from an EM II component, with high
144 $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$. The Upo trend has low $^{206}\text{Pb}/^{204}\text{Pb}$ and
145 high $^{143}\text{Nd}/^{144}\text{Nd}$, consistent with mixing between the Common (C) component and a depleted
146 mantle component (Jackson et al., 2014; Workman et al., 2004). The rejuvenated basalts from
147 Upolu, Savai'i and Tutuila sample a diluted EM I component that also has low $^{206}\text{Pb}/^{204}\text{Pb}$, with
148 lower $^{143}\text{Nd}/^{144}\text{Nd}$ and higher $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ than the Samoan Upo

149 components (Jackson et al., 2014). These four distinct compositional trends have been argued to
150 reflect mixing between “C” and four geochemically-distinct recycled components that are
151 spatially separated in the Samoan mantle plume (Jackson et al., 2014). Their distinct lead isotope
152 geochemistry provides an ideal framework for determining how sulfur from various sources is
153 distributed in this plumbing system.

154 **2 Materials and methods**

155
156 Samples chosen for this study were collected on land and through dredging (AVON2/3
157 cruises) and were characterized for Sr-Nd-Pb-He-Os isotopes, trace elements, and major elements
158 (Workman et al. 2004; Jackson et al., 2007 a,b; Jackson et al., 2010). With the exception of
159 samples from Upolu and Ta’u which show evidence for chemical weathering (Workman et al. 2004),
160 all samples are interpreted to be pristine unaltered basalts (see supplementary information). In
161 preparation for acid digestion, ~ 3-6 grams of whole rock chips from submarine pillow basalt
162 interiors and subaerially-erupted basalts were crushed in a steel mortar and pestle and sieved to
163 <56 microns. Aliquots of ~ 3 grams of homogenized powder were then placed into Teflon
164 reactors with stir bars. The Teflon reactors were subsequently connected to a water trap with
165 plastic tubing and the water trap was connected to an AgNO₃ trap where released sulfide would
166 eventually precipitate as Ag₂S. Prior to acidification, a digestion set-up similar to that presented
167 in Labidi et al. (2012) was purged with N₂ for approximately 10 to 15 minutes. After purging 20
168 ml of CrCl₂, 10 ml of HCl, and 10 ml of HF were injected into the Teflon reactors through a two-
169 way valve with flowing N₂ through a separate port. After acidification, the sample and reagents
170 were heated to ~80 degrees C and stirred with a magnetic stir bar for better powder digestion and
171 to avoid the formation of fluorides which can inhibit the release of sulfide. During this reaction

172 sulfides in the powder are released as H_2S , that is then carried through the water trap to the acid
173 trap, and then bubbled through the AgNO_3 trap to precipitate sulfide as Ag_2S . The reaction ran
174 for ~3 hours. Once the reaction was complete, samples were stored in the dark for a minimum of
175 three days and subsequently rinsed and centrifuged in 1.5 ml Eppendorf tubes six times with
176 Milli-Q water. After rinsing, samples were dried for ~2 hours at 70 degrees C, weighed (to
177 calculate S concentration), and wrapped in foil in preparation for fluorination. S contents of the
178 basalts are estimated from the weight of collected S during extraction. We take our 1 standard
179 deviation uncertainty on S concentration from extractions to be 18 ppm, as determined from
180 repeat extractions (n=4) of AVON 71-22.

181 2.1 Fluorination

182
183 Samples of silver sulfide (~0.2 mg to ~3 mg) in foil packets were placed into nickel
184 reaction tubes and reacted with three to five times excess fluorine overnight to produce SF_6 .
185 Produced SF_6 was first frozen into a liquid nitrogen trap and excess fluorine was passivated
186 through a heated KBr salt. The remaining frozen gas was thawed with an ethanol slush (~-108 to
187 -110 degrees C) to separate SF_6 from HF (also produced during the overnight fluorination). The
188 separated SF_6 was frozen into a separate coil and injected into a gas chromatograph with He
189 flow. Using peak monitoring software, we were able to trap the purified SF_6 with liquid nitrogen
190 in metal coils. After trapping, we manometrically calculated yields of fluorination, which varied
191 from 78% to 108% for this study. Note that excess yields up to 108% in this study can represent
192 either weighing errors or the known slight calibration drift of the pressure gauge that can result in
193 > 100% yields during complete fluorination of standards.

194

2.2 Mass Spectrometry

The purified SF₆ was next analyzed using a ThermoFinnigan MAT 253 dual-inlet gas source mass spectrometer. All samples were analyzed as nine sets of eight 26-second cycles of measurements (of both the reference gas and the sample gas) and bracketed with analyses of a single reservoir of IAEA-S1 standard materials. All samples were first normalized to IAEA-S1 analyses conducted during the analytical session and then subsequently renormalized to IAEA-S1 relative to CDT that places IAEA-S1 at -0.401‰, 0.116‰, 0.796‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ respectively (Antonelli et al., 2014). Generally, our estimated uncertainty on measurements (all 2σ) is 0.3‰, 0.008‰, and 0.3‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ respectively and is estimated from long-term uncertainty on measurements of IAEA-S1. However, for smaller samples (U16, U19, S15), the uncertainty on $\Delta^{33}\text{S}$ is estimated at 0.016‰ as an upper limit. The difference in uncertainty for smaller samples reflects larger analytical uncertainty in measurements on ^{33}S . We note that the uncertainty on $\Delta^{33}\text{S}$ is primarily analytical (Dottin et al., 2020b) whereas the estimated uncertainty reported on $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ includes uncertainty associated with sample processing through wet chemistry and fluorination. Note that in Dottin et al. (2020b) AVON3-63-2 and AVON3-70-9 have $\Delta^{33}\text{S}$ uncertainty of 0.016‰ as a result of shorter analytical sessions.

3 Results

Whole rock S-isotope data and S concentrations from basalts that sample the various Samoan Islands from subaerial and submarine eruptions are presented in figure 3 and table 1. Unlike Hawaii, where shield stage lavas tend to be tholeiitic and rejuvenated stage lavas are

219 alkalic, Samoan shield stage and rejuvenated stage lavas are both overwhelmingly alkalic in
220 composition, and the samples targeted in this study are alkali basalts (see Jackson et al., 2010,
221 2007a; Workman et al., 2006, 2004 for details). While a prior study of Samoan lavas targeted
222 submarine pillow glass (Labidi et al., 2015), here we follow the method of Dottin et al. (2020b)
223 and analyze whole rock basalts for sulfide material. Reduced sulfur concentrations in our
224 samples range from ~ 10 to 1000 ppm. Analyzed subaerial whole rock lavas typically have lower
225 S concentrations relative to the S concentrations from whole rock submarine lavas and glasses,
226 indicative of sulfur loss via degassing. One exception is the western Samoa submarine lava
227 sample ALIA-114-03, where basalts were collected by dredging at ~2500m depth but have S
228 concentrations as low as 32 ppm, which may represent a sample erupted shallowly but then was
229 simply transported downslope following eruption (Supplementary Figure S1).

230 The new data are from Malumalu, Malutut, Savai'i, Upolu, and Tutuila. Submarine
231 samples from Malumalu seamount ($N = 2$) have S-isotope compositions (AVON3-78-1: $\delta^{34}\text{S} =$
232 $1.73\text{‰} \pm 0.30$, $\Delta^{33}\text{S} = 0.000\text{‰} \pm 0.008$, $\Delta^{36}\text{S} = -0.05\text{‰} \pm 0.30$; AVON3-76-9: $\delta^{34}\text{S} = 1.79\text{‰} \pm$
233 0.30 , $\Delta^{33}\text{S} = -0.003\text{‰} \pm 0.008$, $\Delta^{36}\text{S} = 0.01\text{‰} \pm 0.30$ [all 2σ]) that are within the range
234 (including uncertainty) of previously reported data on Malumalu ($\delta^{34}\text{S} = 1.45\text{‰}$ to $2.69\text{‰} \pm 0.24$
235 relative to CDT, $\Delta^{33}\text{S} = 0.004\text{‰}$ to $0.01\text{‰} \pm 0.010$, and $\Delta^{36}\text{S} = -0.01\text{‰}$ to $0.271\text{‰} \pm 0.18$, $n = 6$)
236 which have been reported for sulfur from fresh glass (Labidi et al., 2015) and whole rock
237 powders (Dottin et al. 2020b). Note, estimated S concentrations for the submarine Malumalu
238 samples (AVON3-78-1 = 361 ppm S; AVON3-76-9 = 449 ppm S) are slightly lower, or at the
239 lower end of the range, of S concentrations previously reported on Malumalu samples (393-1693
240 ppm S) (Dottin et al., 2020b; Labidi et al., 2015). The data for the one submarine sample from
241 the Malutut seamount, which is geochemically similar to Malumalu in sampling an EM II

242 component, has a S concentration of 81 ppm (ALIA 108-04) and an S-isotope composition of
243 $\delta^{34}\text{S} = 4.89 \text{‰} \pm 0.30$, $\Delta^{33}\text{S} = 0.008\text{‰} \pm 0.008$, and $\Delta^{36}\text{S} = -0.06\text{‰} \pm 0.30$. Western Samoan
244 submarine lavas from Savai'i have S concentrations of 32 and 219 ppm and S-isotope
245 compositions of $\delta^{34}\text{S} = 1.62 \pm 0.30$, $\Delta^{33}\text{S} = 0.003 \pm 0.008$, $\Delta^{36}\text{S} = -0.10 \pm 0.30$ and $\delta^{34}\text{S} = 4.23 \pm$
246 0.30 , $\Delta^{33}\text{S} = 0.005 \pm 0.008$, $\Delta^{36}\text{S} = -0.12 \pm 0.30$ for ALIA 114-03 and ALIA 128-21,
247 respectively. Tutuila and Upolu subaerial lavas from the Upo trend (DM) have S concentrations
248 that range from 9 to 69 ppm S, with S isotope ratios that range from -0.29 to 1.76, -0.009 to
249 0.006, and -0.17 to 0.14 in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ respectively. Rejuvenated stage subaerial basalts
250 from Savai'i and Upolu have S concentrations that range from 15 to 83 ppm and show a slightly
251 different S-isotope composition with values ranging from -0.28‰ to 1.28‰ in $\delta^{34}\text{S}$, -0.018 to
252 0.011 in $\Delta^{33}\text{S}$, and -0.14 to 0.38 in $\Delta^{36}\text{S}$. Rejuvenated submarine basalt from Savai'i ALIA116-
253 04 has an S-isotope composition of $\delta^{34}\text{S} = +1.99 \pm 0.30$, $\Delta^{33}\text{S} = +0.017 \pm 0.008$, $\Delta^{36}\text{S} = -0.08 \pm$
254 0.30 . The samples from rejuvenated volcanism show the largest range in $\Delta^{33}\text{S}$ for a single
255 geochemical grouping of Samoan basalts reported thus far, with $\Delta^{33}\text{S}$ that ranges from -0.018‰
256 to +0.017‰. The highest and lowest $\Delta^{33}\text{S}$ values in Samoa range from +0.027± 0.016 (Dottin et
257 al. 2020b) to -0.018 ± 0.008 (this study), and the highest and lowest $\Delta^{36}\text{S}$ values are 0.31 ± 0.30
258 (this study) to -0.47 ± 0.18 (Labidi et al., 2015), demonstrating resolvable $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$
259 heterogeneity in the Samoan plume. After filtering subaerially-erupted lavas, which are degassed
260 (and therefore have $\delta^{34}\text{S}$ that no longer represents the mantle source composition), the submarine
261 pillow basalts and pillow basalt glasses exhibit a range in $\delta^{34}\text{S}$ that extends from 0.11 ± 0.24
262 (Labidi et al., 2015) to 4.84 ± 0.30 (this study).

263 **4 Discussion**

264

265 4.1 Variable S contents in submarine basalts

266
267 We analyzed sulfide extracted from submarine and subaerial whole rock powders and
268 determined S contents that range from ~10 to 1000 ppm S. In some cases, the S concentrations
269 reported in submarine whole rocks are lower than the lowest S concentration observed in
270 Samoan glasses (~600 ppm, Labidi et al., 2015). The lower concentrations may simply be an
271 effect of dilution in whole rocks versus glasses but, without extensive knowledge as to where
272 sulfides reside in the rock, an effect of dilution cannot be ruled out. However, the variable S
273 concentrations and S isotope compositions raise the question as to whether there are other
274 processes at play that contribute to the extremely low S contents. For the samples analyzed, we
275 must consider degassing as a means of altering S concentrations and S isotope compositions.

276 Although sulfide segregation is known to occur in Samoan basalts, it is difficult to
277 discern its potential effect on S concentrations as there are no clear links between S contents,
278 eruption depth, MgO and Cu contents (Workman et al., 2006, 2004) (Supplementary Figure S2).
279 Sulfide segregation could produce $\delta^{34}\text{S}$ variations, especially in a system with coexisting sulfide
280 and sulfate assuming the S pools remain in isotopic equilibrium (~3 ‰, Miyoshi et al., 1984;
281 also see Fiege et al., 2014). Sulfate at Samoa was shown to host more positive $\delta^{34}\text{S}$ than the
282 coexisting sulfide (Labidi et al. 2015). If sulfide is lost to a process such as sulfide segregation,
283 the presence an S speciation buffer (such as dissolved Fe) would cause the sulfate/total sulfur
284 ratio to remain constant through sulfate reduction and by mass balance would cause the $\delta^{34}\text{S}$
285 composition of the sulfide in the melt to constantly increase. Labidi et al. (2015) argue however,
286 that sulfides remain unfractionated for $\delta^{34}\text{S}$, at odds with requirement of a S speciation buffer.
287 Thus, although our samples affected by sulfide segregation may have very low S contents, the

288 $\delta^{34}\text{S}$ could conceivably still represent that of the melt composition and not a process associated
289 with sulfide segregation.

290

291 4.1.1 The effect of degassing on $\delta^{34}\text{S}$ and S concentrations

292

293

294 Many of the basalts analyzed here are from subaerial eruptions and likely have
295 experienced modification of the $\delta^{34}\text{S}$ composition from degassing processes. For those samples,
296 we interpret both the $\delta^{34}\text{S}$ data and the S concentrations to reflect sulfur loss from degassing and
297 note that it is problematic to attribute the observed $\delta^{34}\text{S}$ values directly to the original values of
298 the source. We additionally note that some of the submarine basalts host low S concentrations
299 (e.g. sample ALIA114-03, dredged at 2510 m water depth, has 32 ppm S and ALIA 108-04,
300 dredged at 3200m with 81 ppm S; see Table 1) that may reflect degassing or weathering. We do
301 not observe any correlation between indicators of basalt alteration (Ba/Rb), sulfur isotope
302 compositions, and sulfur concentrations, suggesting that weathering is not a key driver for sulfur
303 isotope and sulfur concentration variations (supplementary figure S3). Furthermore, we note that
304 the depth of collection may not always correspond to the depth of eruption. For example, the low
305 S concentrations may be linked to degassing, as a lava dredged at depth may have erupted at
306 shallow levels and was then transported downslope. Alternatively, a volcano can erupt lavas at
307 shallow levels during an early shield stage—where ALIA-114-03 was erupted at ~4 Ma
308 (Koppers et al., 2008) during the early shield stage on Savai'i—and then experience thermal
309 subsidence, thereby explaining a shallow eruption origin for a deeply-sampled basalt. The depth
310 of eruption therefore remains elusive for such samples.

310

311 Degassing is well documented as an agent responsible for modifying both $\delta^{34}\text{S}$ and S
concentrations (e.g. Moore and Fabbi, 1971; Mandeville et al., 2009), including for basalts from

312 Samoa (Dottin et al. 2020b) and the Canary Islands (Beaudry et al., 2018). At the Quartz-
313 Fayalite-Magnetite reaction buffer the speciation of S in the melt is primarily $S^{(2-)}$, SO_2
314 dominates the gas phase, and there is significant loss of SO_2 at pressures less than 100 bars
315 (Burgisser et al., 2015; Gaillard and Scaillet, 2009). Under equilibrium at 1200 degrees C, SO_2 is
316 argued to be ^{32}S -enriched by ~ 0.8 (Marini et al., 2011) or ~ 2 ‰ relative to S^{2-} (Mandeville et
317 al., 2009), resulting in a decrease in $\delta^{34}S$ of residual sulfide as SO_2 is degassed. Alternatively, if
318 gas is rapidly lost, kinetic degassing results in the loss of ^{32}S -enriched SO_2 , and residual sulfide
319 may be enriched in ^{34}S (e.g. de Moor et al., 2013). At more oxidizing conditions (e.g. QFM +1-
320 5) and higher pressures (e.g. 3000 bars) it is expected that loss of SO_2 would result in an increase
321 in $\delta^{34}S$ within the residual melt (e.g. Beaudry et al. 2018) at equilibrium. An additional
322 complication is that the fO_2 of the melt can change drastically upon decompression which can
323 change S speciation in both the melt and gas phase and ultimately change the associated
324 fractionation with S degassing (Beaudry et al., 2018). We observe $\delta^{34}S$ values that range from ~ 0
325 to ~ 5 ‰ among the submarine and subaerial basalts. Subaerial basalts with very low S contents
326 (S ppm < 65) have variable $\delta^{34}S$. With the exception of Ofu 04-15 that shows very positive $\delta^{34}S$
327 of $+4.23$ ‰ with 64 ppm S (Dottin et al., 2020b), all subaerial samples with S ppm < 65 show a
328 dramatic decrease in $\delta^{34}S$ towards increasingly lower values, below $\sim +2$ ‰ (supplementary
329 figure S1b).

330 In consideration of the nature of samples (whole rocks, in some cases erupted subaerially)
331 we are unable to interpret all $\delta^{34}S$ data collected as a representation of the source composition. In
332 particular, for the subaerial basalts, the composition likely represents a mixture of source
333 compositions and degassing. Thus, we only refer to non-degassed samples (excluding lavas
334 erupting at depths $< \sim 1000$ m as they typically show no difference in $\delta^{34}S$ relative to glasses

335 reported in Labidi et al. (2015)) in any discussion of the $\delta^{34}\text{S}$ data. Nonetheless, variations in
336 $\Delta^{33}\text{S}$ are much less susceptible to measurable variations from degassing (although there may be a
337 potential for this to occur during kinetic S loss at unrealistically low temperatures, e.g. (Eiler et
338 al., 2013)) and thus provides an opportunity to explore whether the proposed distinct recycled
339 components at Samoa can be identified with unique $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. For example, in a plot of
340 $\Delta^{33}\text{S}$ for each sample (figure 4), the data appear to present possible differences in composition
341 when grouped according to criteria described in Jackson et al. (2014), making it plausible that
342 relationships may exist between sulfur and the geochemical mixing trends identified in that
343 study.

344 4.2 Evidence for recycled crust in S-isotope compositions

345
346 Crustal recycling is known to modify the S-isotope composition of basalts at Samoa. The
347 Pacific upper mantle S-isotope composition is estimated at $\delta^{34}\text{S} = -0.89 \pm 0.24$ and $\Delta^{33}\text{S} = 0.008$
348 ± 0.012 (all 2σ , Labidi et al., 2014) and the primordial sulfur isotope composition of the mantle
349 is estimated at $\Delta^{33}\text{S} = 0.000 \pm 0.008$ (2σ , Dottin et al., 2020b). With compositional estimates
350 close to the origin for both $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ in the mantle, any measured values that strongly
351 deviate from these estimates are likely due to crustal recycling (with the exception of samples
352 modified syn or post-eruption). At Samoa, the role of recycling has been documented to result in
353 a positive $\delta^{34}\text{S}$ in lavas (Labidi et al., 2015). The $\delta^{34}\text{S}$ compositions are positively correlated with
354 $^{87}\text{Sr}/^{86}\text{Sr}$ in Samoan lavas and have been argued to be linked to a sedimentary protolith with a
355 $\delta^{34}\text{S}$ composition of $\sim +10$ ‰ (Labidi et al. 2015). $\Delta^{33}\text{S}$ values have been documented as
356 generally near zero for Samoan basalts with the exception of 1 sample with slightly positive $\Delta^{33}\text{S}$
357 ($+0.027 \pm 0.016$) that is associated with a HIMU influence (Dottin et al., 2020b).

358 In the following sections we continue to evaluate the role of crustal recycling through
359 characterization of basalts associated with the volcanic trends at Samoa and offer new insights
360 into the role of plume zonation in the distribution of recycled components among the islands.
361 The $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ compositions at Samoa reveal four trends that radiate from a
362 common composition associated with high $^3\text{He}/^4\text{He}$, termed the Common component (Hanan and
363 Graham, 1996; Jackson et al., 2014). The four trends extend from an intersection associated with
364 the Common component to four distinct endmembers that sample a DM component (Upo-trend
365 lavas), a dilute HIMU component (Vai trend lavas), an EM II component (Malu trend lavas), and
366 an EM I component (rejuvenated lavas) (figure 2). We hereby explore the S isotope signatures
367 of these four components below.

368 4.3. Geochemical zones of the Samoan hotspot

369

370 4.3.1 Upo Trend – the DM component

371

372 Shield stage basalts from the Upolu Island and Pago volcanic series from Tutuila
373 represent samples from some of the oldest parts of the hotspot track and exhibit Pb isotope
374 compositions that link them to DM-like components (Jackson et al., 2014). Our three samples
375 from the Upo trend (DM) (U16, U19, and TUT 99-01, all of which erupted subaerially) have
376 $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ within uncertainty of that reported for the MORB mantle. The S-isotope
377 composition of the upper mantle, based on the average S isotope composition of 80 non-
378 degassed MORB samples, is estimated at $\Delta^{33}\text{S}=0.008\text{‰} \pm 0.006$ (1σ) (Labidi and Cartigny,
379 2016) [Note this estimate is published on a different CDT scale relative to UMD results that
380 would result in a positive 0.010‰ shift]. $\delta^{34}\text{S}$ of the upper mantle is generally assumed to be
381 negative as a result of core formation (Labidi et al., 2013) but is variable among multiple

382 localities: $-1.28 \pm 0.33\text{‰}$ (1σ , $n=6$, Labidi et al., 2013) South Atlantic ridge; $-0.89 \pm$
 383 0.11‰ (1σ , $n=28$, Labidi et al., 2014)-Pacific-Antarctic ridge; -0.68 ± 0.33 (1σ , $n=10$, Labidi and
 384 Cartigny, 2016)-Garret transform lavas. At Upolu and Tutuila, representing the Upo Trend
 385 (DM), $\delta^{34}\text{S}$ is variable and higher than the MORB mantle, ranging from -0.29‰ to 1.76‰
 386 (± 0.30). Whether this represents a source signature or degassing in these three subaerial lavas is
 387 unclear. Furthermore, the nature of the depleted component at Upolu and Tutuila is such that it is
 388 the least likely to exhibit evidence for recycling. Thus, without unmodified $\delta^{34}\text{S}$, no clear
 389 connection to DM components can be made, although the positive $\delta^{34}\text{S}$ in these samples may
 390 reflect some contribution of exogenous sulfur. We can however argue that the lack of anomalous
 391 $\Delta^{33}\text{S}$ is consistent with the absence of recycled exogenous sulfur, at least as expected for DM
 392 components (e.g. Labidi et al. 2014).

393 4.3.2 The Vai trend – the HIMU component

394
 395 The Vai trend is composed of six volcanoes: Tama'i seamount, Soso seamount, Tupito
 396 (previously Muli) seamount, Ofu island, Tau island, and Vailulu'u seamount. Radiogenic Pb
 397 isotope data from these volcanoes plot on an array that extends from the Common component to
 398 relatively elevated $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ in samples from Vailulu'u that suggests a dilute
 399 contribution from a HIMU related component. Sulfur isotope compositions of submarine pillow
 400 basalt glasses from the Samoan Vai trend—including Vailulu'u, Tau'u, and Tupito—were
 401 reported in Labidi et al. (2015) and lavas from Vailulu'u and Ofu in Dottin et al. (2020b). The S
 402 isotope data reveal a relationship with radiogenic Pb and He that suggests the observed positive
 403 $\Delta^{33}\text{S}$ measured in samples with relatively high $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ from Vailulu'u reflects
 404 recycled sulfur associated with a HIMU mantle component. $\Delta^{36}\text{S}$ data from Dottin et al. (2020b)
 405 and Labidi et al. (2015) exhibit slightly anomalous compositions in Vailulu'u basalts that

406 supports the contribution of exogenic S to the Vai trend volcanoes. Anomalous S is clearly not
 407 well distributed among Vai trend basalts and such may be the result of geochemical zoning of the
 408 Samoan mantle plume. In this work, we did not analyze additional samples from the Vai trend.
 409 Instead, we provide additional insights into the nature and age of the HIMU component within
 410 the context of recently published work on HIMU-Mangaia (Dottin et al., 2020a).

411 One way to quantify the role of geochemical zoning in the distribution of S isotope
 412 compositions among the Vai trend is through use of measured distance from the Common (C)
 413 component in Pb-isotopic space, using a parameter called $D^{206/206/208Pb}$ (Jackson et al., 2014),
 414 which is expressed as:

$$415 \quad \left[\left(\frac{{}^{206}\text{Pb}/{}^{204}\text{Pb}_S - {}^{206}\text{Pb}/{}^{204}\text{Pb}_R}{X} \right)^2 + \left(\frac{{}^{207}\text{Pb}/{}^{204}\text{Pb}_S - {}^{207}\text{Pb}/{}^{204}\text{Pb}_R}{Y} \right)^2 + \left(\frac{{}^{208}\text{Pb}/{}^{204}\text{Pb}_S - {}^{208}\text{Pb}/{}^{204}\text{Pb}_R}{Z} \right)^2 \right]^{0.5}$$

417 Where R=reference, S=sample, and X, Y and Z represent the absolute difference in the measured
 418 maximum and minimum values (See Jackson et al., 2014 for further details). In a plot of $\Delta^{33}\text{S}$
 419 and $\Delta^{36}\text{S}$ versus $D^{206/207/208Pb}$ for Vai trend lavas (figure 5a,b), $\Delta^{33}\text{S}$ increases and $\Delta^{36}\text{S}$ shows an
 420 increasing range (with lower extreme values) with increasing distance (higher $D^{206/207/208Pb}$) from
 421 the Common component. This relationship demonstrates sulfur isotope mixing among samples in
 422 the Vai trend and shows that increased distance from the Common component towards the
 423 HIMU component results in an increasing contribution of recycled sulfur. $\Delta^{33}\text{S}$ variations are
 424 only produced during low-temperature fractionation processes (e.g. Johnston et al. 2011; Ono et
 425 al., 2012; Farquhar et al., 2014). Therefore, the $\Delta^{33}\text{S}$ -isotope composition from HIMU related
 426 basalts unambiguously requires a contribution of sulfur that was once surface-derived.

427 Although the variations are linked to HIMU components, it is important to emphasize
 428 that the isotopic composition observed is different from those observed in many HIMU OIB

429 elsewhere, where either negative or no $\Delta^{33}\text{S}$ variation is observed (e.g. Cabral et al., 2013; Labidi
430 et al., 2013; Beaudry et al., 2018). The HIMU reservoir, if made of ancient subducted oceanic
431 crust that has been devolatilized, may not be intrinsically homogeneous for S-isotopes as there
432 are resolvable isotopic differences observed at present between the lower oceanic crust
433 (dominated by hydrothermal sulfides, $\delta^{34}\text{S}=+3$, $\Delta^{33}\text{S}=0$; Alt, 1993) and the upper altered oceanic
434 crust (dominated by biogenic sulfides, $\delta^{34}\text{S}=\text{variable}$, $\Delta^{33}\text{S}$ up to +0.16, Ono et al., 2012).
435 However, we acknowledge uncertainty in these compositions as the composition of modern
436 oceanic crust may not be a perfect analogue for oceanic crust in deep time. Such diversity in the
437 S-isotope composition of HIMU related materials is reflected by HIMU-influenced MORBs and
438 the Canary Islands showing no resolvable $\Delta^{33}\text{S}$ variations (Beaudry et al. 2018, Labidi et al.,
439 2014) with rather positive $\delta^{34}\text{S}$ signatures, whereas HIMU at Mangaia whole rock lavas show
440 both negative and positive $\Delta^{33}\text{S}$ anomalies with $\delta^{34}\text{S}$ signatures far lower than the upper mantle
441 (Dottin et al. 2020a).

442 Given the magnitude and direction of the ^{33}S composition at Vailulu'u, it is possible that
443 there is a link between recycled S at Mangaia and the recycled diluted HIMU component at
444 Samoa. However, the major differences in $\delta^{34}\text{S}$ of bulk sulfide measurements (down to ~ -5 ‰ at
445 Mangaia, up to $\sim +2$ at Vailulu'u) and $^{206}\text{Pb}/^{204}\text{Pb}$ (nearly 22 at Mangaia, and just ~ 19.4 at
446 Vailulu'u) make drawing a direct connection complicated, and in fact, may instead suggest that
447 the Samoan HIMU component is most closely linked to the HIMU components characterized at
448 HIMU influenced MORB (Labidi et al. 2014) and the Canary Islands (Beaudry et al. 2018). We
449 may however be able to draw a connection to their materials through relative age constraints.
450 The relative age of the recycled S in Samoa can be illustrated through plots of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$.
451 In this space, Archean sulfur typically plot on a slope of -1, while Proterozoic and Phanerozoic

452 sediments plot on a steeper slope of approximately -7 (e.g. Johnston, 2011). Dottin et al. (2020b)
453 show that the data from Vailulu'u plot on a slope of ~ -7 , which is best attributed to a
454 contribution of post-Archean sulfur at Samoa. Similarly, at Mangaia, bulk S measured in olivine-
455 and clinopyroxene-hosted melt inclusions from pooled magmatic phenocrysts demonstrate a
456 contribution from Proterozoic sulfur (Dottin et al., 2020a). Such commonality in the age of
457 recycled sulfur suggests that at HIMU localities with resolvable $\Delta^{33}\text{S}$, the recycled S is usually of
458 post-Archean nature and the crustal protolith with Archean S that is argued to exist on the basis
459 of large negative $\Delta^{33}\text{S}$ down to -0.35 (Cabral et al., 2013) measured in individual sulfides from
460 Mangaia basalts may not be widely distributed among mantle plumes.

461 4.3.3 The Malu trend: The EM II component

462
463 An extensive dataset from the Malu trend, which is formed by mixing the Samoan
464 Common component with EM II, has been published by Labidi et al. (2015). Additional samples
465 from the Malu trend are presented here with analyses of two additional submarine samples from
466 Malumalu and analyses of two submarine samples from Malutut, another seamount on the Malu
467 volcanic trend. In general, samples from the Malu trend exhibit no resolvable $\Delta^{33}\text{S}$ (-0.003 to
468 0.010) or $\Delta^{36}\text{S}$ (-0.01 to 0.27) and have positive $\delta^{34}\text{S}$ (1.73 to 2.79) (Labidi et al., 2015; this
469 study). ALIA 108-04 is an exception that may have experienced degassing, exhibiting relatively
470 high $\delta^{34}\text{S} = +4.84 \pm 0.30\text{‰}$ and $\Delta^{33}\text{S} = 0.008 \pm 0.008\text{‰}$.

471 The $\delta^{34}\text{S}$ compositions of Samoan basalts from the Malu and Vai trend were previously
472 shown to be correlated with radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (Labidi et al., 2015). This relationship is used to
473 define what is termed the "Mantle-Array" that links MORB S-isotope compositions to EM II S-
474 isotope compositions through mixing with a Proterozoic sedimentary protolith that hosts a $\delta^{34}\text{S}$

475 composition of +10 ‰ and a high S/Sr ratio of 17 (Labidi et al., 2015). A sample analyzed in this
476 study from Malumalu (78-1) has $^{87}\text{Sr}/^{86}\text{Sr}$ that is more radiogenic than samples previously
477 analyzed for S-isotopes and offers an opportunity to test whether the hypothesized crustal
478 protolith is best associated with the material proposed by Labidi et al. (2015). In figure 6 we plot
479 $\delta^{34}\text{S}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for all submarine samples analyzed in Labidi et al. (2015), Dottin et al.
480 (2020b) and this study (subaerial samples, which have experienced significant degassing and
481 fractionation of $\delta^{34}\text{S}$, are not plotted in Figure 6). Interestingly, the most positive $\delta^{34}\text{S}$ is a
482 western Samoan lava dredged at Savai'i that has $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7125, the most extreme high
483 $^{87}\text{Sr}/^{86}\text{Sr}$ EM II lavas characterized for S isotopes. With the exception of the potentially degassed
484 sample from Malutut (ALIA108-04; see Section 4.1.1), our data appear to be consistent with the
485 model proposed by Labidi et al. (2015), demonstrating that $\delta^{34}\text{S}$ increases with increasing
486 $^{87}\text{Sr}/^{86}\text{Sr}$.

487 On a plot of $\Delta^{33}\text{S}$ versus $D^{206/207/208\text{Pb}}$, the Malu trend data do not reproduce a relationship
488 like that seen for the Vai trend (figure 5c): $\Delta^{33}\text{S}$ does not vary at a given $D^{206/207/208\text{Pb}}$. The lack of
489 any anomalous $\Delta^{33}\text{S}$ associated with Malu trend basalts confirms previous suggestions that the
490 EM II component has $\Delta^{33}\text{S} = 0$ (Labidi et al. 2015). This value is distinct from those associated
491 with the Vai trend. Furthermore, when we consider the strongly positive $\delta^{34}\text{S}$ of the Malu-trend
492 basalts (relative to Vai basalts), the S-isotope composition of Malu basalts is unambiguously
493 different from the Vai trend basalts and confirms the Samoan mantle plume is geochemically
494 zoned in terms of recycled components.

495 4.3.4 Rejuvenated Lavas – the EM I component

496
497 Volcanism at Samoa consists of a shield stage that is followed by a period of quiescence
498 (~1 Ma; Reinhard et al., 2019), and lastly, rejuvenated volcanism. At Samoa, subaerial
499 rejuvenated volcanism occurs on the islands of Savai'i, Upolu, and Tutuila, which are located >
500 180 km from the current location of the Samoan mantle plume (which is inferred to lie below the
501 volcanically-active Vailulu'u seamount). The source of rejuvenated volcanism at Samoa is not
502 well understood, but has been discussed elsewhere (Natland, 1980; Workman et al., 2004;
503 Konter and Jackson, 2012; Reinhard et al., 2019). It has been proposed that rejuvenated
504 volcanism at Samoa may be driven by mantle melting from plate flexure of the lithosphere due to
505 subduction at the Tonga Trench (Konter and Jackson, 2012; Natland, 1980). Others have
506 proposed that the Samoan rejuvenated volcanism may be driven by decompression melting of the
507 lithosphere and westwardly swept Samoan plume material due to subduction induced mantle
508 upwelling and toroidal flow around the down going Pacific lithosphere (Strak and Schellart,
509 2018). Although at this time we cannot discount the hypothesis of the latter proposal, the
510 hypothesis is difficult to reconcile with the Pb and S isotope geochemistry and the current
511 location of the Samoan mantle plume. The EM I component in Samoan rejuvenated lavas is not
512 observed in shield lavas and these materials are erupted > 180 km away from active plume
513 upwelling. The Pacific lithosphere in the Samoan region was argued to have passed over the
514 Cook-Austral hotspots (which have erupted volcanoes that host EM I signatures), including the
515 EM I Rarotonga hotspot, prior to passage over the Samoan hotspot. The Cook-Austral hotspots
516 may have contributed EM I mantle compositions to the lithosphere, and thus may be the source
517 of the dilute EM I- type mantle signatures of Samoan rejuvenated lavas (Jackson et al., 2014;
518 Konter and Jackson, 2012). While the presence of a distinct Rarotonga hotspot is currently

519 uncertain (Chauvel et al., 1997; Jackson et al., 2020), this hypothesis provides a possible
 520 mechanism for generating the EM I signature in Samoan rejuvenated lavas. Regardless of the
 521 origin of EM I, we can use S-isotopes to constrain the source of the materials erupted during
 522 Samoan rejuvenated volcanism.

523 We present data on rejuvenated basalts ($N = 6$) from Samoa that are from the Savai'i,
 524 Upolu, and Tutuila Islands and test whether rejuvenated basalts exhibit evidence for a
 525 contribution from a sulfur source that is distinct from that associated with the Samoan mantle
 526 plume. With the exception of ALIA 116-04 ($\delta^{34}\text{S}=1.99$, $\Delta^{33}\text{S}=0.017$, and $\Delta^{36}\text{S} = -0.076$), a
 527 submarine rejuvenated lava, all data on Samoan rejuvenated lavas are from subaerial eruptions
 528 and have compositions that range from -0.28 to 1.28, -0.018 to 0.011, and -0.14 to 0.38 in $\delta^{34}\text{S}$,
 529 $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ respectively. Upo-7A exhibits the lowest measured $\Delta^{33}\text{S}$ (-0.018 ± 0.008) at
 530 Samoa to date. Note, as discussed in Section 4.2, the $\delta^{34}\text{S}$ compositions in the subaerial lavas
 531 likely do not reflect that of the parental melt composition due to degassing. Therefore, we focus
 532 solely on the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in this portion of the discussion, but we do note that the single
 533 submarine rejuvenated lavas—ALIA 116-04—does have a positive $\delta^{34}\text{S}$ (1.99) value that
 534 suggests the mantle source of Samoan rejuvenated lavas has a positive $\delta^{34}\text{S}$ composition.

535 The rejuvenated lavas analyzed in this study do not span a wide range of $D^{206/207/208\text{Pb}}$.
 536 Consequently, in plots of $\Delta^{33}\text{S}$ versus $D^{206/207/208\text{Pb}}$, the data reveal significant variation of $\Delta^{33}\text{S}$
 537 within a narrow range of $D^{206/207/208\text{Pb}}$ ($D^{206/207/208\text{Pb}} = 0.5$ to 0.7 , figure 5e). The behavior of $\Delta^{33}\text{S}$
 538 at a given $D^{206/207/208\text{Pb}}$ is different from that observed for sulfur associated with the Malu and Vai
 539 trends. Like arguments made for the Malu trend and Vai trend data, when mixing with the
 540 Common component, any relationships should converge on $\Delta^{33}\text{S}=0$ at low values of the distance
 541 parameter ($D^{206/207/208\text{Pb}}$). Considering $\Delta^{33}\text{S}$ values measured in rejuvenated lavas do not

542 converge on $\Delta^{33}\text{S}=0$ as the distance parameter decreases it is possible that the EM I component is
543 isotopically heterogeneous (it has both positive and negative $\Delta^{33}\text{S}$) and is not mixing with a
544 significant amount of the common plume component, if any at all; extreme high $^3\text{He}/^4\text{He}$
545 signatures have never been identified in any Samoan rejuvenated lavas, including those with low
546 $\text{D}^{206/207/208\text{Pb}}$ that plot close to the Common component, consistent with the hypothesis that the
547 rejuvenated lavas may not sample the Samoan plume's high $^3\text{He}/^4\text{He}$ Common component. As
548 far as we know, the distinctly negative $\Delta^{33}\text{S}$ values are among the first observed with gas source
549 mass spectrometry in a magmatic system (with one observation at Mangaia, Cabral et al. 2013).

550 Nonetheless, the significant variability in $\Delta^{33}\text{S}$ among rejuvenated lavas suggests that the
551 origin of EM I component at Samoa is associated with the incorporation of surface derived
552 materials. Again, this is because $\Delta^{33}\text{S}$ variations are widespread in sedimentary materials of all
553 age (e.g. Johnston, 2011) and no $\Delta^{33}\text{S}$ variations are known to be produced strictly by mantle
554 processes. S with variable $\Delta^{33}\text{S}$ may be of recycled origin reflecting either biogenic sulfur (which
555 generates relatively small magnitude $\Delta^{33}\text{S}$ anomalies) or sulfur fractionated through UV-
556 photolysis (which generates large magnitude $\Delta^{33}\text{S}$ anomalies). Note, that sulfur derived from UV
557 photolysis would require the observed sulfur to be of Archean age, whereas biogenic sulfur can
558 be of nearly any age (Farquhar et al., 2000, 2007). Our data show rejuvenated lavas are
559 consistent with a post-Archean relationship for $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ (Figure 3b).

560 Whether the rejuvenated S-isotope composition observed at Upolu is related to the
561 compositions at EM I-flavored Pitcairn remains an outstanding question. At Pitcairn, Delavault
562 et al. (2016) report negative $\Delta^{33}\text{S}$ (down to $-0.85\text{‰} \pm 0.13$) on sulfides from Pitcairn basalts
563 measured via SIMS that are linked to recycled Archean sulfur. In contrast, Discovery lavas,
564 another EM I type hotspot, shows $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values that are strictly indistinguishable from

565 0‰ (Labidi et al., 2013), suggesting the EM I S isotope composition is variable. The negative
566 $\Delta^{33}\text{S}$ composition in UPO-7A (-0.018) is in the correct direction if trying to link to EM I
567 components at Pitcairn. However, the magnitude of the $\Delta^{33}\text{S}$ and the measured $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ in the
568 Samoan EM I would suggest that here, S is instead of post-Archean origin. This signature is
569 distinct from Pitcairn, where Archean sulfur is required, and is distinct from Discovery, where
570 $\Delta^{36}\text{S}-\Delta^{33}\text{S}$ signatures indistinguishable from average MORB were observed (Labidi et al., 2013).

571 Our unique $\Delta^{33}\text{S}$ signatures may potentially be linked to the proposed metasomatized
572 lithospheric mantle beneath the Savai'i and Upolu islands. Hauri et al. (1993) observed extreme
573 carbonatite metasomatism in mantle peridotite xenoliths hosted in Samoan rejuvenated lavas,
574 interpreted to reflect modification of oceanic lithospheric mantle beneath Samoa by carbonatite
575 melts derived from the Samoan plume (Hauri and Hart, 1994). Note, however that our observed
576 $\Delta^{33}\text{S}$ variability is different from that observed in mantle xenoliths with EM signatures ($\Delta^{33}\text{S}= 0$
577 to $+0.10\pm 0.08\%$ (Giuliani et al., 2016)) but may be linked to a separate source of material.
578 Konter and Jackson (2012) argued that prior passage of the oceanic mantle lithosphere over
579 another plume (e.g., Rarotonga) may have imparted a geochemically heterogeneous signature on
580 the lithosphere before it arrived in the Samoan region, separating the rejuvenated lava signature
581 from those erupted during the shield stage associated with the Samoan mantle plume. If Samoan
582 rejuvenated lavas sample the oceanic mantle lithosphere, the metasomatic signatures in the
583 lithosphere beneath Samoa may be reflected in S isotope compositions. In order to satisfy
584 observations of a distinct S-isotope composition potentially linked to young biogenic sulfides
585 without an influence from Samoan plume material, a post-Archean subduction zone could have
586 delivered biogenic sulfides into the deep mantle (Luguet et al., 2008), where the sulfides were
587 subsequently entrained by an upwelling plume (not necessarily associated with the Samoan

588 plume, but one associated with Rarotonga, for example) and transported to the surface.
589 Subsequently, tectonic stresses associated with the subducting and tearing of the Pacific plate
590 would have contributed to mobilizing this metasomatized lithosphere component, which was
591 melted and contributed to Samoan rejuvenated lavas (Konter and Jackson, 2012; Reinhard et al.,
592 2019).

593 **5 Conclusions**

594

- 595 • We present S-isotope compositions on basalts from the Vai Trend, Malu Trend, Upo
596 Trend, and rejuvenated basalts to test for unique S-isotope compositions associated with
597 each islands' associated geochemical trend. Most data collected, including those with
598 DM-like components, show $\Delta^{33}\text{S}$ values within uncertainty of the origin $\Delta^{33}\text{S}=0$.
599 Exceptions are seen in two samples from the Vai trend and two in rejuvenated lavas.
- 600 • The different compositional trends appear to have unique S-isotope characteristics that
601 we link to multiple recycled S sources. Through the use of the Pb distance parameter, we
602 argue that S is also geochemically zoned, resulting in unique S isotope compositions
603 delivered to distinct groups of islands.
- 604 • As previously argued in Dottin et al (2020b), the anomalous $\Delta^{33}\text{S}$ in the Vai trend is
605 linked to recycled HIMU related sulfur that is mixed with sulfur associated with the
606 Common component ($\Delta^{33}\text{S}=0$). Here we show, that the HIMU component is spatially zoned
607 from the Common component and other recycled materials in the Samoan plume.
- 608 • From Malu trend basalts we confirm assertions by Labidi et al., (2015) who argue that the
609 EM II component is heavily influenced by a continental crustal component with strongly
610 positive $\delta^{34}\text{S}$ (estimated at + 10‰) and S/Sr of 17 that define the “Mantle-Array”. We

611 show that the array extends out to $\delta^{34}\text{S}$ values of $\sim +5\%$ seen in a Savai'i submarine
 612 shield stage lava, that suggest the $\delta^{34}\text{S}$ is of the EM II component is indeed much more
 613 positive than that measured in basalts from Malumalu.

- 614 • The data collected on Rejuvenated lavas show both positive and negative $\Delta^{33}\text{S}$ associated
 615 with recycled EM I materials. The $\Delta^{33}\text{S}$ variability suggests a separate source of S is
 616 contributed during rejuvenated volcanism. We argue that the variability may be linked to
 617 subducted EM I components associated with a different slab system that were upwelled
 618 and rafted into the Samoan region.

619

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627

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Figure Captions

749 Figure 1. Map of Samoa. Stars denote islands or seamounts of samples characterized in this
 750 project. This map was generated using the GeoMap App.
 751

752 Figure 2. $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot of Samoan basalts highlighting the geochemical trends
 753 (Vai, Malu, DM, and Rejuvenated) and the Common component after Jackson et al. (2014). We
 754 also highlight the samples analyzed (symbols with full color) for this study to demonstrate the
 755 variety of compositions analyzed. Large symbols represent spiked Pb isotope measurements via
 756 TIMS (Thermal Ionization Mass Spectrometry) and MC-ICPMS (Multi Collector-Inductively
 757 Coupled Mass Spectrometry). Small symbols represent un-spiked Pb isotope TIMS data. The
 758 shaded regions are a representation of the 99% confidence interval around the best fit line plotted
 759 through each group of data (Jackson et al. 2014). Note that we do not plot data from MORB and
 760 Hawaii like that shown in Jackson et al. (2014)-this results in the grey shaded region extending
 761 further past what is plotted here.

762 Figure 3. Sulfur isotope data for reduced sulfur from Samoan basalts. A.) $\Delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ of
 763 Samoan basalts. B.) $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ of Samoan basalts. Data presented are from this study (whole
 764 rock powders), Labidi et al. (2015) (glasses) and Dottin et al. (2020b) (whole rock powders).
 765 Error bars represent 2 sigma uncertainty. Large symbols indicate sulfide data from whole rocks
 766 (Dottin et al. 2020b, this study). Small symbols indicate sulfide data from glasses (Labidi et al.
 767 2015). Note that we have not removed subaerial lavas from this plot which are highly degassed
 768 and likely have modified $\delta^{34}\text{S}$ compositions. Muli is renamed as Tupito. The slopes plotted
 769 represent the slope for the Archean ($m = -1$) and post-Archean ($m = -7$) sedimentary rock data
 770 compilations (e.g. Johnston, 2011).

771

772

773 Figure 4. $\Delta^{33}\text{S}$ of each sample and their associated geochemical trend. Data from the Vai Trend
 774 and Malu trend include data collected in Labidi et al. (2015) and Dottin et al. (2020b). Large
 775 symbols represent whole rock analyses. Small symbols represent glasses. S isotope data are from
 776 reduced sulfur in whole rocks and glasses. Muli is renamed as Tupito.

777

778 Figure 5. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ versus $D^{206,207,208\text{Pb}}$ for basalts from the Vai trend, Malu trend, and
 779 rejuvenated lavas. $D^{206,207,208\text{Pb}}$ data is from Jackson et al. (2014). S -isotope data are from Dottin
 780 et al. (2020b), Labidi et al. (2015) and this study. Data from the Vai trend illustrate an increase in
 781 $\Delta^{33}\text{S}$ and decrease in $\Delta^{36}\text{S}$ with increasing distance from the Common component. Malu trend
 782 basalts outline essentially no trend among the samples. The rejuvenated lavas show a steeper
 783 relationship between $\Delta^{33}\text{S}$ and $D^{206,207,208\text{Pb}}$ than that seen in the Vai trend, and potentially does
 784 not converge on a compositional relationship that involves significant influence from the
 785 Common component with $\Delta^{33}\text{S}=0$. Muli seamount is renamed as Tupito. S isotope data are from
 786 reduced sulfur in whole rocks and glasses. For each panel, note the difference in scales on the Y-
 787 axis which are set to best illustrate the degree of isotopic variation (or lack thereof).

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789

790 Figure 6. $\delta^{34}\text{S}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for Samoan basalts analyzed in this study and Dottin et al.,
 791 (2020b) (large symbols represent whole rock analyses) and Labidi et al. (2015) (small symbols
 792 represent glasses). MORB data from Labidi et al. (2013). Subaerial basalts are omitted from this
 793 plot as they likely host modified $\delta^{34}\text{S}$. Large symbols from the Vai and Malu trends represent
 794 whole rock analyses. Small symbols from the Vai and Malu trends represent glasses. MORB data
 795 are from glasses. All other data (rejuvenated lavas and Savai'i submarine lavas) are whole rock
 796 analyses. All S isotope data are from extracted sulfide.

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798

799 Table 1. Compilation of S-isotope compositions for Samoan basalts

Sample	Dredge Depth (m)	Location	S (ppm)	$\delta^{34}\text{S}$		$\Delta^{33}\text{S}$		$\Delta^{36}\text{S}$	
				$\delta^{34}\text{S}$	2σ	$\Delta^{33}\text{S}$	2σ	$\Delta^{36}\text{S}$	2σ
<i>Rejuvenated Lavas</i>									
UPO-7A	subaerial	Upolu	45	0.28	0.30	0.018	0.008	0.31	0.30
S 11	subaerial	Savai'i	28	0.94	0.30	0.006	0.008	-0.14	0.30

	S 15	subaerial	Savai'i	15	1.26	0.30	0.011	0.008	0.03	0.30
	S 12	subaerial	Savai'i	31	0.37	0.30	0.014	0.008	0.27	0.30
	S 32M	subaerial	Savai'i	83	1.28	0.30	0.010	0.008	-0.13	0.30
	S 26S	subaerial	Savai'i	52	0.15	0.30	0.008	0.008	0.38	0.30
	ALIA 116-04	2510	Savai'i	655	1.99	0.30	0.017	0.008	-0.08	0.30
<i>Upo Volcanic Lineament</i>										
	U 16	subaerial	Upolu	11	0.09	0.30	0.000	0.008	0.12	0.30
	U19	subaerial	Upolu	9	0.29	0.30	0.009	0.008	0.14	0.30
	TUT 99-01	subaerial	Tutuila	69	1.76	0.30	0.006	0.008	-0.17	0.30
<i>Malu Volcanic Lineament</i>										
	AVON3-78-1	2264	Malumalu	361	1.73	0.30	0.000	0.008	-0.05	0.30
	AVON3-76-9	2393	Malumalu	449	1.79	0.30	0.003	0.008	0.01	0.30
†	AVON3-77-1	3605	Malumalu	393	1.97	0.30	0.004	0.008	-0.01	0.30
*	AVON3-76-11	2393	Malumalu	1693	2.79	0.24	0.010	0.010	0.059	0.18
*	AVON3-76-13	2393	Malumalu	1289	1.55	0.24	0.005	0.010	0.271	0.18
*	AVON3-76-3	2393	Malumalu	1348	2.00	0.24	0.008	0.010	0.099	0.18
*	AVON3-76-6	2393	Malumalu	1514	2.45	0.24	0.006	0.010	0.211	0.18
*	AVON3-76-8	2393	Malumalu	1435	1.98	0.24	0.009	0.010	0.129	0.18
	ALIA108-04	3200	Malutut	81	4.84	0.30	0.008	0.008	-0.06	0.30
<i>Vai Volcanic Lineament</i>										
†	OFU-04-15	subaerial	Ofu	64	4.23	0.30	0.001	0.008	0.22	0.30
†	OFU-04-06	subaerial	Ofu	29	1.08	0.30	0.004	0.008	0.13	0.30
	AVON3-71-22 (Avg)	4170	Vailulu'u	1038	1.97	0.30	0.016	0.008	-0.19	0.3
†	AVON3-63-2	920	Vailulu'u	809	1.23	0.30	0.019	0.016	-0.47	0.30
†	AVON3-70-9	1130	Vailulu'u	201	2.30	0.30	0.027	0.016	-0.22	0.30
†	AVON3-73-1	960	Vailulu'u	214	1.88	0.30	0.01	0.008	-0.02	0.30
*	AVON3-71-13	4170	Vailulu'u	1755	1.52	0.24	0.010	0.010	0.063	0.18
*	AVON3-71-11	4170	Vailulu'u	1794	1.62	0.24	0.001	0.010	0.017	0.18
*	AVON3-71-2	4170	Vailulu'u	1768	1.26	0.24	0.005	0.010	0.020	0.18
*	AVON3-68-3	780	Vailulu'u	800	0.35	0.24	0.008	0.010	0.106	0.18

*	AVON3-73-12	960	Vailulu'u	600	0.11	0.24	0.022	0.010	0.112	0.18
*	AVON3-75 2	2675	Ta'u	651	1.18	0.24	0.002	0.010	0.030	0.18
*	AVON3-75-10	2675	Ta'u	819	0.62	0.24	0.001	0.010	0.072	0.18
*	AVON3-75-15	2675	Ta'u	945	1.45	0.24	0.007	0.010	-	0.18
*	AVON3-74-2	2544	Ta'u	1575	0.77	0.24	0.003	0.010		
*	AVON3-79-4	3484	Tupito	880	2.45	0.24	0.009	0.010	0.080	0.18

Submarine western Samoan lavas

	ALIA 114-03	2510	Savai'i submarine	32	1.62	0.30	0.003	0.008	-0.10	0.30
	ALIA 128-21	2560	Savai'i submarine	219	4.23	0.30	0.005	0.008	-0.12	0.30

800 † Data from Dottin et al., 2020b; * Data from Labidi et al., 2015. Avg=average of n=2 analyses

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802

Figure 1.

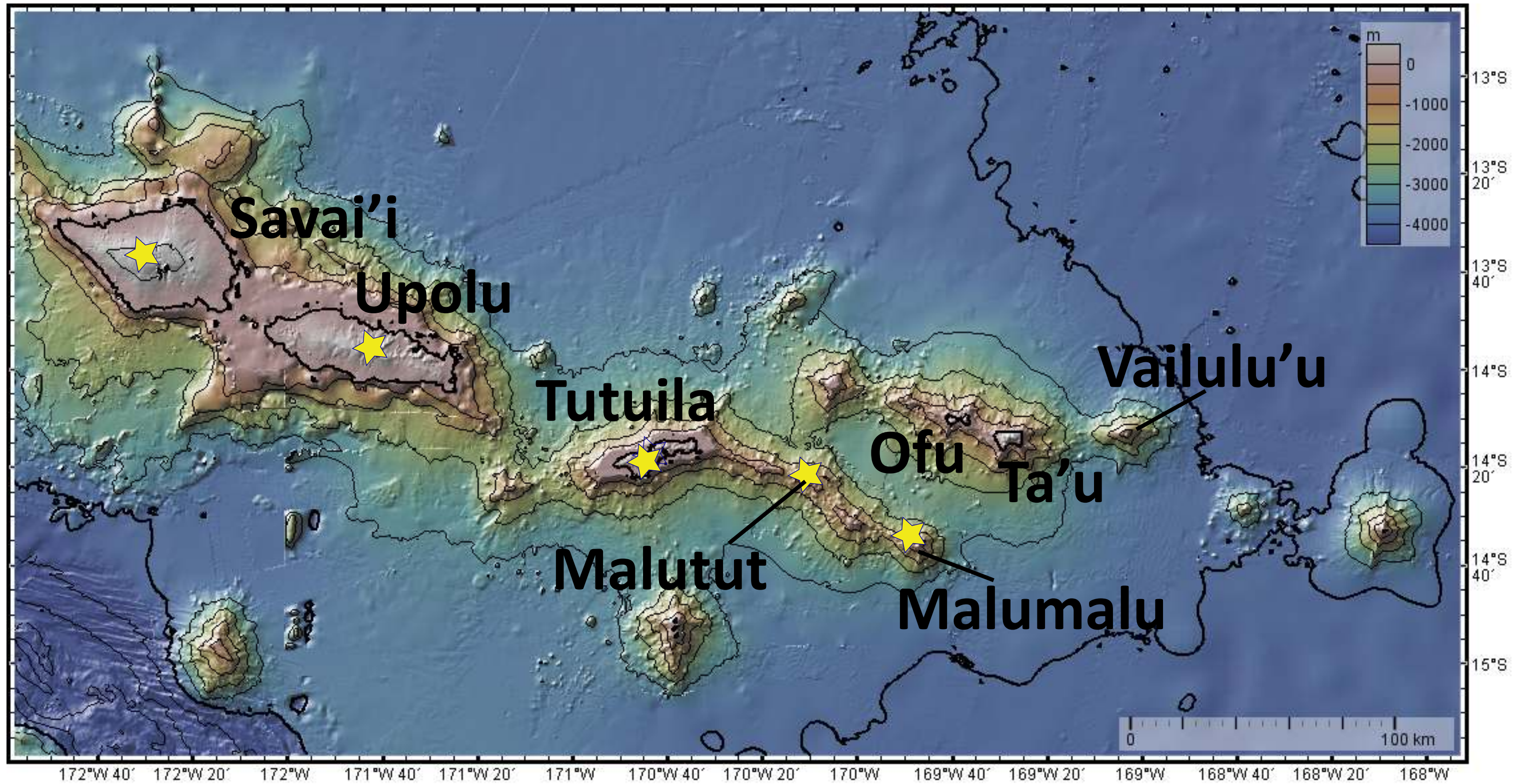
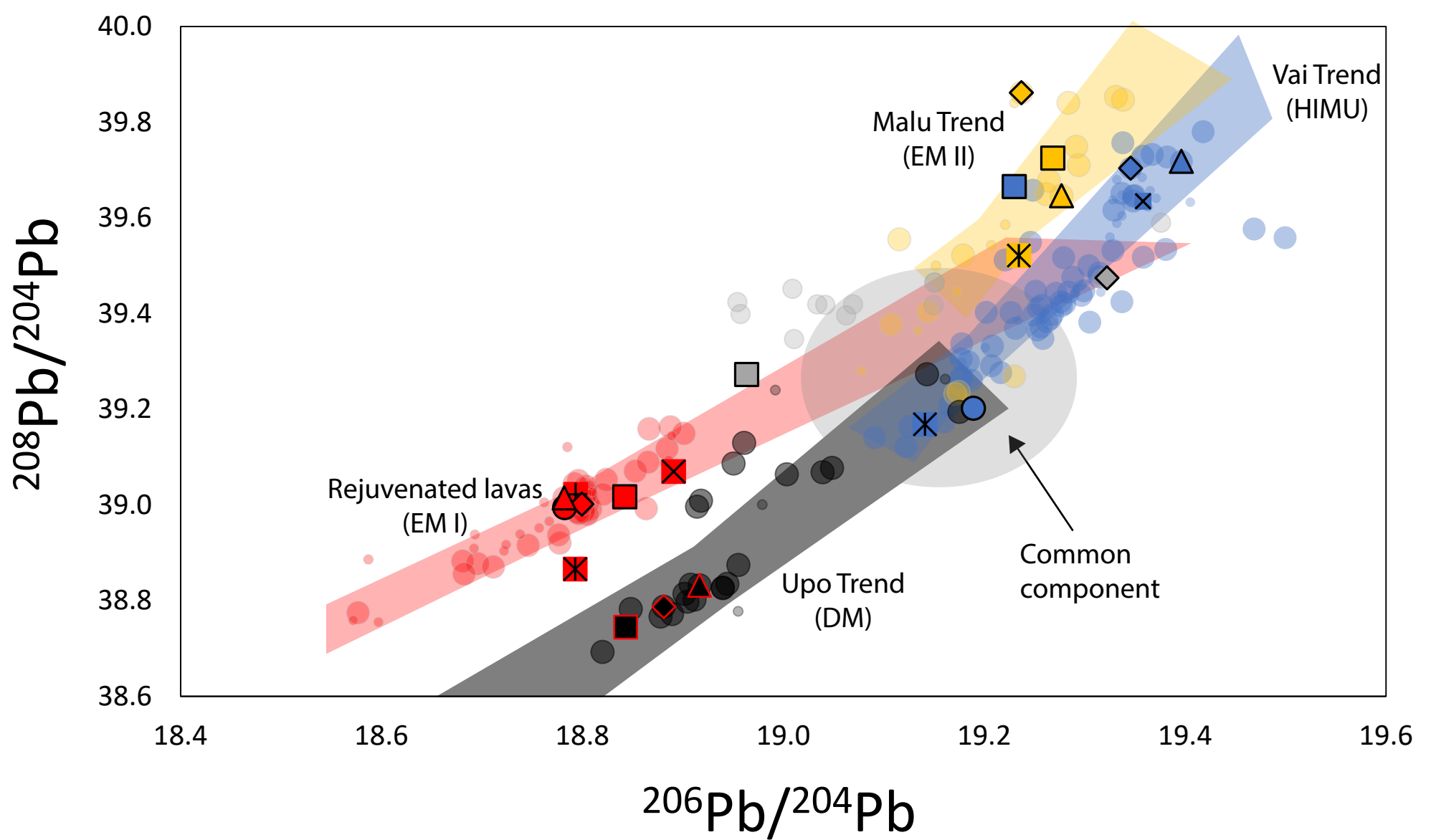
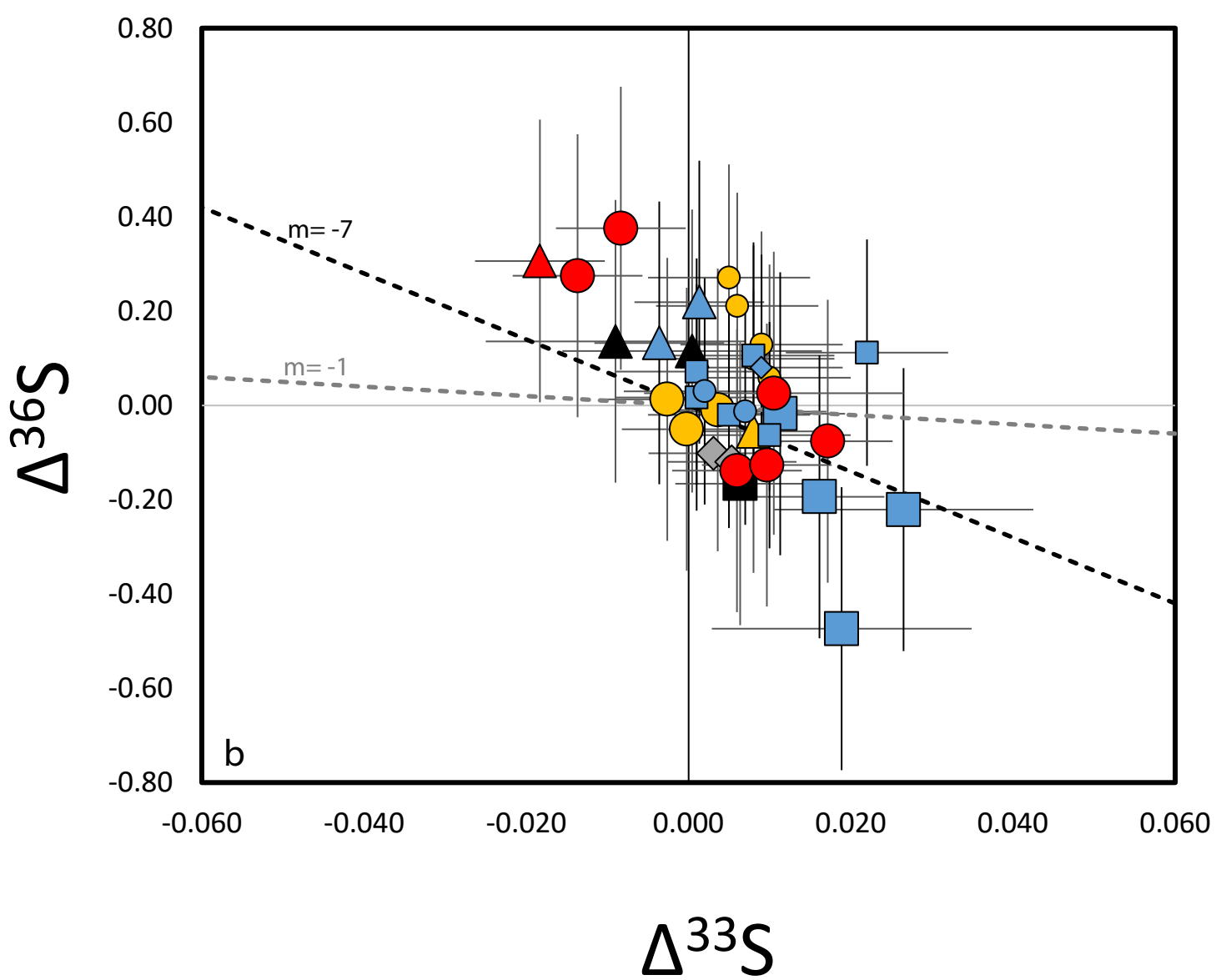
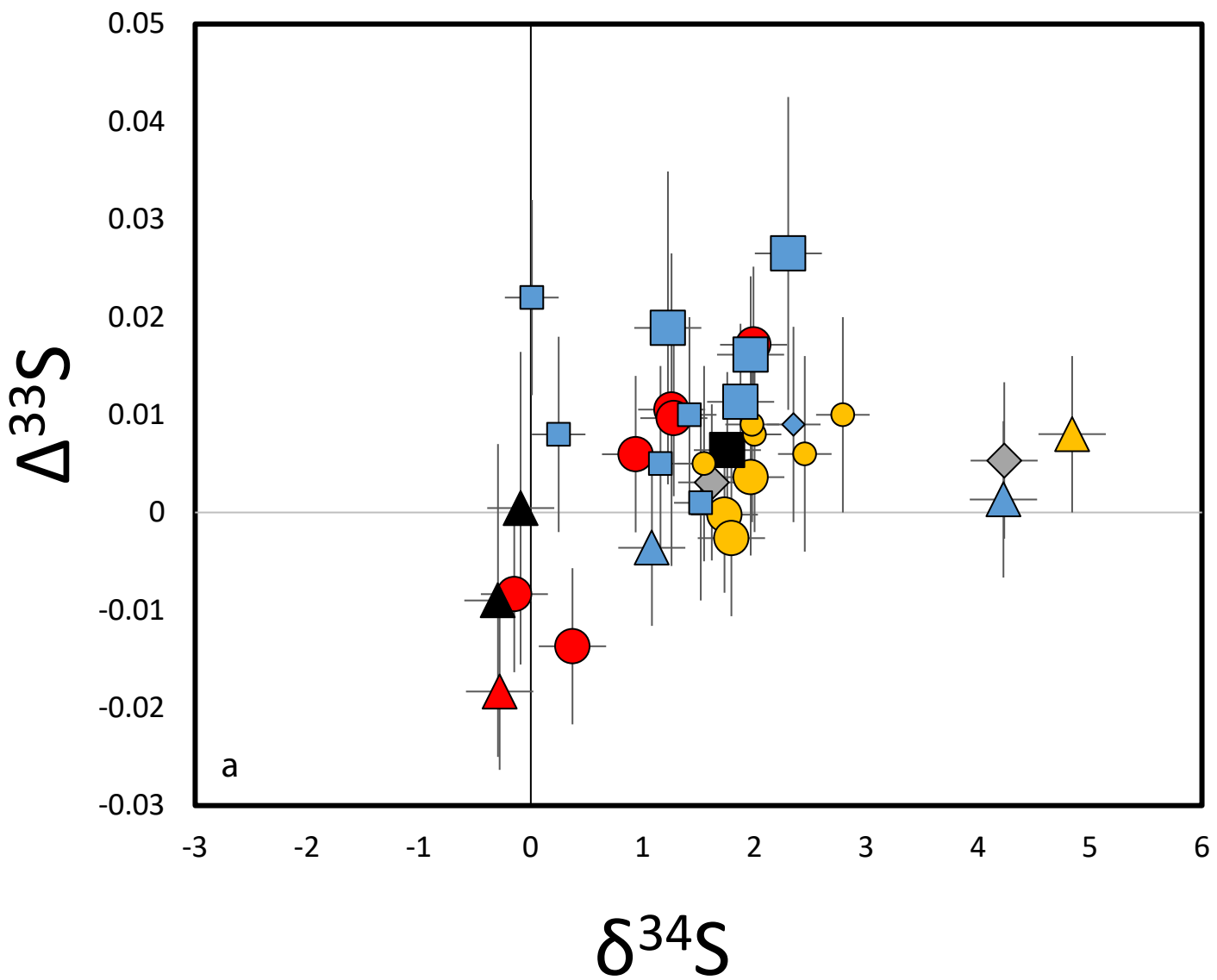


Figure 2.



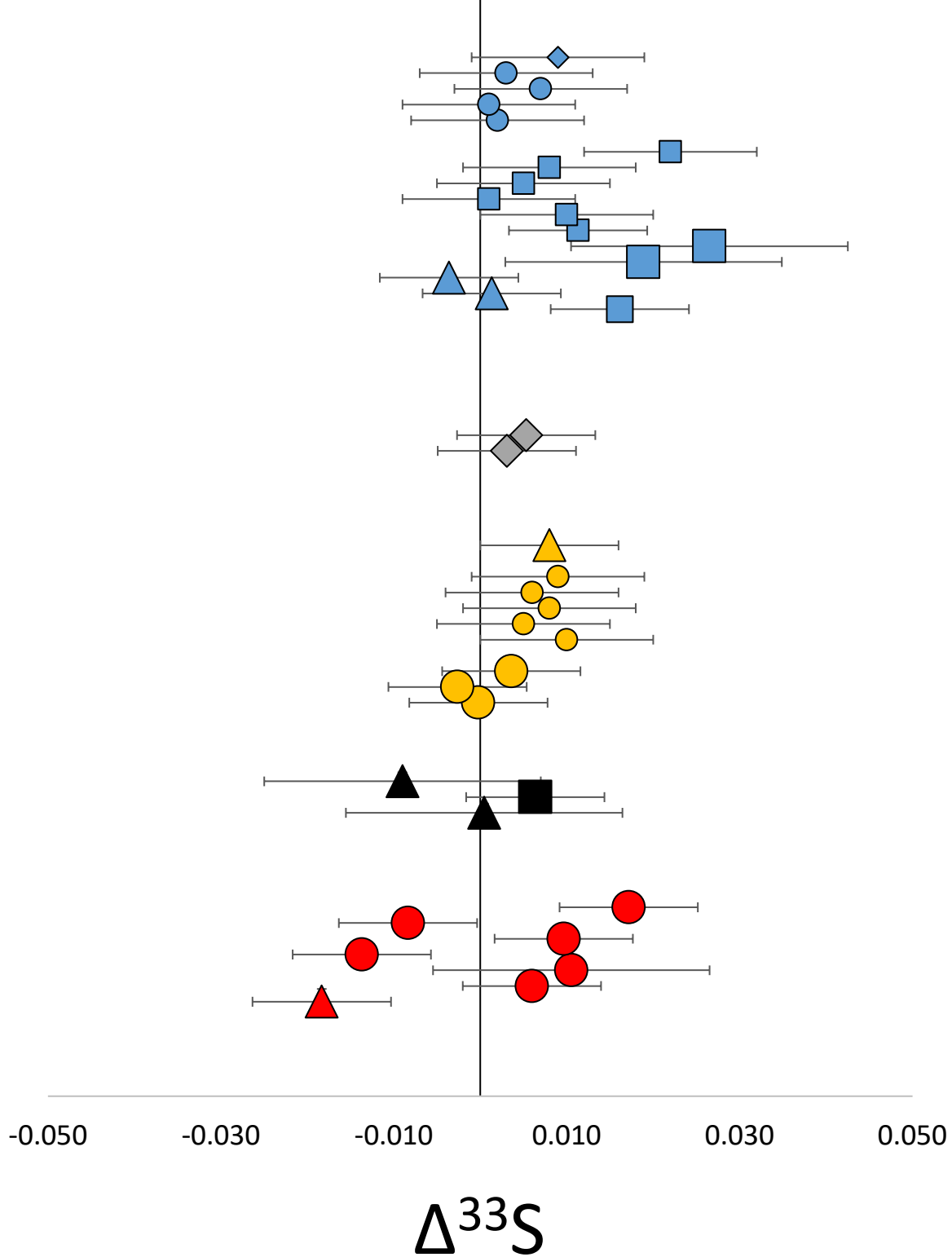
- | | | | | |
|---------------|----------------|------------|----------------------|---------------------------|
| ● Vai (HIMU) | ● Malu (EM II) | ● Upo (DM) | ● Rejuvenated (EM I) | ● Submarine Western Samoa |
| ● Ofu 05-18 | ▲ AVON3-76-9 | ■ TUT99-01 | ■ UPO-7a | ◆ ALIA 114-03 |
| ✱ Ofu 04-15 | ■ AVON3-77-1 | ◆ U16 | ◆ S 11 | ■ ALIA 128-21 |
| ■ AVON3-73-1 | ◆ AVON3-78-1 | ▲ U19 | ◆ S 12 | |
| ▲ AVON3-70-9 | ✱ ALIA 108-04 | | ■ S 15 | |
| ✱ AVON3-71-22 | | | ✱ S 26S | |
| ◆ AVON3-63-2 | | | ■ S 32M | |
| | | | ▲ ALIA 116-04 | |

Figure 3.



- | | | | |
|---------------------------|--------------------|---|----------------------------|
| ● Tau-glass |] Vai Trend (HIMU) | ▲ Upolu rejuvenated-whole rock |] Rejuvenated Lavas (EM I) |
| ◆ Tupito-glass | | ● Savai'i rejuvenated-whole rock | |
| ■ Vailulu'u-glass | | ● Malumalu-glass |] Malu Trend (EM II) |
| ■ Vailulu'u-whole rock | | ● Malumalu-whole rock | |
| ▲ Ofu-whole rock | | ▲ Malutut-whole rock | |
| ▲ Upolu-whole rock |] Upo Trend (DM) | ◆ Savai'i submarine shield stage-whole rock | |
| ■ Tutuila Pago-whole rock | | | |

Figure 4.



- | | | | |
|---------------------------|-----------------------|---|-------------------------------|
| ● Tau-glass |] Vai Trend
(HIMU) | ▲ Upolu rejuvenated-whole rock |] Rejuvenated Lavas
(EM I) |
| ◆ Tupito-glass | | ● Savai'i rejuvenated-whole rock | |
| ■ Vailulu'u-glass | | ● Malumalu-glass |] Malu Trend
(EM II) |
| ■ Vailulu'u-whole rock | | ● Malumalu-whole rock | |
| ▲ Ofu-whole rock | | ▲ Malutut-whole rock | |
| ▲ Upolu-whole rock |] Upo Trend
(DM) | ◆ Savai'i submarine shield stage-whole rock | |
| ■ Tutuila Pago-whole rock | | | |

Figure 5.

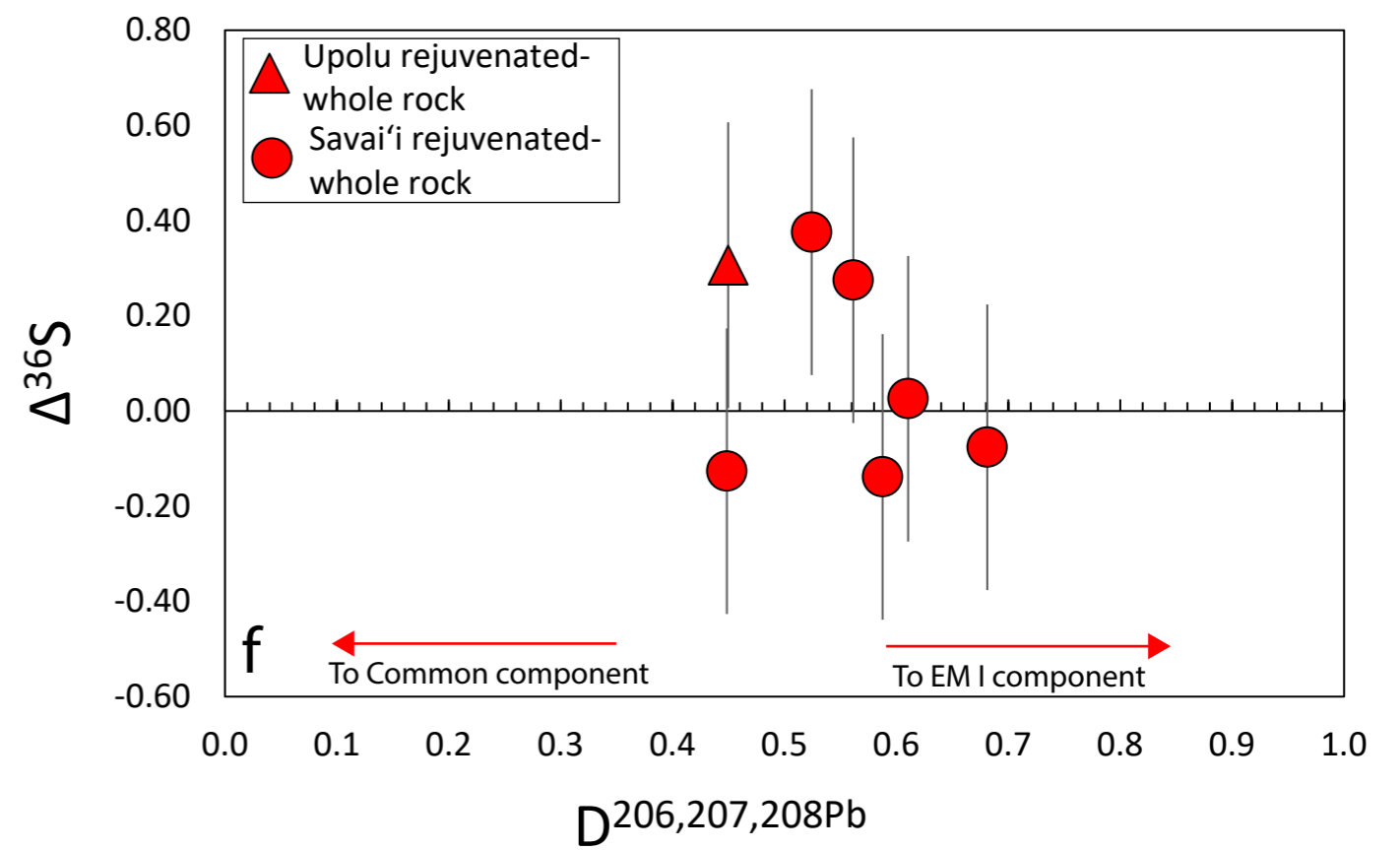
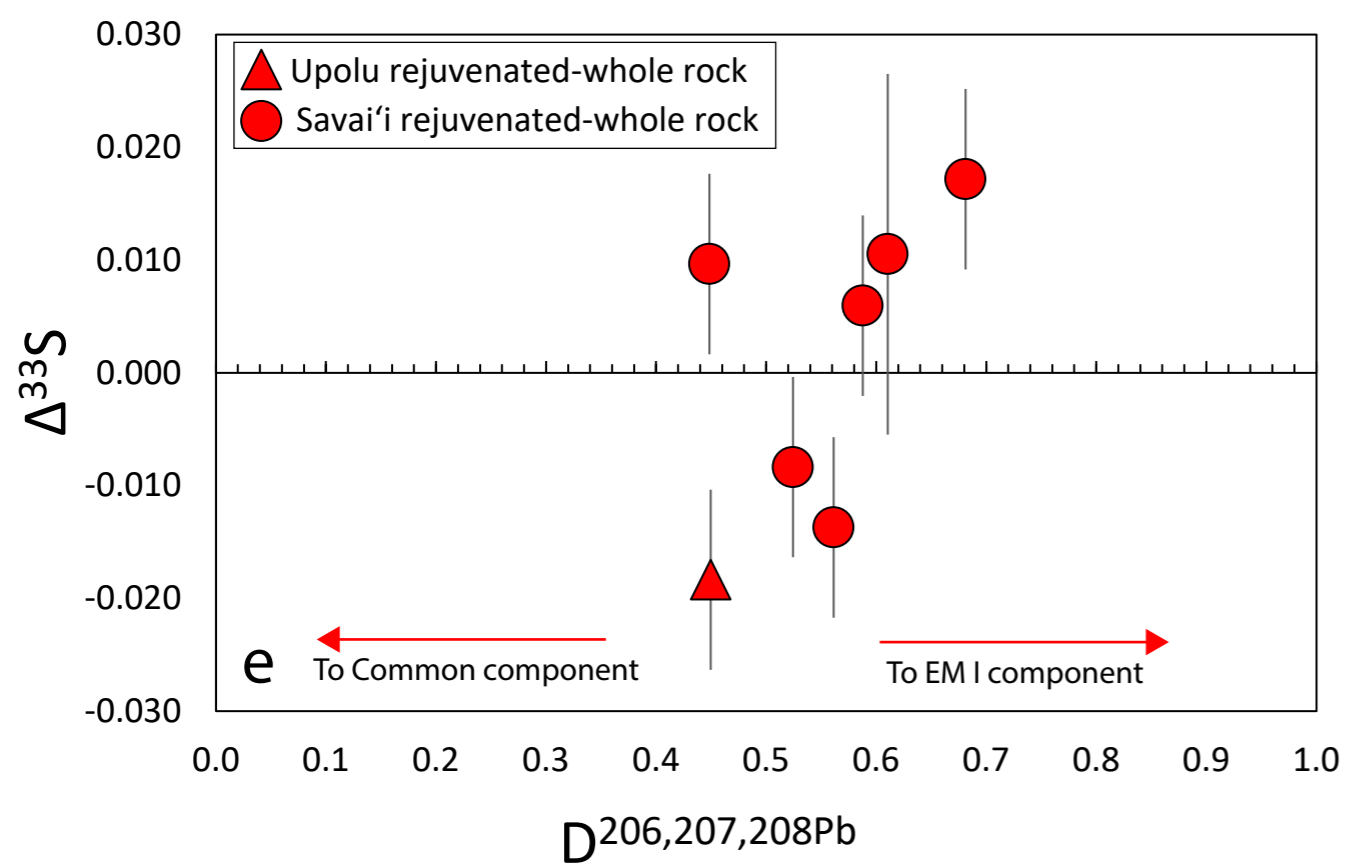
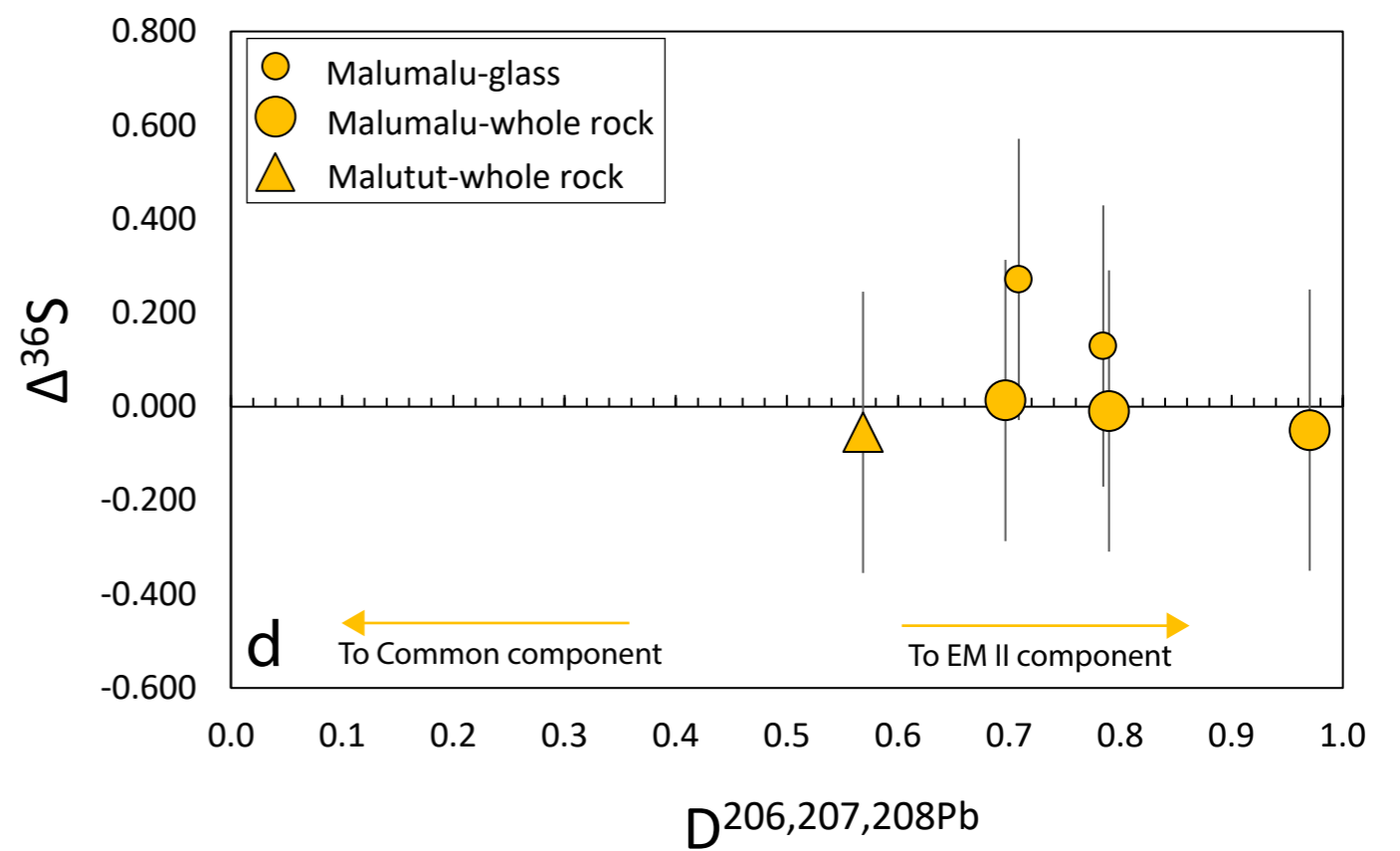
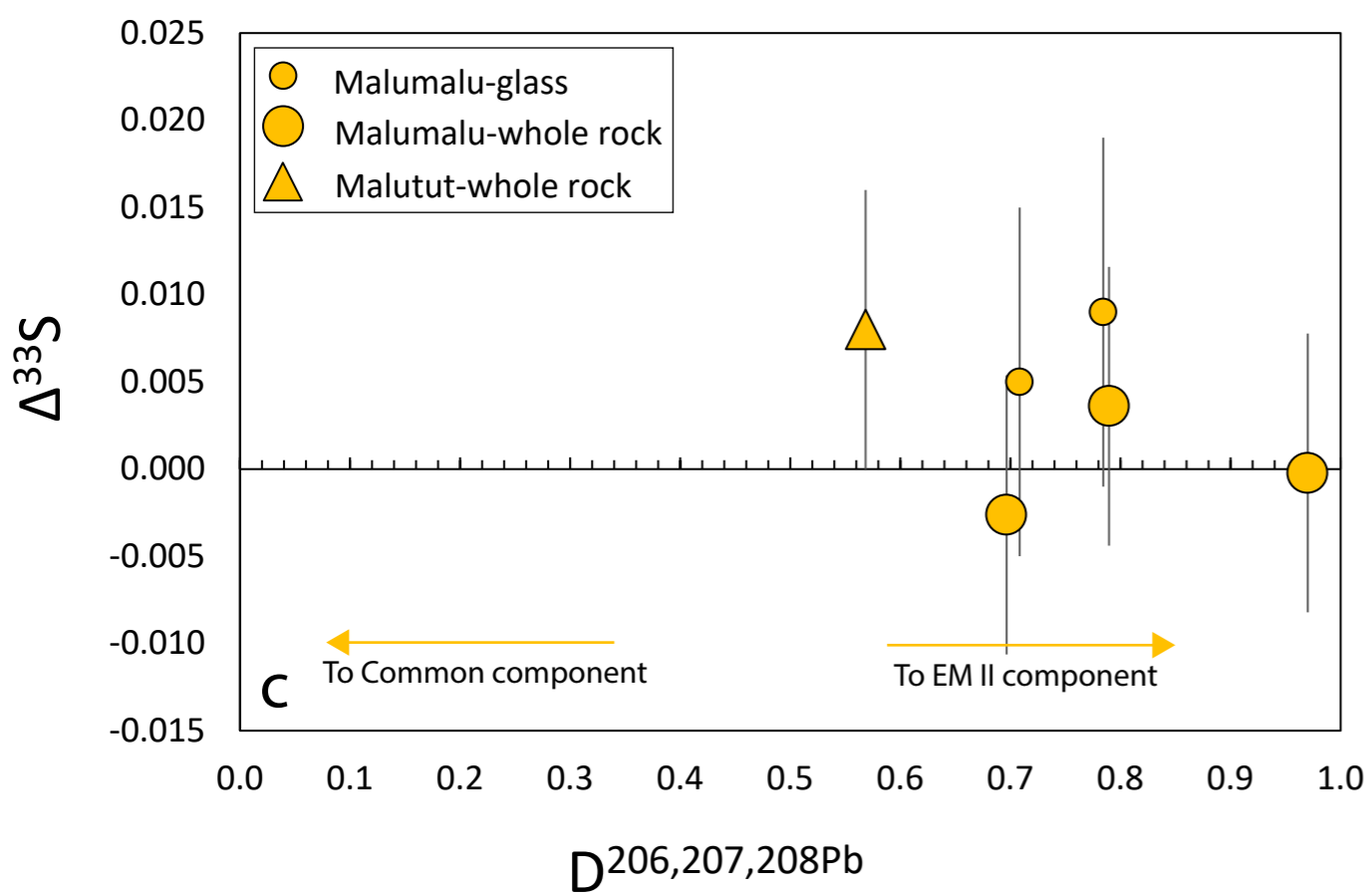
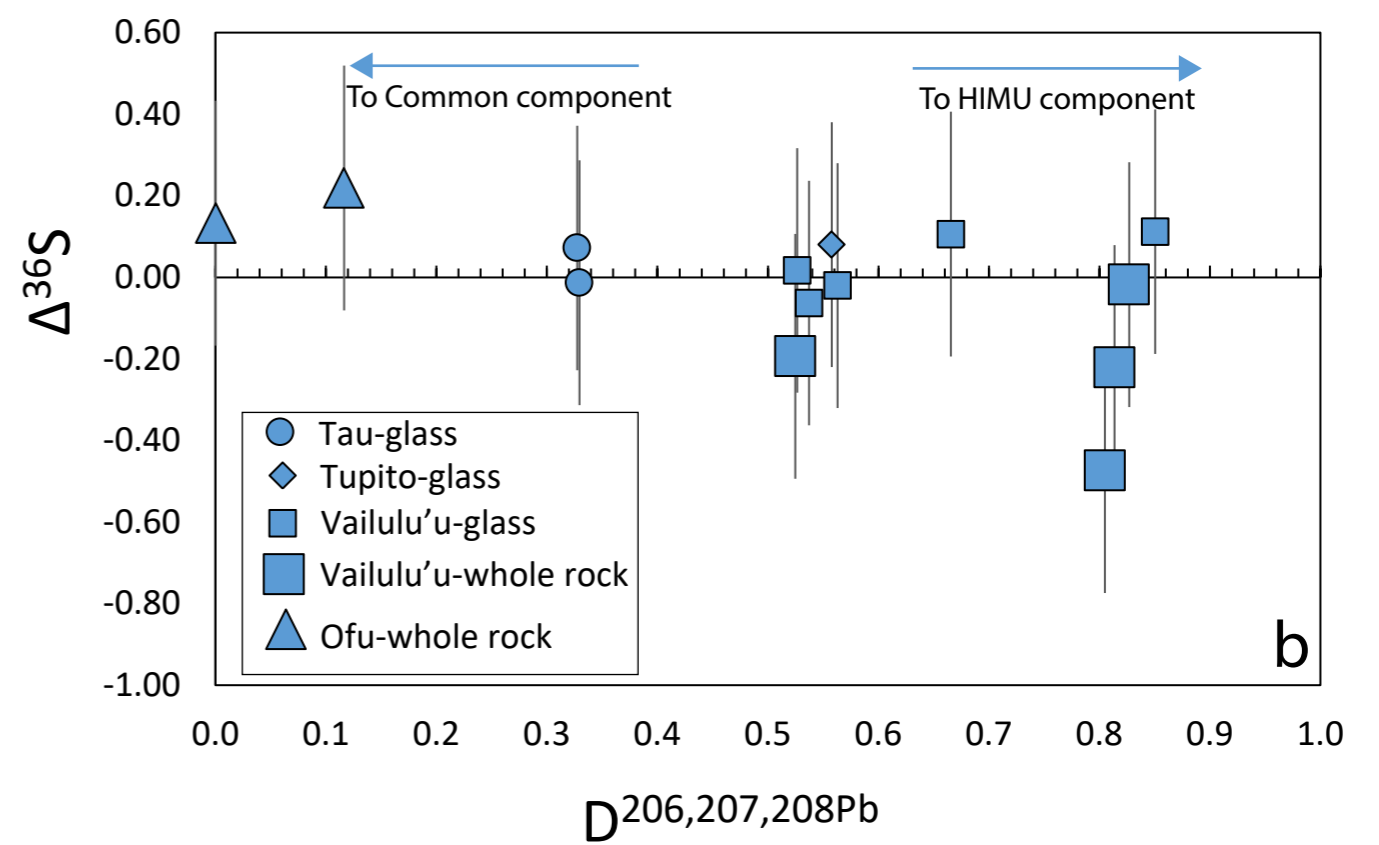
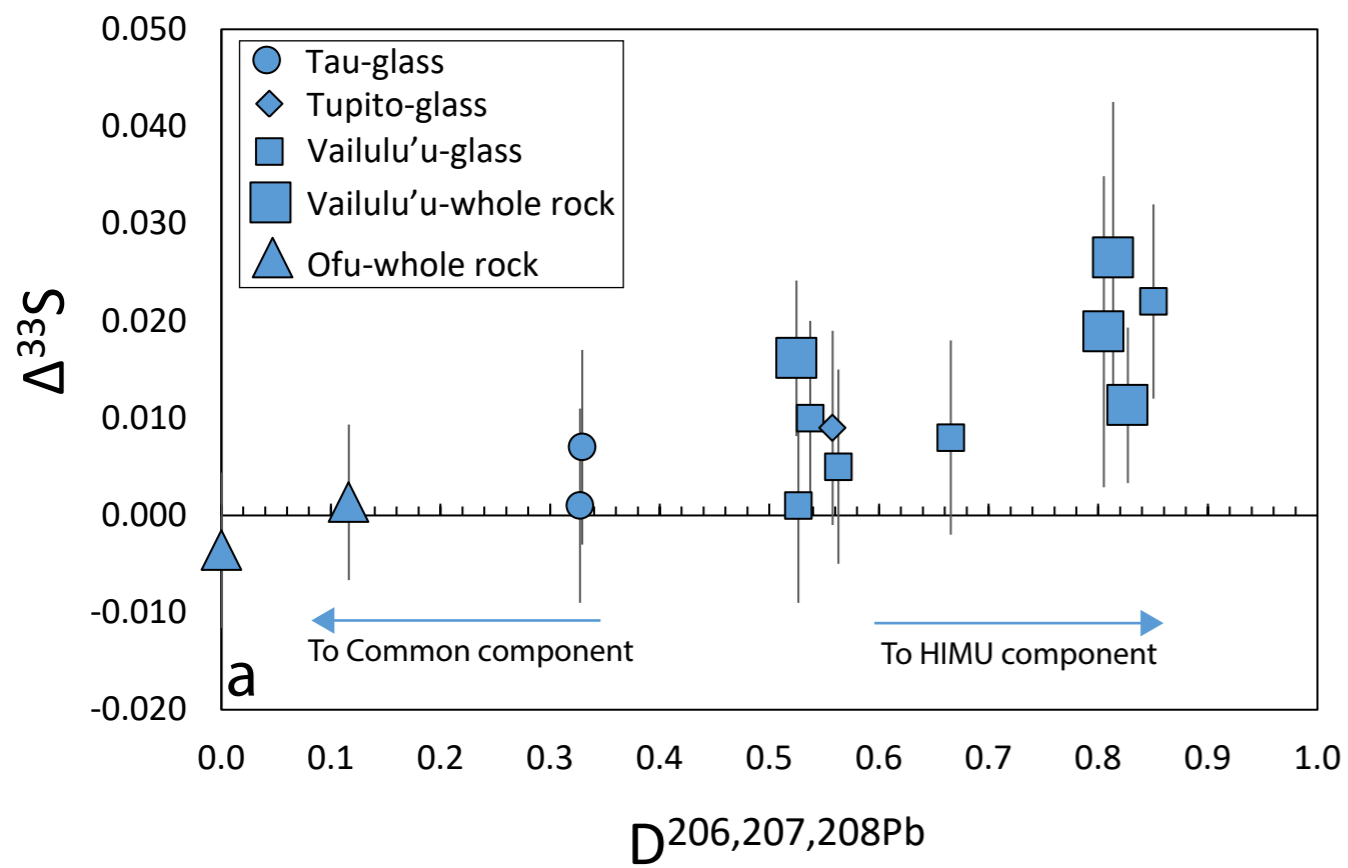
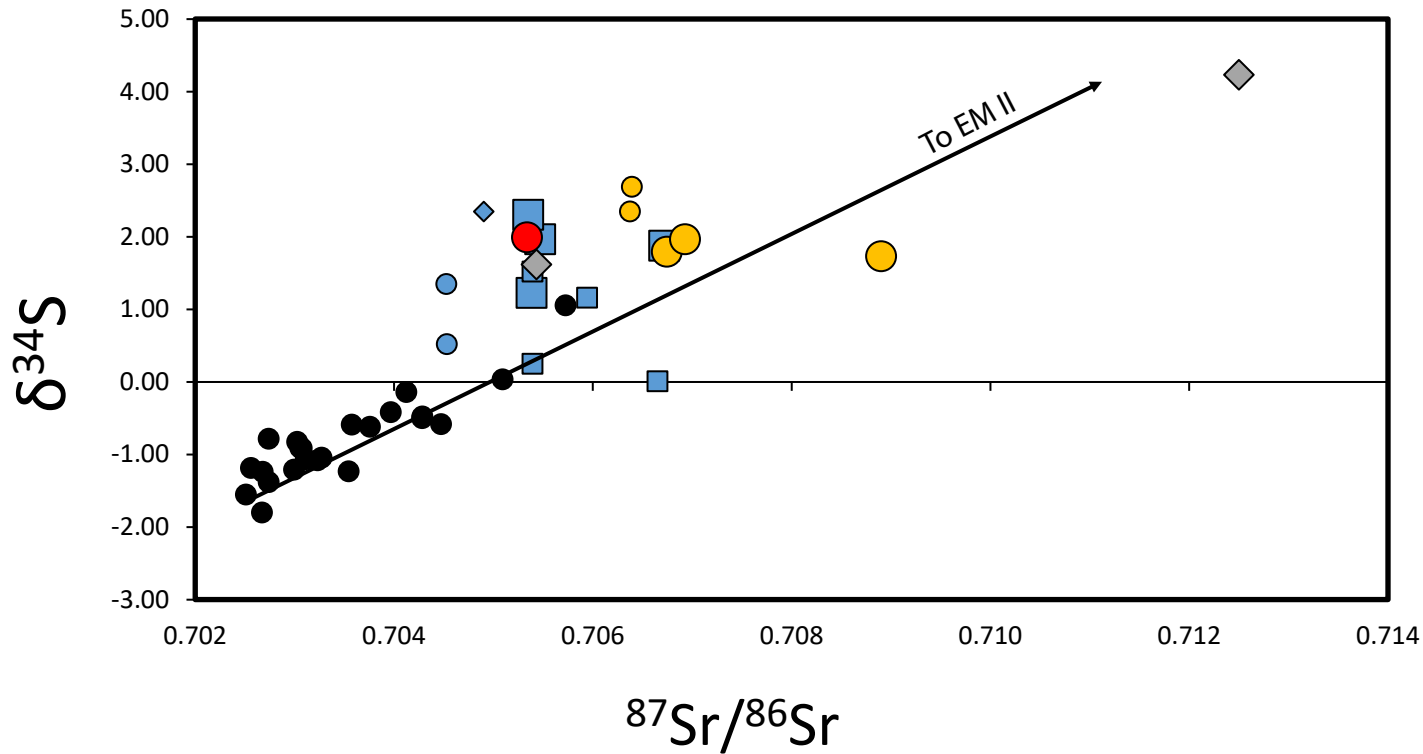


Figure 6.



● Tau-glass

◆ Tupito-glass

■ Vailulu'u-glass

■ Vailulu'u-whole rock

Vai
(HIMU)

● Malumalu-glass

● Malumalu-whole rock

Malu
(EM II)

◆ Savai'i submarine shield stage

● Savai'i rejuvenated-whole rock

Rejuv.
(EM I)

● MORB-glass