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## Near-zero $^{33}\text{S}$ and $^{36}\text{S}$ anomalies in Pitcairn basalts suggest Proterozoic sediments in the EM-1 mantle plume

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26 a  $\sim 1\text{‰}$   $^{34}\text{S}$  enrichment compared to Pacific upper mantle. The  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$   
27 signatures average at  $+0.024\pm 0.007\text{‰}$  and  $+0.02\pm 0.07\text{‰}$  vs. CDT, respectively  
28 (all  $1\sigma$ ). Only  $\Delta^{33}\text{S}$  is statistically different from MORBs, by  $+0.02\text{‰}$ . The  $\Delta^{33}\text{S}$   
29 enrichment is invariant across degassing and sulfide segregation. We suggest it  
30 reflects a mantle source enrichment rather than a high-temperature fractionation  
31 of S in the basalts. Despite the small magnitude of the  $^{33}\text{S}$ - $^{36}\text{S}$  variations, our data  
32 require a substantial amount of recycled sulfur overwhelm the Pitcairn mantle  
33 source. We show that models involving metasomatized peridotites, lower crust  
34 units, or Archean sediments, may be viable, but are restricted to narrow sets of  
35 circumstances. Instead, scenarios involving the contribution of Proterozoic  
36 marine sediments appear to be the most parsimonious explanation for the EM-1  
37 signature at Pitcairn.

38

## 39 **1. Introduction**

40 Ocean Island Basalts (OIB) sample a variety of mantle reservoirs, often deep  
41 seated in Earth's mantle (Weis et al., 2011). Erupted basalts at volcanic islands and  
42 seamounts originate from the partial melting of upwelled mantle sources, and  
43 reveal a complex history of the deep mantle. The isotopic compositions of basalts  
44 show that OIB mantle sources incorporate both primordial noble gases  
45 (Mukhopadhyay, 2012; Mukhopadhyay and Parai, 2019; Parai et al., 2019) as well  
46 as lithophile elements that are evidently recycled from Earth's surface (Weis et al.,  
47 2011; Willbold and Stracke, 2006).

48 Pitcairn is an island in the South-Pacific ocean, with basalts that host

49 moderately primordial neon (Honda and Woodhead, 2005) associated with a  
50 notoriously radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  signature, at some of the least  
51 radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  (Woodhead and Devey, 1993). This signature is coined  
52 Enriched Mantle 1 (EM-1) and likely results from recycling crustal components  
53 into a mantle source (Zindler and Hart, 1986). The EM-1 signature requires a low  
54 time-integrated  $^{238}\text{U}/^{204}\text{Pb}$  associated with high time-integrated  $^{87}\text{Rb}/^{86}\text{Sr}$  and  
55  $^{234}\text{Th}/^{238}\text{U}$ . Various crustal materials have been proposed as the recycled material,  
56 including but not limited to a metasomatized lithospheric mantle, oceanic  
57 sediments, and components from the lower continental crust (Chauvel et al., 1992;  
58 Eisele et al., 2002; Gibson et al., 2005; Turner et al., 2017; Willbold and Stracke,  
59 2006; Woodhead et al., 1993).

60 Sulfur isotope signatures may place constraints on the type of material  
61 recycled into the Pitcairn mantle plume. Ion probe measurements on sulfide  
62 inclusions in olivine, plagioclase, and the matrix from submarine pillow interiors  
63 (Delavault et al., 2016) show negative  $^{33}\text{S}$  anomalies, down to  $-0.85 \pm 0.25\%$ . This  
64 requires surface-derived sulfur of Archean age is hosted within the Pitcairn  
65 mantle source (Delavault et al., 2016). The available ion-probe dataset however  
66 lacks  $^{36}\text{S}$  measurements. Given that Archean sediments have unique  $^{33}\text{S}$ - $^{36}\text{S}$   
67 relationships compared to Proterozoic rocks (Farquhar et al., 2007; Johnston,  
68 2011), determining  $\Delta^{36}\text{S}$  would allow testing relative age difference among  
69 various recycled materials in the mantle. In order to better constrain the origin of  
70 sulfur in the Pitcairn source, we use gaseous source mass spectrometry in dual  
71 inlet mode and document high-precision  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and importantly  $\Delta^{36}\text{S}$   
72 signatures of Pitcairn basalts. We evaluate whether crustal, peridotite and/or

73 sedimentary components contribute to the EM-1 mantle source erupted at  
74 Pitcairn.

75

## 76 **2. Samples**

77 The Pitcairn hotspot is located in the south Pacific, on oceanic crust that is  
78 approximately 25 million years old. Active submarine volcanoes are located about  
79 80 km east of the island of Pitcairn (Hekinian et al., 2003). The active seamounts  
80 offer fresh basaltic glassy material that may host geochemical characteristics of  
81 the hotspot. Our Pitcairn samples are fresh glasses from the Polynaut cruise  
82 (1999). We analyzed glassy rims of pillow basalts sampled with the *Nautilé*  
83 submersible from the flanks of Bounty, Adam and “volcano 5”, at various depths  
84 between 3,100 and 1,000 meters below seawater level (Hekinian et al., 2003).

85

## 86 **3. Methods**

87 Sulfur was extracted for isotopic analysis via wet chemistry (Labidi et al.,  
88 2012). Briefly, centimeter size pieces of glassy basalts were chosen, cleaned and  
89 crushed to a grain size < 63 microns. The samples were digested in 20 mL of 2.1  
90 M CrCl<sub>2</sub> solution with 5 ml of 12 M HCl and 5 ml of 29 M HF in a Teflon vessel under  
91 continuous flushing of pure N<sub>2</sub>. Reduced sulfur was extracted as H<sub>2</sub>S, bubbled  
92 through a water trap and subsequently into a sulfide trap filled with AgNO<sub>3</sub> (0.3  
93 M) where H<sub>2</sub>S reacted to precipitate Ag<sub>2</sub>S. Sulfate occurrence was anticipated as  
94 sulfate is often observed in OIB (Jugo et al. 2010). Here, bulk sulfur concentrations  
95 are estimated with an electron microprobe, while reduced sulfur is quantified

96 with our wet chemistry protocol (Labidi et al., 2012). Any sulfates potentially  
97 present in glasses remained in the digestion solution (Labidi et al. 2012). We infer  
98 the  $S^{2-}/S_{\text{tot}}$  ratios by mass balance, with a relative uncertainty of  $\sim 10\%$ .

99 The sulfur isotope measurements were performed using a dual inlet MAT  
100 253 gas-source mass spectrometer. Once  $\delta^{34}\text{S}$  are determined ( $n = 33, 34, 36$ ),  $\Delta^{33}\text{S}$   
101 and  $\Delta^{36}\text{S}$  are calculated ( $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000((\delta^{34}\text{S}/1000 + 1)^{0.515} - 1)$  and  $\Delta^{36}\text{S} =$   
102  $\delta^{36}\text{S} - 1000((\delta^{34}\text{S}/1000 + 1)^{1.90} - 1)$ ). Aliquots of Canyon Diablo Troilite (CDT)  
103 analyzed relative to the IPGP reference gas give average  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values of -  
104  $0.024 \pm 0.004\text{‰}$  and  $-0.13 \pm 0.04\text{‰}$  ( $1\sigma$ ,  $n=11$ ). Repeated analyses of IAEA-S1  
105 versus the IPGP in-house  $\text{SF}_6$  tank give  $\Delta^{33}\text{S} = +0.082 \pm 0.004\text{‰}$ ,  $\Delta^{36}\text{S} =$   
106  $-0.91 \pm 0.11\text{‰}$  (all  $1\sigma$ ,  $n=43$ ,  $\delta^{34}\text{S}_{\text{S1}}$  is fixed at  $-0.30\text{‰}$  and hereafter defines the V-  
107 CDT scale). In the following, all  $\delta^{34}\text{S}$  are reported against V-CDT and all  $\Delta^{33}\text{S}$  and  
108  $\Delta^{36}\text{S}$  values are anchored on the CDT scale. Ten of the basalts had their S isotope  
109 measurement replicated (supplementary table 1). Most duplicates had  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$   
110 and  $\Delta^{36}\text{S}$  values indistinguishable within  $\sim 0.1$ ,  $0.012$ , and  $0.1\text{‰}$  respectively ( $1\sigma$ ),  
111 similar to the uncertainty obtained on basalt standards (Labidi et al., 2012). The  
112 average value for replicates is given in Table 1, and raw data can be found in the  
113 supplementary online file.

114 More details on the characterization of the glasses can be found in the  
115 supplementary material. Briefly, major element, sulfur, copper and chlorine  
116 abundance analyses of the glasses were performed using electron microprobe  
117 (EMP) techniques on polished sections using a Cameca SX100 at the CAMPARIS  
118 facility (Sorbonne Université, Pierre et Marie Curie Campus) under standard  
119 conditions described elsewhere (e.g., Labidi et al., 2012). Water concentrations

120 were quantified on a vacuum line as detailed elsewhere (Clog et al., 2013, 2012).  
121 The Sr-Nd-Pb isotope ratios on a selection of Pitcairn glasses were acquired  
122 following standard techniques in the Magma-Ocean laboratory, Brest, France,  
123 following a published protocol (Mougel et al., 2014).

## 124 **4. Results**

### 125 **4.1 Major elements**

126 Samples from Adam and Bounty seamounts have MgO contents between  
127 4.5 and 6.0 wt% except for PN14-04 that has an MgO concentration of 2.6 wt%  
128 (Fig. 1). Three samples from Volcano 5 show MgO content of ~2.5 wt%.  
129 Concentrations in FeO are nearly constant at variable MgO (Fig. 1a), reflecting Fe  
130 oxides on the liquid line of descent. We also observe near-constant Al<sub>2</sub>O<sub>3</sub>  
131 concentrations of ~15 wt% across varying MgO (Table 1, Fig. Supp 1), indicating  
132 the suppression of plagioclase crystallization. These two observations are  
133 consistent with a calc-alkaline differentiation trend (Zimmer et al., 2010). All  
134 samples have high concentrations of incompatible major elements. The K<sub>2</sub>O  
135 content is > 0.8 wt% (up to 2.8 wt%), and Na<sub>2</sub>O concentrations are > 3.5% for most  
136 samples (Table 1). High concentrations of K<sub>2</sub>O and Na<sub>2</sub>O are characteristics of  
137 alkali basalts and reflect low partial melting fractions, below < 8% (Aubaud et al.,  
138 2006; Hekinian et al., 2003) as well as crystal fractionation. High K<sub>2</sub>O/TiO<sub>2</sub> ratios  
139 of ~ 0.4 are observed for samples with MgO > 4 wt%. (Fig. 1b). High K<sub>2</sub>O/TiO<sub>2</sub>  
140 likely represent a mantle source enrichment associated with the Pitcairn hotspot  
141 (Jackson and Dasgupta, 2008). For samples with MgO < 4 wt%, K<sub>2</sub>O/TiO<sub>2</sub> are even  
142 higher, likely reflecting the late onset of titanomagnetite precipitation at MgO ~

143 4% which causes  $\text{TiO}_2$  fractionation and hence increases even further the  
144  $\text{K}_2\text{O}/\text{TiO}_2$  ratios.

145

## 146 **4.2 Volatile and supporting minor elements in Pitcairn basalts**

147 We report chlorine contents of  $< 800$  ppm for all Pitcairn lavas (Table 1).  
148 Combined with  $\text{K}_2\text{O}$  abundances determined here,  $\text{Cl}/\text{K}$  ratios are  $< 0.05$  for  
149 Bounty,  $< 0.04$  for Adam, and  $< 0.02$  for volcano 5 (Table 1). Water contents range  
150 between 5,700 and 12,100 ppm. The average  $\text{H}_2\text{O}$  content is  $8304 \pm 1983$  ppm ( $1\sigma$ ).  
151 The observed  $\text{H}_2\text{O}$  concentrations are typical of OIB (Dixon et al., 2002; Workman  
152 et al., 2006) and overall higher than MORB (Clog et al., 2013; Michael, 1995;  
153 Sobolev and Chaussidon, 1996).

154 In Bounty lavas, bulk S contents vary between  $512 \pm 50$  and  $1416 \pm 50$  ppm S  
155 (Fig. 2). Among Bounty lavas, samples from dive 3 have homogeneous major  
156 element compositions, but display most of the S content variability, with values  
157 ranging from  $738 \pm 50$  to  $1416 \pm 50$  ppm S (Table 1). The glasses collected from dive  
158 3 also have S contents that are correlated with eruption depth (Fig. 3). At Adam,  
159 two glasses show S contents of  $799 \pm 50$  and  $762 \pm 50$  ppm S. At Volcano 5, two  
160 glasses show S contents of  $573 \pm 50$  and  $602 \pm 50$  ppm S.

161 The  $\text{S}^{2-}/\text{S}_{\text{tot}}$  ratios of 12 out of the 15 Pitcairn lavas are within uncertainty of  
162 1, indicating a small amount (if any) of dissolved sulfate. Three other lavas, all  
163 from Bounty, picked in the dive 3, show  $\text{S}^{2-}/\text{S}_{\text{tot}}$  ratios of  $0.76 \pm 0.04$ , indicating  
164 measurable sulfate abundances. No correlations appear between  $\text{S}^{2-}/\text{S}_{\text{tot}}$  ratios  
165 and bulk S content, or between  $\text{S}^{2-}/\text{S}_{\text{tot}}$  ratios and eruption depths.

166 In lavas with  $\text{MgO} > 4$  wt%, Cu contents range between  $60 \pm 10$  and  $33 \pm 10$

167 ppm Cu (Fig. 4). For the more evolved bounty sample (PN14-04) and lavas from  
168 volcano 5 (PN08-01 and 08-07), Cu contents are below 10 ppm.

169

#### 170 4.3 Sulfur isotopes ratios

171 Sulfur isotope ratios are given here as  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$  values for reduced  
172 S, which for most samples correspond to bulk sulfur (Fig. 5A). The  $\delta^{34}\text{S}$  values  
173 range between -1.3‰ and +1.6‰, averaging at  $-0.4 \pm 1.0$ ‰ (n=15). For Bounty,  
174  $\delta^{34}\text{S}$  values vary between -1.3‰ and +0.7‰, with an average of  $-0.7 \pm 0.7$ ‰. The  
175 2 samples from Adam have  $\delta^{34}\text{S}$  values of -1.2‰ and -1.1‰. For volcano 5, the  
176 two glasses both have  $\delta^{34}\text{S}$  values of +1.6‰. As shown on figure 5B, our  $\delta^{34}\text{S}$   
177 values do not duplicate the largely negative  $\delta^{34}\text{S}$  values on individual sulfide  
178 inclusions from Bounty pillow lavas obtained by ion probe measurements  
179 (Delavault et al., 2016).

180 Reduced sulfur displays rather homogenous  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  among all basalts (Fig.  
181 5A and Fig. 6).  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  averages are  $+0.023 \pm 0.007$ ‰ and  $+0.02 \pm 0.07$ ‰ vs.  
182 CDT, respectively (1 s.d.). Our  $\Delta^{33}\text{S}$  data are inconsistent with the substantially  
183 negative  $\Delta^{33}\text{S}$  ion probe estimates on individual sulfide inclusions (Delavault et al.,  
184 2016). For the dive 3 at Bounty, the  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  average values are  
185  $+0.026 \pm 0.004$ ‰ and  $+0.07 \pm 0.04$ ‰ (1 s.d.). The  $\Delta^{36}\text{S}$  values at Pitcairn extend to  
186 values that are somewhat higher than MORB estimates of  $-0.04 \pm 0.08$ , (1 s.d.)  
187 (Labidi and Cartigny, 2016) but average values remain similar within the  $1\sigma$  level.  
188 The  $\Delta^{33}\text{S}$  average of  $+0.023 \pm 0.007$ ‰ is distinctly higher than MORB average of  
189  $+0.007 \pm 0.006$ ‰ (1 s.d., Labidi and Cartigny, 2016) at both 1 and  $2\sigma$  confidence  
190 level. We note that the sample PN14-04, from Bounty, has a MORB-like  $\Delta^{33}\text{S}$  value.

191 Should it be excluded, the  $\Delta^{33}\text{S}$  average at Pitcairn would become  $0.024 \pm 0.006\text{‰}$ .

192 Simple t-tests on both  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values would suggest a significant  
193 difference between Pitcairn and MORB may exist, but would not take into account  
194 analytical error. We use a Monte-Carlo approach to evaluate whether the  
195 differences in the averages are statistically significant and consider analytical  
196 uncertainties. We generate simulated datasets for the MORB and Pitcairn samples,  
197 based on sampling a normal distribution for each sample with an average equal to  
198 the measured value and a standard deviation equal to the corresponding  
199 analytical uncertainty. We then run a Welch's t-test and repeat the process 10,000  
200 times. Histograms and kernel density plots are shown in Fig. 7. For  $^{36}\text{S}$ , Pitcairn  
201 melts show an average value significantly distinct ( $p < 0.05$ ) from MORBs only in  
202 40% of the simulations. Thus, we suggest MORB and Pitcairn  $\Delta^{36}\text{S}$  are not  
203 significantly different. In contrast, the means of the  $\Delta^{33}\text{S}$  values are significantly  
204 distinct ( $p < 0.05$ ) in 99.9% of the simulation runs, confirming the  $\Delta^{33}\text{S}$  enrichment  
205 at Pitcairn is statistically significant.

206

#### 207 **4.4 Radiogenic isotopes**

208 We analyzed the Sr-Pb-Nd isotopic composition with a focus on the samples  
209 from the dive 03, from the Bounty seamount, which has the least differentiated  
210 basalts. For all samples but PN14-04, the  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$   
211 ratios are homogeneous, with values ranging between 0.704466 and 0.704624,  
212 0.512537 and 0.512944, and 17.74 and 17.92, respectively (Fig. Supp 3). We  
213 observe relatively high  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ .  
214 The radiogenic isotope data are in agreement with previous work performed on

215 the same glasses (Bourdon and Van Orman, 2009), or on different samples from  
216 Pitcairn (Woodhead et al., 1993, Delavault et al, 2016). For almost all samples, the  
217 data is consistent with an extreme EM-1 endmember. Only PN14-04, from Bounty,  
218 has a  $^{206}\text{Pb}/^{204}\text{Pb}$  higher than 18.0 and a  $^{87}\text{Sr}/^{86}\text{Sr}$  lower than 0.7041 (see below).  
219 This illustrates a slightly distinct mantle source, somewhat less affected by the  
220 EM-1 signature.

221

## 222 **5. Discussion**

223 The lavas studied here underwent a complex history prior to eruption. This  
224 involves mantle source enrichment with an EM-1 component, low partial melting,  
225 magmatic differentiation following a calc-alkaline trend, and various amounts of  
226 volatile losses via degassing. Below, we constrain the magmatic behavior of sulfur  
227 in our samples and identify the respective contributions of sulfide fractionation  
228 and sulfur degassing. Ultimately, we estimate the sulfur isotope composition of the  
229 mantle source for  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$  signatures.

### 230 **5.1 Limited crustal assimilation**

231 Hydrothermal brine assimilation may be sporadically associated with  
232 contamination by hydrothermal sulfides (Labidi et al., 2014). Cl and K have a  
233 similar incompatible behavior during mantle melting and basalt differentiation  
234 (Michael and Cornell, 1998; Michael and Schilling, 1989). However, Cl is enriched  
235 in the hydrated oceanic crust and in brines. Thus, elevated Cl/K ratios in basalts  
236 are treated as evidence for crustal assimilation. Here, the Cl/K are  $< 0.05$  for  
237 Bounty,  $< 0.04$  for Adam, and  $< 0.02$  for volcano 5 (Table 1). The Cl/K for the three

238 localities are below the threshold of 0.1, above which lavas are argued to undergo  
239 contamination by Cl-rich brines (Michael and Cornell 1998). We conclude our  
240 samples unlikely assimilated hydrothermal components prior to eruption, and  
241 thus we assume their S isotope composition has remained unaffected by  
242 potentially contaminant sulfides from the crust.

243

## 244 **5.2. Sulfide saturation in Pitcairn melts**

245 Pitcairn lavas have MgO < 6 wt% (Fig. 1), indicative of substantial crystal  
246 fractionation, with near-constant FeO concentrations of ~9.5% across the range  
247 in MgO (Fig. 1). In tholeiitic basalts, FeO concentration is the prime factor  
248 controlling sulfur content at sulfide saturation (Mathez, 1976). If this relationship  
249 is at all maintained in calc-alkaline melts, one would anticipate invariable S  
250 concentrations at a particular value defined by the sulfur solubility at sulfide  
251 saturation. These are, however, not observed: we observe variation of S  
252 concentrations over almost a factor of 3 at a given FeO (or MgO) content (Fig. 2).

253 Sulfide fractionation could explain the dramatic variation in sulfur  
254 concentration in Pitcairn melts (Fig. 2). Although challenging to quantify (Jenner  
255 et al., 2010; Yierpan et al., 2019), sulfide fractionation may be singled out via the  
256 copper systematics : the partition coefficient of Cu is  $\sim 10^{-1}$  and  $\sim 10^3$  for  
257 crystal/melt and sulfide/melt, respectively (Lee et al., 2012). Thus, in the absence  
258 of sulfides on the liquidus, copper behaves as a moderately incompatible element  
259 and increases with decreasing MgO, as observed in arc-magmas and other OIB.  
260 Once sulfide saturation is met, Cu abundances drop as copper is readily  
261 partitioned into sulfides (Lee et al., 2012, Labidi et al., 2015). This behavior of Cu

262 is not observed at Pitcairn. Here, Cu concentrations appear coincidentally similar  
263 to MORBs, with a near-constant Cu concentration across most of the MgO range  
264 (Fig. 4). The data appear more consistent with a liquid line of descent that is  
265 typical of MORB, where a roughly constant rate of sulfide fractionation occurs  
266 during magmatic differentiation range (Labidi et al., 2014). We thus argue that  
267 while sulfides existed on the liquidus of Pitcairn melts, dramatic sulfide  
268 fractionation is not the cause of varying S concentration at a given FeO, observed  
269 on Fig. 2.

270

### 271 5.3. Magmatic degassing

272 Sulfur degassing could account for the variable sulfur concentrations  
273 observed on Fig. 2. We focus on samples from the dive 3 from Bounty, because  
274 these lavas are comparable in terms of major elements and radiogenic isotope  
275 compositions (Table 1), so their sulfur concentrations prior to eruption can be  
276 assumed at zero-order to be homogeneous. Basalts from the dive 3 however were  
277 erupted at various depths on the flank of the volcano (Hekinian et al., 2003).  
278 Dissolved sulfide ( $S^{2-}$ ) abundances range from  $1300 \pm 50$  ppm to  $550 \pm 50$  ppm and  
279 are correlated with the depth of eruption: the shallowest samples have the lowest  
280 S concentrations (Fig. 3). We interpret this relationship as evidence for sulfur  
281 degassing upon eruption. We quantify the residual sulfur fraction  $f$  as the ratio of  
282 the observed S concentration to the highest S concentration observed here,  $\sim 1300$   
283 ppm S. For S concentrations between  $1300 \pm 50$  ppm and  $550 \pm 50$  ppm S, we infer  $f$   
284 values are between 1 and 0.45. Note that the starting S concentration could be

285 even higher than ~1300 ppm, but this does not fundamentally change our results  
286 below.

287 Sulfur degassing is consistent with water behavior in our melts. Across  
288 decreasing depths, the H<sub>2</sub>O abundances decrease from ~9500±500 ppm to  
289 5500±500 ppm water (Fig 3). The H<sub>2</sub>O/K<sub>2</sub>O range between 0.69 and 0.35 (Table  
290 1), decreasing by a factor of ~2 across the depth rise (Fig 3). Water and potassium  
291 oxide have comparable incompatible behaviors (Danyushevsky, 2001; Michael,  
292 1995) and may not be substantially fractionated from each other by crystal  
293 fractionation. Instead, observed decreasing H<sub>2</sub>O/K<sub>2</sub>O at increasingly shallow  
294 eruption depths is compatible with H<sub>2</sub>O degassing. Importantly, sulfur  
295 concentrations are correlated with H<sub>2</sub>O/K<sub>2</sub>O ratios (Supp Fig. 4). The simplest  
296 explanation involves the concomitant degassing of water and the reduced fraction  
297 of sulfur from the melts during eruption. We note that the concomitant degassing  
298 of reduced S and water during eruption is not unique to Bounty. A similar  
299 degassing trend featuring sulfur and water was observed in Hawaii basalts  
300 (Brounce et al., 2017; Dixon et al., 1991).

301

#### 302 **5.4. Interpreting <sup>34</sup>S/<sup>32</sup>S ratios in Pitcairn glasses**

303 The δ<sup>34</sup>S values of reduced S from all Pitcairn basalts analyzed here range  
304 between -1.3‰ to +1.6‰. At Bounty, values are between -1.3‰ and +0.7‰.  
305 Bounty basalts from the dive 3 have homogeneous Cu concentrations at a given  
306 MgO content, suggesting they underwent comparable amounts of immiscible  
307 sulfide losses (Table 1). Isotope fractionation during sulfide segregation is

308 therefore discarded to explain the variable  $\delta^{34}\text{S}$  values seen in basalts from the  
309 dive 3. In figure 8, we plot  $\delta^{34}\text{S}$  values against  $f$  values calculated for samples from  
310 the dive 3.  $\delta^{34}\text{S}$  appear increasingly negative at lower  $f$  and may be interpreted in  
311 terms of isotopic fractionation associated with degassing under open-system  
312 distillation (Fig. 8A). One possibility involves two starting endmember  
313 compositions, with two steep trends. To cause the decrease in  $\delta^{34}\text{S}$  in the residual  
314 melt, the vapor phase must preferentially partition heavy  $^{34}\text{S}$  isotopes, under a  
315 bulk isotope fractionation of 2‰ ( $\alpha_{\text{gas-melt}} = 1.002$ ). This happens to be  
316 indistinguishable from predicted  $\text{SO}_2\text{-S}^{2-}$  isotopic fractionation at equilibrium at  
317 1,200 °C (Mandeville et al. 2009). This average melt-gas isotope fractionation  
318 would suggest  $\text{SO}_2$  is the dominant S-bearing species during equilibrium  
319 degassing. A similar suggestion was made for basalts from the Canary Islands  
320 (Beaudry et al., 2018). It is unclear whether equilibrium  $\text{SO}_2$  degassing could also  
321 offer a possible explanation for the low  $\delta^{34}\text{S}$  observed in sulfides from Pitcairn  
322 pillows (Delavault et al., 2016) as they do not report S concentrations of the  
323 basalts they analyzed. The eruption of depths of the Bounty basalts studied by  
324 Delavault et al., (2016) is  $\sim 1,000$  meters, substantially shallower than our samples,  
325 consistent with a pattern of more pronounced  $\text{SO}_2$  degassing.

326 A caveat in our degassing interpretation comes from observation of  
327 variable  $\delta^{34}\text{S}$  at a given  $f$ , on Fig. 8. This inevitably requires multiple starting  
328 compositions. The scenario of equilibrium  $\text{SO}_2$  degassing requires two starting  
329 compositions of  $\sim -0.7$  and  $\sim +0.2$ ‰ (Fig. 8) for  $\delta^{34}\text{S}$ . The data may alternatively  
330 be interpreted as degassing under much smaller isotope fractionations. Most  
331 basalts have  $\delta^{34}\text{S}$  compositions that can be explained as the result of S degassing

332 under a near-zero gas-melt isotope fractionation of  $-0.1\text{‰}$  ( $\alpha_{\text{gas-melt}} = 1.0001$ ),  
333 with a starting  $\delta^{34}\text{S}$  of  $-0.9\text{‰}$ , indistinguishable from the Pacific MORB mantle  
334 (Labidi et al., 2014), as illustrated on Fig. 8B. The degassing fractionation is  
335 consistent with  $\text{S}^{2-}\text{-H}_2\text{S}$  isotopic fractionation at equilibrium (Beaudry et al., 2018,  
336 Mandeville et al. 2009). However, when three glasses with high  $\delta^{34}\text{S}$  at a given  $f$   
337 are included, this degassing scenario suggests no less than three initial starting  
338 compositions. In summary, the data appear to inevitably argue in favor of multiple  
339 starting  $\delta^{34}\text{S}$  compositions for the Bounty melts, spread over  $\sim 1\text{‰}$  above the  
340 MORB estimates and our isotope data alone may not unambiguously disambiguate  
341  $\text{H}_2\text{S}$  and  $\text{SO}_2$  degassing scenarios.

## 342 **5.5. The recycled component at Pitcairn mantle sources**

343 The parental melts at Pitcairn show a  $\delta^{34}\text{S}$  range, restricted between  $-1\text{‰}$   
344 and  $+0.5\text{‰}$  (Fig. 8). Our  $\delta^{34}\text{S}$  estimate points to values above the MORB range, for  
345 basalts with EM-1 signatures. In consideration of the vulnerability of our  
346 degassing scenarios (section 5.4), and the uncertainty associated with estimated  
347 starting compositions, we are unable to interpret all  $\delta^{34}\text{S}$  data as a straightforward  
348 representation of source composition. In the following, we focus on  $\Delta^{36}\text{S}\text{-}\Delta^{33}\text{S}$  data  
349 which remain unmodified by degassing, as attested by a lack of correlation  
350 between on  $\Delta^{36}\text{S}\text{-}\Delta^{33}\text{S}$  and  $f$  values (Table 1). Our  $\Delta^{36}\text{S}$  and  $\Delta^{33}\text{S}$  are homogeneous  
351 (with one outlier with a MORB-like  $\Delta^{33}\text{S}$  signature, PN14-04), but the average  $\Delta^{33}\text{S}$   
352 is statistically distinct from MORB (Fig. 5, 7). Pitcairn samples show a small  
353 positive  $\Delta^{33}\text{S}$  anomaly of  $\sim 0.02\text{‰}$ . We attribute the small-magnitude  $\Delta^{33}\text{S}$   
354 enrichment to subducted sulfur, associated with the recycled component  
355 responsible for the EM-1 Pitcairn signatures. Our  $\Delta^{33}\text{S}$  values, duplicated for most

356 basalts (supplementary table 1), are not consistent with large negative  $\Delta^{33}\text{S}$   
357 anomalies reported elsewhere via ion probe measurements on individual sulfides  
358 from Bounty basalts (Delavault et al., 2016). In the following, we provide  
359 interpretations for our dataset and briefly discuss if our data may be reconciled  
360 with suggestions made in Delavault et al., (2016).

361 We plot our  $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$  data on Fig. 9, together with a compilation of  
362 sediments from the literature (Johnston, 2011). The plot shows the difference  
363 between Archean components, with  $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -1$ , and post-Archean rocks, with  
364  $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -7$  (Farquhar et al., 2007). Post-Archean rocks show a much smaller  
365  $\Delta^{33}\text{S}$  range than Archean sediments. We posit that the recycled endmember at  
366 Pitcairn falls within the existing fields defined by literature data on surface rocks  
367 shown on Fig. 9. Our approach relies on the assumption that no systematic  $\Delta^{33}\text{S}$ -  
368  $\Delta^{36}\text{S}$  isotope fractionation may be associated with metamorphism and slab  
369 devolatilization (Dottin III et al., 2020a). We examine various mixing scenarios. In  
370 all, we discuss the prospect of two-component mixing between a mantle peridotite  
371 with a recycled component. A mass balance is considered successful if can fit the  
372 observed  $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$  compositions at Pitcairn with a reasonable set of restrictions.

373 The Pitcairn  $\Delta^{33}\text{S}$  enrichment is associated with a near-invariant, MORB-  
374 like  $\Delta^{36}\text{S}$  signature (Fig. 5-7). For recycled sulfur to be of Proterozoic age and plot  
375 within the field defined by published sedimentary data (Fig. 9), the  $\Delta^{33}\text{S}$  signature  
376 of the Pitcairn endmember is allowed to be between  $\sim 0.03$  and  $\sim 0.10\text{‰}$  with a  
377  $\Delta^{36}\text{S}$  between  $\sim -0.4$  and  $\sim 0.4\text{‰}$  ('plausible Pitcairn endmember' on Fig. 9A). This  
378 is well within the  $\Delta^{33}\text{S}$  range in the Proterozoic of  $\sim 0.20\text{‰}$  (Fig. 9). This is also

379 consistent with the frequent near-zero  $\Delta^{36}\text{S}$  at a varying  $\Delta^{33}\text{S}$  observed in the  
380 geological record, especially when sedimentary sulfates are considered (Fig. 9A).  
381 Archean signatures are far more variable in  $\Delta^{33}\text{S}$ , such that a 0.020‰  $^{33}\text{S}$   
382 enrichment at Pitcairn is minuscule compared to most Archean anomalies (Fig.  
383 9B). The Pitcairn endmember could be a diluted Archean signature, which would  
384 happen to mimic the magnitude of Proterozoic sediment. In this case, our  
385 observation of an invariant  $\Delta^{36}\text{S}$  requires the Archean signature to have a  $\Delta^{36}\text{S}$   
386 between  $\sim -0.4$  and  $\sim 0.4$ ‰. Positive  $\Delta^{33}\text{S}$  at near-zero  $\Delta^{36}\text{S}$  exist in the Archean,  
387 if  $\Delta^{33}\text{S}$  remains in a restricted range between 0.1 and  $\sim 1.0$ ‰ ('plausible Pitcairn  
388 endmember' Fig. 9B). This exercise illustrates that although the magnitude of  
389 Proterozoic sediments appears more consistent with the Pitcairn  $^{33}\text{S}$  data than  
390 Archean rocks, both Archean and Proterozoic components could theoretically  
391 account for the signatures at Pitcairn. However, Archean signatures have  
392 implications that may be harder to reconcile with the geological record. This is  
393 detailed below in the context of the various geochemical models that account for  
394 the nature of EM-1.

### 395 **5.5.1 The metasomatism hypotheses for EM-1 at Pitcairn**

396 Delamination of lithospheric mantle has been suggested to yield EM-1  
397 signatures. This is an umbrella concept, involving either sub-oceanic or sub-  
398 continental depleted peridotites. The peridotites would develop EM signatures  
399 after experiencing metasomatism by either low-degree silicate melts or by slab-  
400 derived fluids (Hart et al., 1986; McKenzie and O'nions, 1983). One suggestion is  
401 that EM-1 originates from the Sub-Continental Lithospheric Mantle (SCLM), after  
402 it experienced metasomatism by melts from the asthenosphere (Hoernle et al.,

403 2011; McKenzie and O’Nions, 1995). This mechanism was found to generate EM-  
404 1 components in convergent margins, where it is clear that no contributions  
405 occurred from subducted components (Turner et al., 2017). In light of this  
406 hypothesis, we anticipate a scenario in which low-degree melts from the  
407 asthenosphere would deliver sulfur with MORB-like  $\Delta^{33}\text{S}$  of  $\sim 0.007 \pm 0.006\text{‰}$   
408 (Labidi and Cartigny, 2016), in conflict with the  $\Delta^{33}\text{S}$  excess in the Pitcairn basalts.

409 The SCLM may alternatively experience metasomatism by subduction fluids.  
410 Gibson et al. (2005) and Meyzen et al., (2005) reviewed evidence for peridotites  
411 metasomatized by subduction fluids, and showed they are dominated by EM-2  
412 signatures, but EM-1 compositions are also observed. This metasomatized  
413 component could for instance contribute to the EM-1 Tristan mantle source at  
414 about  $\sim 10\%$  (Gibson et al., 2005). A similar scenario was suggested for Pitcairn,  
415 on account of the absence of oxygen isotope variations in basalts associated with  
416 extreme EM-1 compositions (Eiler et al., 1995, 1997). This idea has the advantage  
417 of offering a mechanism to deliver surface-derived S (thus showing variable  $^{33}\text{S}$   
418 signatures) inherited from either sediments or the altered oceanic crust, to a  
419 lithospheric unit. We consider the sulfur isotope consequences of such a two-  
420 component mixing, assuming a contribution of metasomatized peridotites of  $\sim$   
421  $10\%$  (Gibson et al., 2005) mixed with  $90\%$  of a deep mantle source showing a  
422 MORB-like  $\Delta^{33}\text{S}$  (Dottin III et al., 2020b) and  $200\text{ ppm S}$  concentration (Lorand  
423 and Luguet, 2016; Nielsen et al., 2014). The metasomatized peridotites are  
424 assigned the entirety of the  $\Delta^{33}\text{S}$  anomaly, and S concentrations between  $50$  and  
425  $400\text{ ppm S}$ , as observed in natural samples (Lorand and Luguet, 2016). These  
426 endmember concentrations reflect how much a SCLM experiences sulfur  
427 depletion by partial melting prior to being metasomatized (Lorand and Luguet,

428 2016). There are no constraints on which endmember scenario may be more  
429 relevant for Pitcairn, and therefore we explore the two possibilities with no *a*  
430 *priori* estimate on how they may remain viable for other trace elements. Taking  
431 400 ppm for [S], the 10%-90% two-component mixing requires the SCLM to show  
432 an average  $\Delta^{33}\text{S}$  of  $\sim 0.09\text{‰}$  to account for the  $\sim 0.02\text{‰}$  enrichment at Pitcairn.  
433 Taking 50 ppm S, the required  $\Delta^{33}\text{S}$  value becomes  $\sim 0.55\text{‰}$ . This illustrates that  
434 again, both Archean and post-Archean sulfur could explain the data in the SCLM  
435 scenario.

436 Scenarios requiring melt depletion followed by fluid-driven enrichments are  
437 not supported by trace element signatures at Pitcairn. Notably, systematic  
438 enrichments or depletions of fluid mobile elements are not observed in the  
439 Pitcairn source (e.g. Nb anomalies, Willbold and Stracke, 2006). The integrated  
440 dataset therefore does not argue in favor of a scenario involving a subduction-  
441 imprinted SCLM in the Pitcairn source.

#### 442 **5.5.2 The effect of incorporating Lower Continent Crust**

443 Delamination of the lower continental crust (LCC) could be a viable  
444 alternative to account for EM-1 signatures in plumes (Willbold and Stracke, 2006).  
445 Meyzen et al., (2005) showed granulites from the lower continental crust develop  
446 signatures far closer to EM-1 than samples from the SCLM. Only  $\sim 2\%$  of LCC is  
447 necessary to contribute to any mantle source to generate the Pitcairn EM-1  
448 signature (Willbold and Stracke, 2006). In addition, the somewhat variable trace  
449 element signature of various LCC units offers an explanation for the irregular trace  
450 element patterns among EM-1 hotspots (Willbold and Stracke, 2006).

451 We consider the sulfur isotope consequences of a two-component mixing  
452 scenario where the LCC contributes 2% of the bulk mass of the Pitcairn source

453 (Willbold and Stracke, 2006). Assuming a concentration of 350 ppm S in the LCC  
454 (Rudnick et al., 2003), mass balance requires the average LCC to show a  $\Delta^{33}\text{S}$  of  
455  $\sim 0.7\text{‰}$  to account for the  $\sim 0.020\text{‰}$   $^{33}\text{S}$  excess observed in the Pitcairn source.  
456 This would put the LCC unit in the Archean domain (Fig. 9B).

457 The LCC reservoir is severely under-constrained, with a  $^{33}\text{S}$  isotope  
458 composition remaining virtually unknown. Mafic granulites essentially carry  
459 igneous sulfur, with a MORB-like  $\delta^{34}\text{S}$  signature (Wedepohl, 1995), consistent  
460 with the common idea that they result from crustal underplating by  
461 asthenosphere melts (Rudnick et al., , 2003). If so, the lower crust would have  
462 MORB-like  $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$  signatures. This would render the LCC unable to account for  
463 the  $^{33}\text{S}$  isotope anomaly that characterize the Pitcairn source. Felsic granulites also  
464 exist in the lower crust. They apparently show non-mantle  $\delta^{34}\text{S}$  signatures,  
465 illustrated by a modest  $^{34}\text{S}$  enrichment of  $\sim 3\text{‰}$  (Wedepohl, 1995). A complex  
466 model where delaminated felsic granulites would happen to have a  $\Delta^{33}\text{S}$  of  $\sim 0.7\text{‰}$ ,  
467 inherited from Archean rocks, could be invoked to account for the data at Pitcairn.  
468 However, it would be inconsistent with the few available data on Archean crustal  
469 melts, with near-zero  $\Delta^{33}\text{S}$  values (Bucholz et al., 2020). We cannot exclude that at  
470 an unconstrained location and time, an analogous process in a hypothetical LCC  
471 resulted in felsic components with a high  $\Delta^{33}\text{S}$  average value of exactly  $0.7\text{‰}$ , but  
472 this scenario appears restrictive and speculative.

473

### 474 **5.5.3 A sedimentary origin: Archean exhalates in Pitcairn?**

475 SIMS measurements on sulfides from other Pitcairn lavas from Bounty  
476 (Delavault et al., 2016) yielded  $\Delta^{33}\text{S}$  values down to  $\sim -0.85 \pm 0.25\text{‰}$ . The

477 substantial  $^{33}\text{S}$  anomaly was attributed to the contribution of Archean exhalates,  
478 an uncommon type of Archean chemical sediments that so far were only observed  
479 in the Abitibi greenstone belt (Delavault et al., 2016). Our high-precision  $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$   
480 data do not reproduce the large negative  $\Delta^{33}\text{S}$  anomalies observed by Delavault et  
481 al., (2016). Instead, the data establish the Pitcairn source to have positive  $^{33}\text{S}$   
482 anomalies, at odds with Archean exhalates. Furthermore, although exhalates may  
483 be enriched in trace elements, their rare earth patterns do not match any  
484 reconstructed slab component contributing to the Pitcairn mantle source  
485 (Delavault et al., 2016). Thus, ad-hoc modification during subduction (e.g., fluid  
486 losses causing trace element fractionation) was invoked to account for the EM-1  
487 trace element data (Delavault et al., 2016). Again however, the Pitcairn trace  
488 element compositions lack the typical fluid-loss signatures like Nb anomalies  
489 (Willbold and Stracke, 2006). Up to about  $\sim 20\%$  of a component resulting from  
490 the processing of the exhalates was suggested in the Pitcairn mantle source  
491 (Delavault et al., 2016). It is unclear whether this may be reconcilable with a  
492 mantle source suggested to be almost exclusively dominated by peridotites  
493 (Jackson and Dasgupta, 2008), perhaps with a minor pyroxenitic component  
494 (Nebel et al., 2019). It also appears to conflict with the absence of O isotope  
495 anomalies in Pitcairn basalts, that would likely be observed for any sediment  
496 contribution higher than 2% (Eiler et al., 1995). As it stands, although the S isotope  
497 compositions measured by Delavault et al. suggest a contribution from Archean  
498 exhalates, the majority of geochemical data published on Pitcairn basalts suggests  
499 otherwise.

#### 500 **5.5.4 The return of conventional marine sediments**

501 Invoking the subduction of marine sediments has been a classic scenario in

502 chemical geodynamics (Hofmann and White, 1982). As for the SCLM or the LCC  
503 scenarios, sediment recycling is a viable hypothesis that requires a specific mixing  
504 ratio. Here, we assume a 2% contribution of sediment into Pitcairn source (Eisele  
505 et al., 2002). Note that variations between 1 and 4%, in the range of reasonable  
506 predictions for EM signatures (Jackson and Dasgupta, 2008), would yield  
507 comparable results.

508 From our data we can establish a first-order mass balance scenario from the  
509 standpoint of S concentrations. Taking 2% contribution of sediment into a 98%  
510 peridotite source, and S concentrations in the sediments ranging between 2,500  
511 and 10,000 ppm S, sediments with  $\Delta^{33}\text{S}$  of +0.10‰ and +0.025‰ would result in  
512 mixtures with  $\Delta^{33}\text{S} \sim 0.02\text{‰}$ . This would match our  $^{33}\text{S}$  observations in basalts.  
513 Should the sediments also show a  $\Delta^{36}\text{S}$  between  $\sim -0.4$  and  $\sim 0.4\text{‰}$  as illustrated  
514 in Fig. 9A, the  $^{36}\text{S}$  data in basalts would also be accounted for. The concentrations  
515 between 2,500 and 10,000 ppm, required by the mass balance, are in the wide  
516 range shown by Proterozoic sediments showing typically between 100 and 30,000  
517 ppm S (Poulton et al., 2004). This simple mass balance calculation shows that  
518 Proterozoic sediments with moderate S concentrations may contribute to the  
519 Pitcairn source for the S isotope basalt data to be accounted for. Concluding on  
520 whether or not the required S concentrations are significantly low compared to  
521 non-subducted sediments, perhaps because of sulfur losses during subduction,  
522 appears unwarranted. However, we note that the mass balance exercise does not  
523 require having to generate any hypotheses on the sulfur behavior in ancient  
524 subduction zones. Considering how contentious the notion of sulfur losses in  
525 subduction is, even for well-studied subduction zones in the Phanerozoic (Li et al.,  
526 2020, Walters et al., 2020), the lack of strict restrictions of our mass balance with

527 regard to sulfur behavior in subduction is noteworthy.

528 In a similar exercise for Archean sediments, we find the maximum plausible  
529  $\Delta^{33}\text{S}$  of  $\sim 1\text{‰}$  for recycled S, as required by the invariant  $\Delta^{36}\text{S}$  and the field of  
530 Archean signatures (Fig. 9B). For a  $\Delta^{33}\text{S}$  between  $+0.2\text{‰}$  and  $+1\text{‰}$ , the S  
531 concentration of the recycled component is between  $\sim 1000$  and  $\sim 200$  ppm,  
532 respectively. These concentrations exist in the Archean record, but remain  
533 uncommon:  $>99\%$  of Archean sediments have S concentrations between 500 and  
534 20,000 ppm S (Reinhard et al., 2013). The simple mass balance shows that  
535 recycled Archean sediments would be required to have low S concentrations to  
536 account for the data in Pitcairn basalts, perhaps indicating a role for sulfur losses  
537 during subduction. We cannot rule out this scenario, but we note that it adds a  
538 level of restriction compared to the mass balance involving Proterozoic sediments.

539 To summarize, 2% of marine sediments with variable S concentrations,  
540 recycled in the Pitcairn mantle source, could easily explain the S isotope signature  
541 of Pitcairn basalts. We find that requiring a Proterozoic age for recycled sediments  
542 allows a rather large range of plausible S concentrations, and a tight range of S  
543 isotope composition within the post-Archean isotope field (Fig. 9A). The mass  
544 balance exercise allows for (but does not require) higher sulfur contents prior to  
545 subduction, should sulfur losses be substantial during slab devolatilization.  
546 Assuming an Archean age requires the small  $^{33}\text{S}$  enrichment at Pitcairn results  
547 from the dilution of an Archean component in the Pitcairn mantle source, resulting  
548 in an average  $^{33}\text{S}$  enrichment resembling in magnitude what is observed in  
549 Proterozoic sediments. For a dilution of a putative Archean signature to be  
550 achieved, low S concentration in the recycled sediment is required. In other words,  
551 this model requires a tight range of S isotope compositions within the known

552 Archean field (Fig. 9B), but also demands a narrow range of sulfur concentrations.  
553 Although Archean sediments are not ruled out, the scenario of Proterozoic  
554 sediment appears the least restrictive, and therefore the most parsimonious  
555 hypothesis to account for the Pitcairn EM-1 signature.

556

#### 557 **5.5.5. Implications on other geochemical signatures**

558 The absence of resolvable  $^{18}\text{O}$  isotopes variations in basalts (Eiler et al., 1995,  
559 1997) was suggested to argue against sediment recycling in the Pitcairn source.  
560 However, the cut-off sensitivity threshold of O isotopes is at  $\sim 2\%$  sediment  
561 contribution (Eiler et al., 1995). It is conceivable that  $\leq 2\%$  sediment may not be  
562 detected, even with precise  $^{18}\text{O}$  measurements. Another critique of the sediment  
563 model came from Willbold and Stracke (2006). Various EM-1 hotspots have  
564 irregular trace element patterns, notably in terms of Ba and Rb enrichments  
565 (Willbold and Stracke, 2006); Pitcairn is peculiar in that it shows the lowest Ba  
566 enrichment of all EM-1 signatures, with Ba/La ratio of  $\sim 9$  only, much lower than  
567 what is seen at Tristan (Ba/La  $\sim 17$ , Willbold and Stracke, 2006). This variability  
568 across various EM-1 hotspots is a problem for any unifying model aimed at  
569 lumping together all EM-1 compositions as a family of mantle signatures. This was  
570 considered evidence against sediment recycling (Willbold and Stracke, 2006),  
571 since sediments are thought to have unimodal Ba enrichments (Plank and  
572 Langmuir, 1998). The unimodal distribution however does not erase the  
573 substantial sedimentary variability for Ba enrichments. In fact, the Ba/La ratios of  
574 various sedimentary piles varies greatly, between 8 (MAR 800) and 171 (Central  
575 America) (Plank and Langmuir, 1998). Any sediments with a Ba/La  $< 50$ , largely  
576 in the range of modern sediments (Plank and Langmuir, 1998), would explain the

577 low Ba/La ratio at Pitcairn. Worldwide EM-1 components with variable Ba/La  
578 ratios may simply reflect the natural variability of sedimentary protoliths, as  
579 illustrated by modern sediments.

580 The lead isotope systematics can provide constraints on time-integrated  
581 elemental ratios, as well as model ages of recycled components (Chauvel et al.,  
582 1992). Delavault et al., (2016) suggested taking  $\mu$  values ( $^{238}\text{U}/^{204}\text{Pb}$ ) of  $\sim 6$  and  $\kappa$   
583 values ( $^{232}\text{Th}/^{238}\text{U}$ ) of  $\sim 7$  could yield a model age for the recycled sediment  
584 between 2.4 and 2.8 Ga. Here, we suggest relaxing the constraint of an Archean  
585  $\Delta^{33}\text{S}$  signature. Considering that most sediment columns in modern trenches have  
586  $\mu$  between  $\sim 1$  and 13, and  $\kappa$  values between  $\sim 1$  and 9 (Plank and Langmuir, 1998),  
587 we suggest that any combination of  $\kappa > 5$  and  $\mu < 10$  yields the EM-1  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  
588  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  signatures at Pitcairn with model ages lower than 2  
589 Ga, consistent with a post-Archean  $\Delta^{33}\text{S}$  signature.

590

## 591 **6. Conclusions**

592 We report on 15 submarine alkaline basalts at Pitcairn of EM-1 type. Low  
593 copper concentrations suggest all the samples were sulfide saturated upon  
594 eruption. The basalts show evidence for sulfur and water degassing, likely causing  
595  $\delta^{34}\text{S}$  fractionation. Accurately estimating the  $\delta^{34}\text{S}$  value of undegassed melts is  
596 challenging but they are likely between  $-1$  and  $+0.7\text{‰}$ , higher than the Pacific  
597 upper mantle estimates of  $-0.9 \pm 0.1\text{‰}$ . The samples have no resolvable  $^{36}\text{S}$   
598 variation relative to MORBs. In contrast, reduced sulfur displays homogenous  $\Delta^{33}\text{S}$ ,  
599 averaging at  $+0.024 \pm 0.006\text{‰}$  vs. CDT. This is higher than the  $\Delta^{33}\text{S}$  MORB average

600 of  $+0.007 \pm 0.006\%$ , by  $\sim 0.015\text{-}0.020\%$ . We attribute the small  $^{33}\text{S}$  anomaly to the  
601 recycling of surface-derived sulfur in the mantle source of Pitcairn. We show that  
602 metasomatized peridotites or components from the lower continental crust,  
603 appear inconsistent with the S isotope data, or would require narrow sets of  
604 unlikely circumstances. Archean sediments with large positive  $^{33}\text{S}$  anomalies  
605 could explain the data, but also present tight requirements. The contribution of  
606  $\sim 2\%$  Proterozoic sediments in the Pitcairn mantle source represents the simplest  
607 explanation, with the lowest amounts of restrictions.

608

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616

617

#### 618 **Captions**

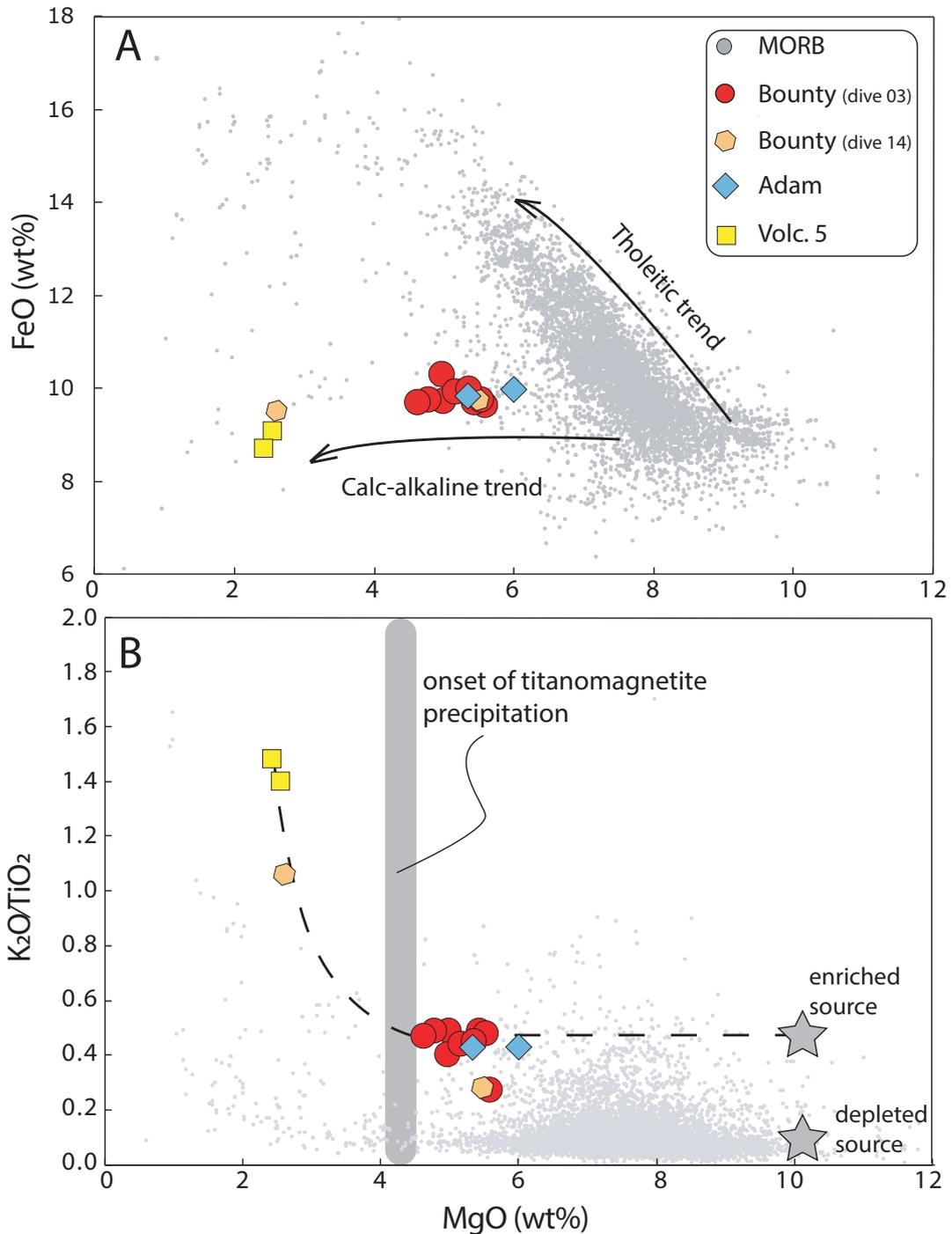
sample ID	pn02-01	pn02-05	pn03-08	pn03-10	pn03-01	pn03-02	pn03-03	pn03-04	pn03-05	pn03-07	pn03-11	pn14-04	pn14-07	pn08-01	pn08-07
seamount	adam	adam	bounty	bounty	bounty	volc. 5	volc. 5								
depth (m)	1595	1001	2250	2165	2508	2508	2500	2480	2408	2275	1957	1705	1513	3103	
Na <sub>2</sub> O	3.7	3.7	4.2	3.5	4.2	4.2	4.2	3.6	3.9	3.9	4.0	4.2	3.5	4.2	4.2
SiO <sub>2</sub>	48.4	48.3	48.8	50.6	47.8	47.9	47.7	49.0	47.8	47.5	48.9	54.2	50.3	54.3	54.4
K <sub>2</sub> O	1.5	1.4	1.6	0.8	1.4	1.4	1.5	1.3	1.4	1.4	1.6	2.3	0.9	2.8	2.7
Al <sub>2</sub> O <sub>3</sub>	15.5	15.5	16.2	15.1	16.0	16.0	15.8	15.8	15.4	15.3	15.3	15.3	15.1	16.2	16.1
CaO	9.0	8.9	8.1	8.6	9.1	9.1	9.1	9.4	9.8	9.7	8.7	5.4	8.6	4.9	4.9
MgO	5.3	6.0	5.0	5.6	5.4	5.5	4.8	5.0	5.2	5.4	4.6	2.6	5.5	2.4	2.6
P <sub>2</sub> O <sub>5</sub>	0.8	0.8	0.8	0.5	0.7	0.7	0.8	0.7	0.7	0.7	0.8	1.2	0.5	1.3	1.2
FeO	9.8	10.0	9.7	9.6	9.7	9.8	9.7	10.3	9.9	10.0	9.7	9.5	9.7	8.7	9.1
MnO	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2
TiO <sub>2</sub>	3.5	3.3	3.3	3.1	2.9	2.9	3.0	3.1	3.1	3.1	3.4	2.2	3.1	1.9	1.9
total	97.6	97.9	97.9	97.6	97.5	97.6	96.8	98.3	97.2	97.1	97.2	97.0	97.3	97.0	97.2
Cl (ppm)	463	465	459	324	502	494	498	471	426	424	417	750	276	495	493
Cu (ppm)	50	60	33	37	59	50	52	37	50	56	50	11	34	4	3
H <sub>2</sub> O (ppm)			9099	5696	9192	9807	9662	7195	8512	8125	5667	12123	6266		
S <sup>2-</sup> (ppm)	815	861	738	1017	1279	1299	1133	893	953	875	569	507	970	608	602
K <sub>2</sub> O/TiO <sub>2</sub>	0.43	0.43	0.49	0.27	0.49	0.48	0.49	0.40	0.44	0.45	0.47	1.06	0.28	1.48	1.40
CaO/Al <sub>2</sub> O <sub>3</sub>	0.58	0.57	0.50	0.57	0.57	0.57	0.58	0.60	0.63	0.63	0.57	0.36	0.57	0.31	0.30
Cl/K	0.04	0.04	0.03	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.04	0.04	0.02	0.02
S <sup>2-</sup> /S <sup>6+</sup>	102	113	100	95	97	98	80	77	95	91	72	99	95	106	100
δ <sup>34</sup> S (‰)	-1.2	-1.1	-1.0	-1.2	0.1	0.2	-1.0	-0.3	-1.2	-1.3	-1.2	0.7	-1.2	1.6	1.6
Δ <sup>34</sup> S (‰)	0.017	0.017	0.027	0.030	0.020	0.028	0.025	0.021	0.028	0.012	0.031	0.007	0.028	0.027	0.026
Λ <sup>34</sup> S (‰)	-0.08	-0.09	0.06	0.06	0.08	0.08	0.05	-0.01	0.13	0.08	0.06	-0.06	-0.11	0.01	0.02
<sup>206</sup> Pb/ <sup>203</sup> Pb	17.747	17.926	17.742	17.742	17.742	17.749	17.791	17.816	17.809	17.770	18.1982335				
<sup>207</sup> Pb/ <sup>203</sup> Pb	15.475	15.493	15.470	15.470	15.474	15.474	15.476	15.482	15.479	15.479	15.5167915				
<sup>208</sup> Pb/ <sup>203</sup> Pb	38.644	38.798	38.569	38.570	38.579	38.592	38.645	38.658	38.658	38.668	38.9161373				
<sup>143</sup> Nd/ <sup>142</sup> Nd	0.512537					0.512567	0.512573	0.512599	0.512583	0.512944	0.512762				
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.704624		0.704481	0.704463	0.704477	0.704485	0.704466	0.704482	0.704498	0.704531	0.704002				
<sup>87</sup> Sr/ <sup>86</sup> Sr*	0.70463		0.70447				0.70446								0.70530

a. data from bourdon et al., 2009

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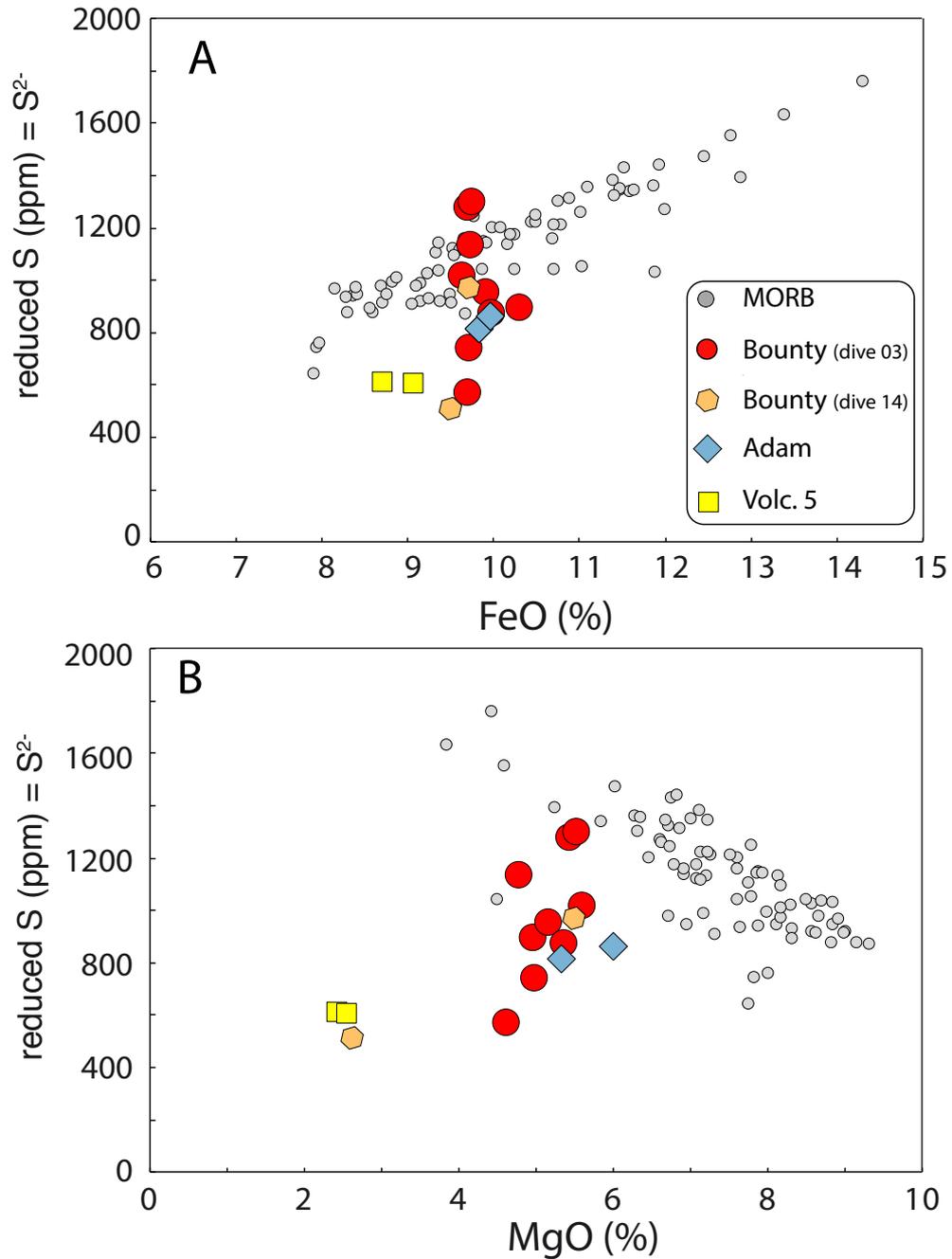
**Table 1** – Major element, radiogenic isotopes, volatile concentration and sulfur isotope data of 15 submarine glasses from Pitcairn.



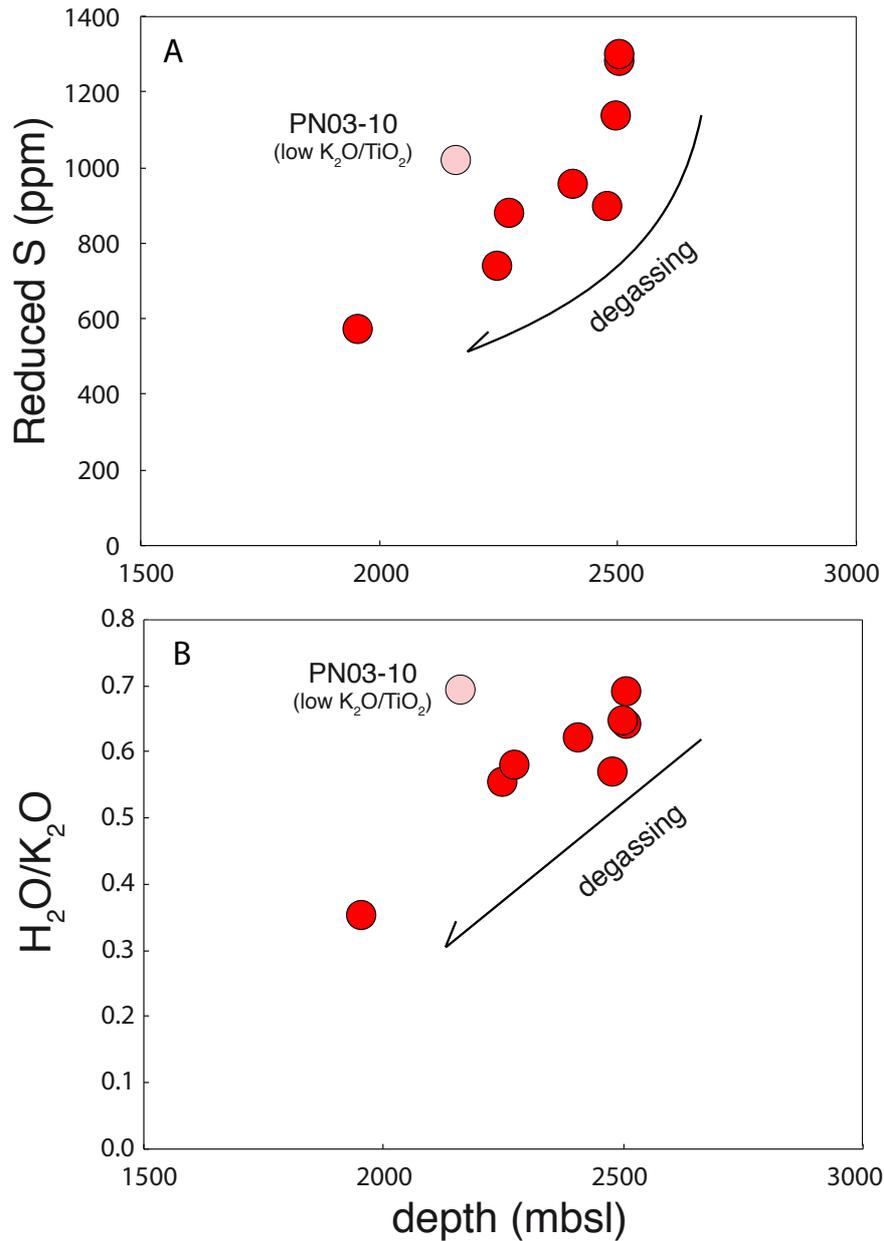
622

623 **Figure 1** – A: iron and magnesium oxides concentrations for various basalts. B: ratio of potassium  
 624 to titanium oxides, shown against magnesium oxide concentrations, for various basalts. MORB data  
 625 are compiled using the PetDB database ([www.earthchem.org/petdb](http://www.earthchem.org/petdb), Lehnert et al., 2000). On  
 626 panel A, Pitcairn basalts are shown to differ from MORBs in that they undergo magmatic  
 627 differentiation on a calc-alkaline trend, maintaining near-constant FeO concentrations at variable  
 628 MgO contents. On panel B, Pitcairn basalts are shown to have rather high K<sub>2</sub>O/TiO<sub>2</sub> ratios,  
 629 illustrating a mantle source enrichment. The onset of titanomagnetite precipitation at MgO ~4%  
 630 likely explains the extremely elevated K<sub>2</sub>O/TiO<sub>2</sub> ratios for the most evolved basalts. A hypothetical  
 631 liquid line of descent is illustrated as the dashed line.

632

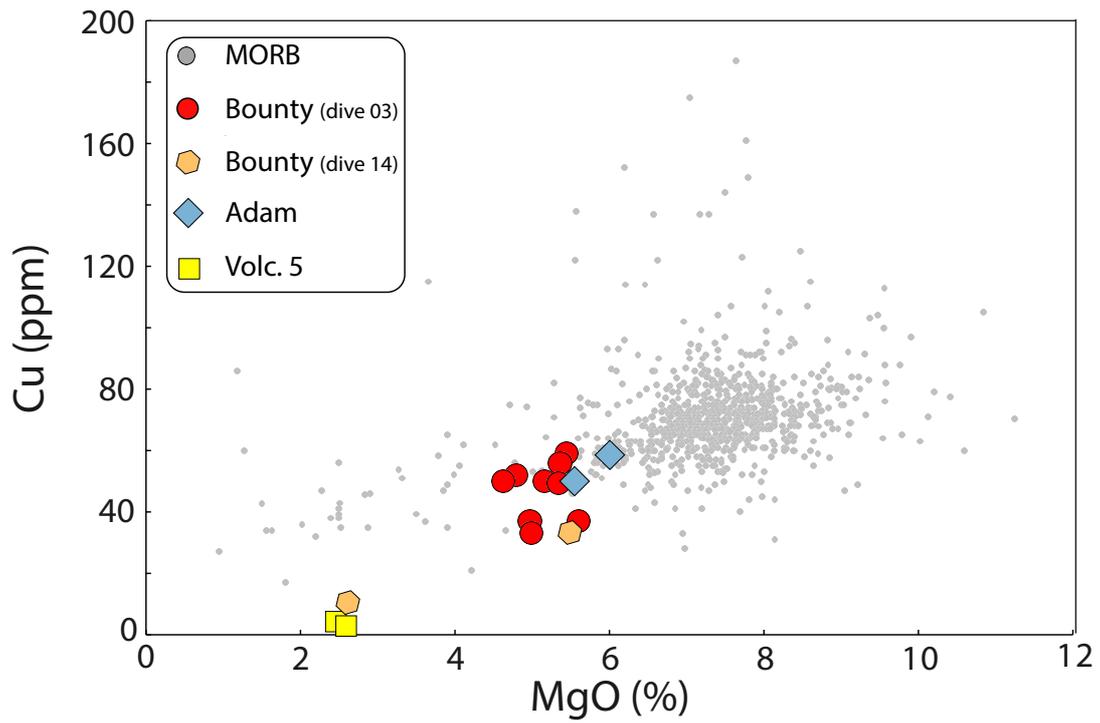


633  
 634 **Figure 2** – reduced sulfur concentrations of MORB and Pitcairn basalts shown against A: iron and  
 635 B: magnesium oxides concentrations. The error bar is MORB data acquired with the same  
 636 techniques are the literature (Labidi et al., 2014, 2013). On panel A, Pitcairn basalts are shown to  
 637 have a higher maximum in S solubility at a given FeO, relative to MORBs. The highest concentration  
 638 of reduced sulfur observed here, at sulfide saturation, is  $\sim 1300 \pm 50$  ppm S at a FeO  $\sim 9.8$  wt%.  
 639 This concentration is an excess of  $\sim 200$  ppm S relative to sulfur concentrations at sulfide  
 640 saturation in tholeiitic melts (Mathez, 1976). Commonly, such high concentrations would likely be  
 641 attributed to the solubility of bulk sulfur which is enhanced by sulfate occurrence (Jugo et al., 2010).  
 642 Here, the high S concentration is observed in melts that appear to show limited sulfate abundances  
 643 (Table 1). It is not clear whether the high S concentration illustrates the combined effects of minute  
 644 sulfate abundances, magmatic temperatures and alkaline chemistry on the sulfide solubility in  
 645 alkaline melts (Fortin et al., 2015). Independently of the reason for relatively high S concentrations  
 646 in some of the Pitcairn melts, the near-vertical S concentrations at a given FeO (panel A) and MgO  
 647 (panel B) shows sulfur loss occurred in the basalts. The sulfur loss may reflect S degassing or  
 648 sulfide fractionation (see sections 5.2 and 5.3)



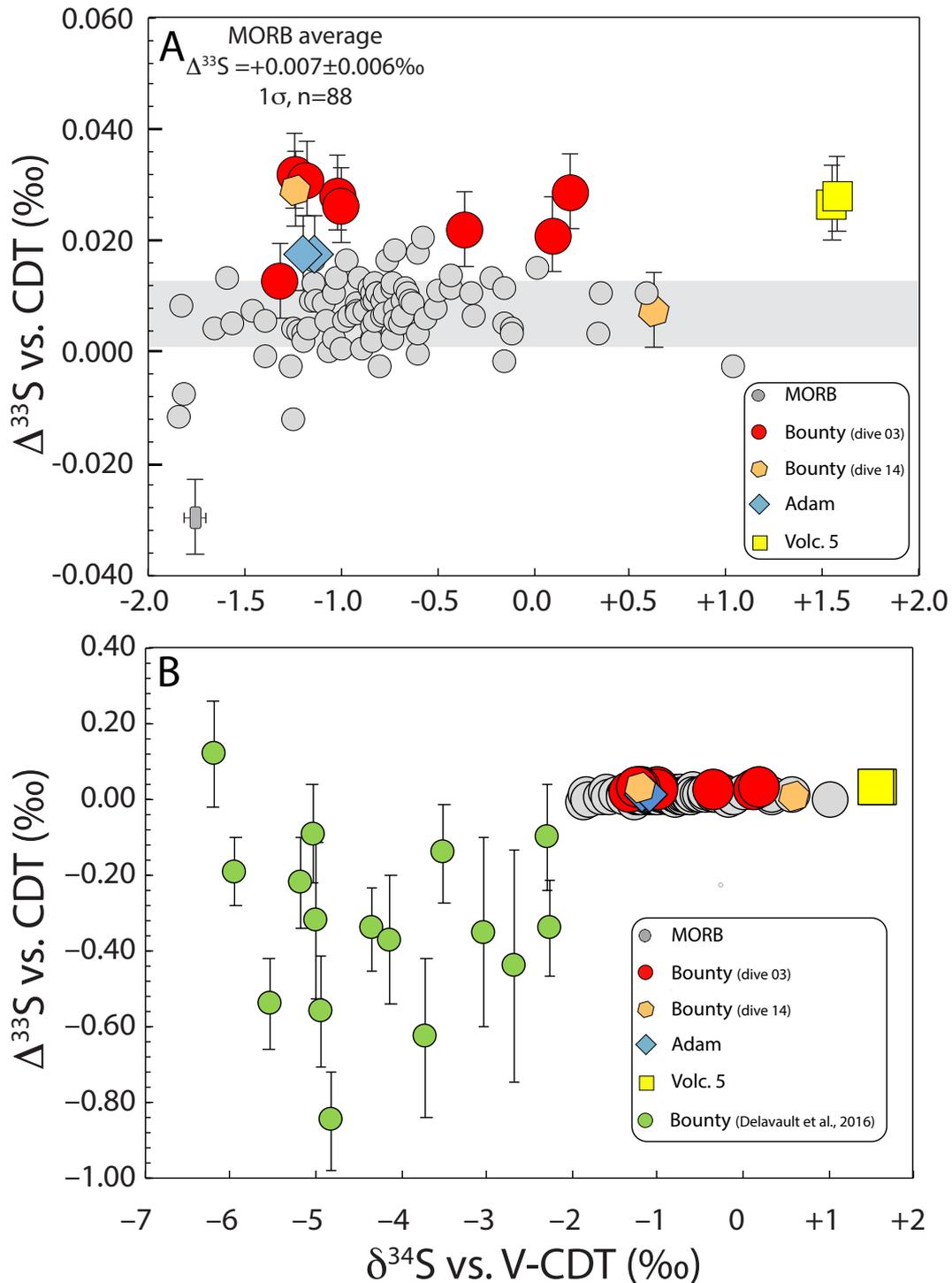
649

650 **Figure 3** - reduced sulfur concentrations and H<sub>2</sub>O/K<sub>2</sub>O ratios of Pitcairn basalts from the dive 03  
 651 only, for which all samples have broadly homogeneous major element concentrations. For those  
 652 samples that were carefully picked at a given location on the flank of Bounty (Hekinian et al., 2003),  
 653 we assume the S concentration prior to degassing to be comparable. In contrast, we anticipate the  
 654 variable major element compositions of other samples from Bounty (dive 14), Adam and Volc. 5 to  
 655 cause variable pre-eruptive S concentration owing to the intricate link between sulfur solubility in  
 656 silicate melts and basalt chemistry. At a given major element concentration but variable eruption  
 657 depths for dive 03 basalts, the positive correlations are consistent with magmatic degassing upon  
 658 eruption. Only PN03-10 is an outlier. This is the only sample from this seamount with a K<sub>2</sub>O/TiO<sub>2</sub>  
 659 ratio of ~0.25, where all others have K<sub>2</sub>O/TiO<sub>2</sub> ~0.45 (Fig. 1). We attribute the outlier to a distinct  
 660 mantle source composition in terms of volatile elements.



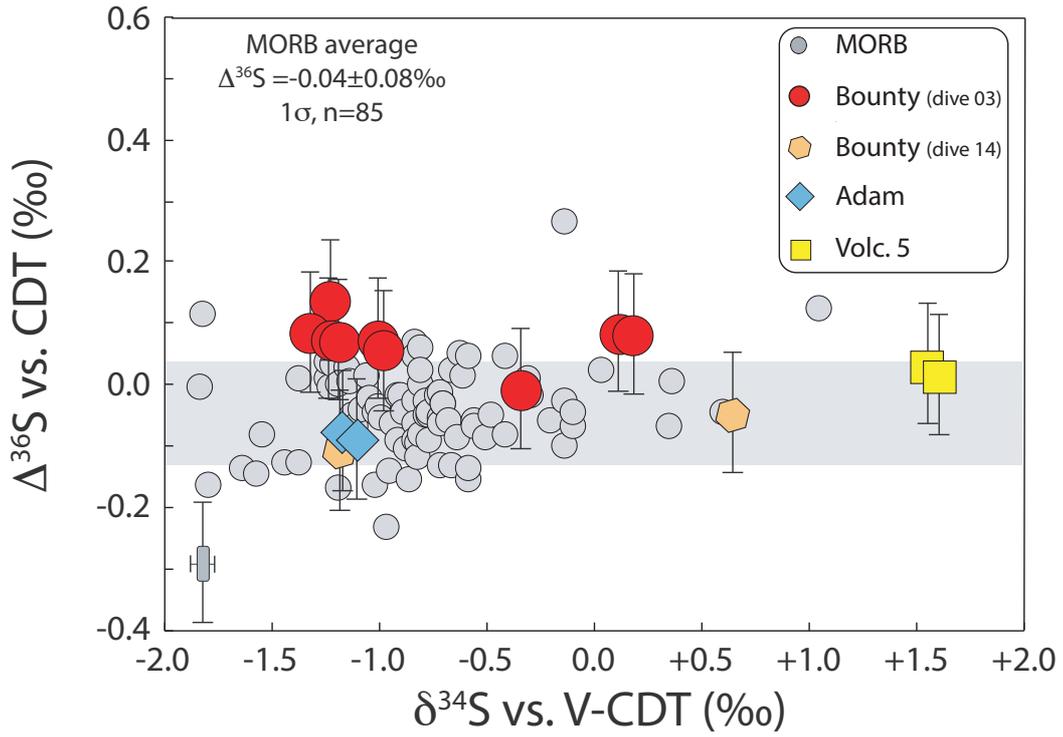
661

662 **Figure 4** – copper concentrations of MORBs and Pitcairn basalts shown against MgO contents. The  
 663 Cu concentrations happen to be consistent with a MORB fractionation trend. This indicates sulfide  
 664 fractionation is comparable in most samples from Bounty and Adams samples.



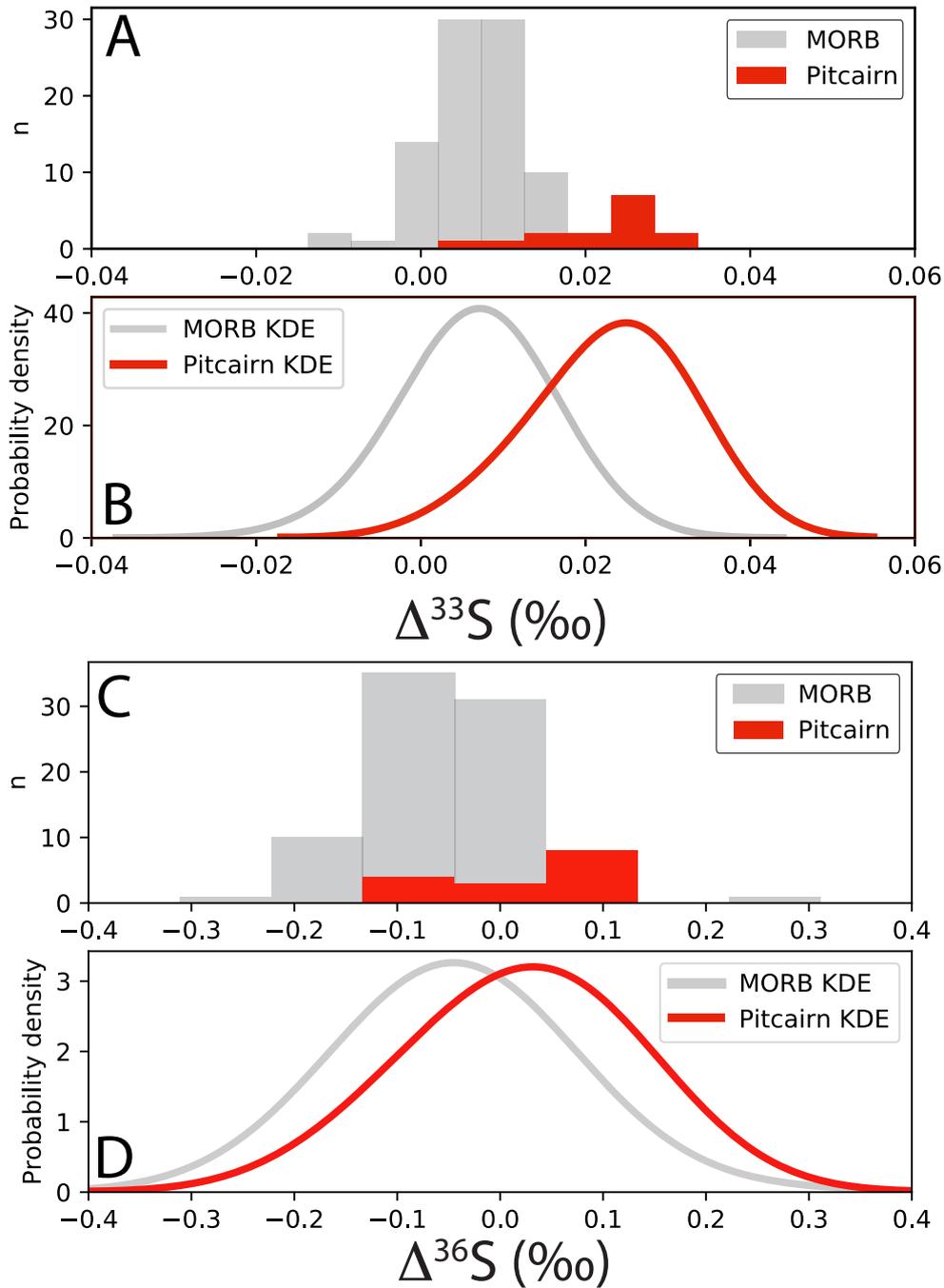
665

666 **Figure 5** –  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  of Pitcairn basalts compared to published MORB data (Labidi et al., 2014,  
 667 2013, 2012; Labidi and Cartigny, 2016). Panel A and B show the same geochemical space, but panel  
 668 B incorporates the dataset from Delavault et al. (2016) obtained on individual sulfides from other  
 669 basalts from the Bounty seamount. On Panel A, our data for Pitcairn basalts are shown to have an  
 670 average  $\Delta^{33}\text{S}$  of  $+0.024 \pm 0.007\text{‰}$ , higher than the MORB average value by  $\sim 0.02\text{‰}$ . the error bars  
 671 of MORB measurements are shown on the bottom left. On Panel B, the data of Delavault et al.,  
 672 (2016) are plotted next to ours. The ion probe data from Delavault et al., (2016) show substantially  
 673 negative  $\Delta^{33}\text{S}$  values, down to  $-0.85 \pm 0.25\text{‰}$ , which are not duplicated by our measurements.



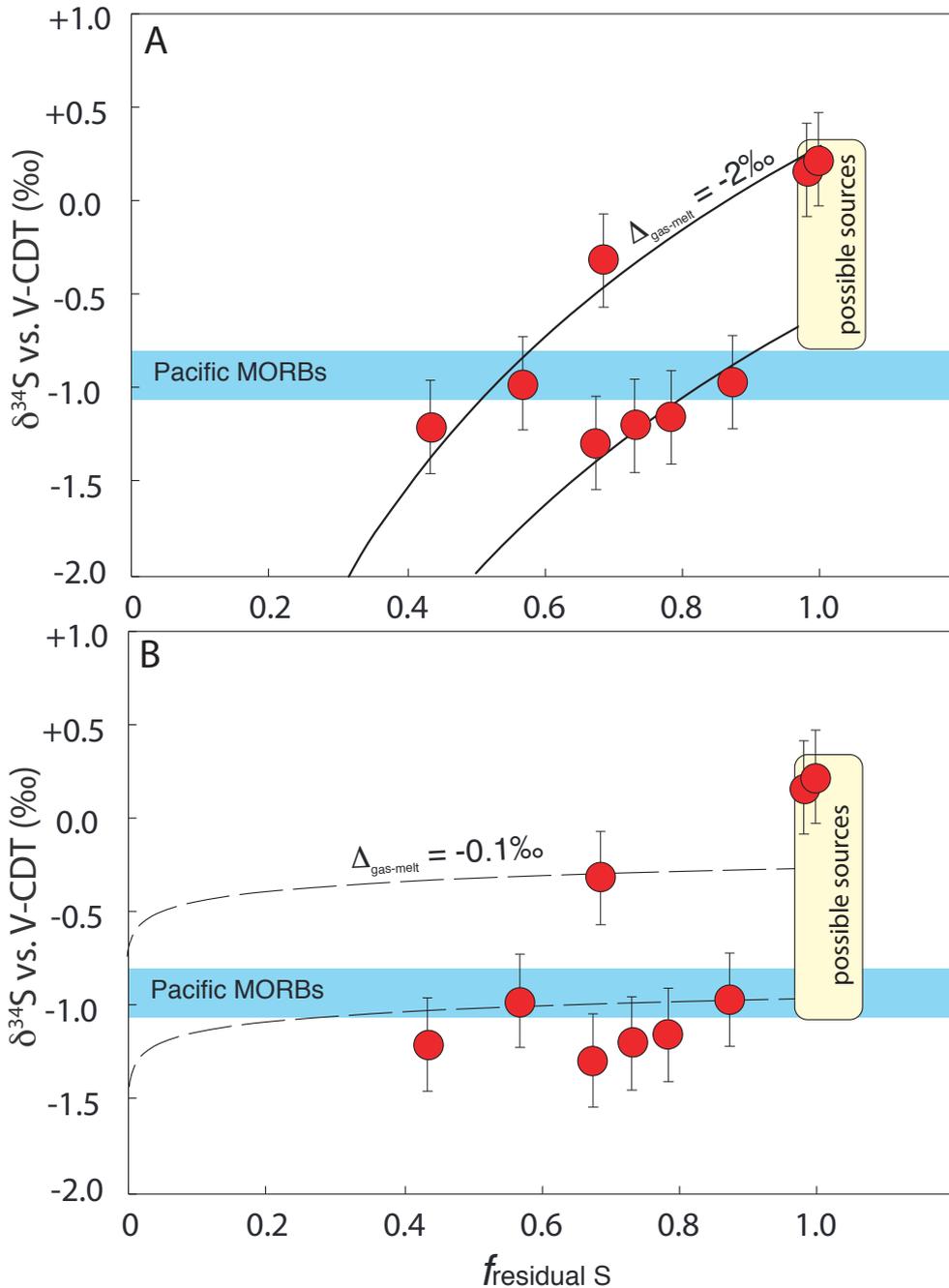
674

675 **Figure 6** –  $\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}$  of Pitcairn basalts compared to published MORB data (Labidi et al.,  
 676 2014, 2013, 2012; Labidi and Cartigny, 2016). Pitcairn basalts show no clearly discernable  $^{36}\text{S}$   
 677 anomaly relative to MORBs.



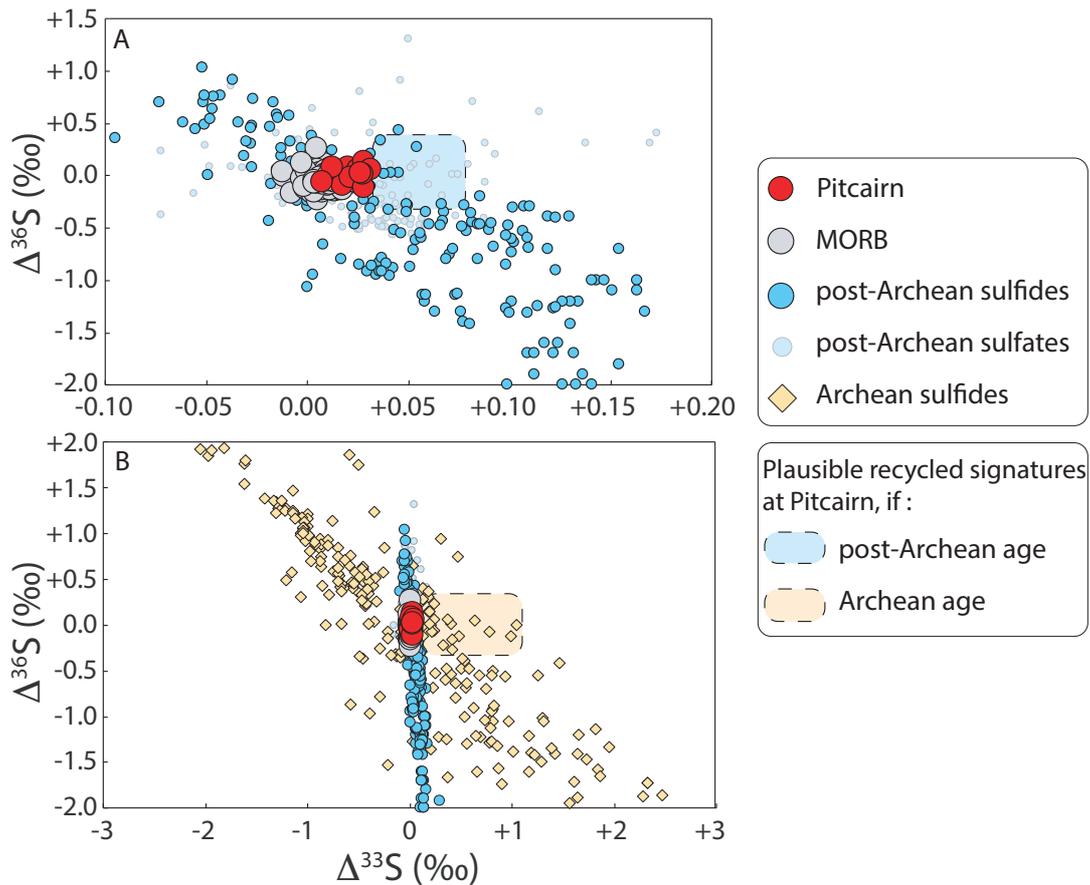
678

679 **Fig. 7** – data distribution for  $^{33}\text{S}$  and  $^{36}\text{S}$  signatures of MORB and Pitcairn samples. Panels A and C  
 680 show data histograms and B and D show Kernel density plots (KDE), with a bandwidth equal to  
 681 the analytical uncertainty. Only for  $^{33}\text{S}$  is the mean value of the Pitcairn samples statistically  
 682 distinct from MORB.



683

684 **Figure 8** –  $\delta^{34}\text{S}$  values shown against the fractions of residual  $\text{S}^{2-}$  in glasses, for samples undergoing  
 685 varying volatile losses via degassing. Sulfur isotope ratios vary as a function of the extent of  
 686 degassing, recording a mass-dependent fractionation associated with volatile losses. On panel A,  
 687 the data are fit with a gas-melt fractionation of 2‰, consistent with  $\text{S}^{2-}$ – $\text{SO}_2$  equilibrium isotope  
 688 fractionation. Two  $\delta^{34}\text{S}$  source compositions appear to be required to fit the data. They are both  
 689 higher than the pacific upper mantle value of  $-0.9 \pm 0.1\text{‰}$  (Labidi et al., 2014). Alternatively, as  
 690 shown on panel B, the data may be fit with a gas-melt fractionation of 0.1‰, consistent with  $\text{S}^{2-}$ –  
 691  $\text{H}_2\text{S}$  equilibrium isotope fractionation. In this case, three  $\delta^{34}\text{S}$  source compositions would be  
 692 required. Most basalts would be consistent with the  $\delta^{34}\text{S}$  estimate of the pacific upper mantle value.



693

694 **Figure 9** – Sulfur isotope ratios of Pitcairn basalts compared to MORB (data from Labidi et al., 2012,  
 695 2013, 2014, Labidi and Cartigny, 2016), Archean sediments and post-Archean sediments (data  
 696 compilation from Johnston, 2011).

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