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Olivia E Anderson, Matthew G Jackson, Ayla S Pamukçu, Estelle F. Rose-Koga, Véronique Le Roux, et al.. Extensive H₂O degassing in deeply erupted submarine glasses inferred from Samoan melt inclusions: The EM2 mantle source is damp, not dry. *Chemical Geology*, 2024, 651, pp.121979. 10.1016/j.chemgeo.2024.121979 . insu-04516946

HAL Id: insu-04516946

<https://insu.hal.science/insu-04516946>

Submitted on 22 Mar 2024

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1 **Extensive H₂O degassing in deeply erupted submarine glasses inferred from**
2 **Samoan melt inclusions: The EM2 mantle source is damp, not dry**

3 **O. E. Anderson^{1*}, M. G. Jackson¹, A. S. Pamukçu^{2,3}, E. F. Rose-Koga⁴, V. Le Roux², F.**
4 **Klein², K. T. Koga⁴, G. A. Gaetani², A. A. Price¹**

5 ¹Isotope Geochemistry Facility – Global Center for Mantle Zoology (GCMZ), University of
6 California Santa Barbara, Department of Earth Science, Santa Barbara, CA, USA ²Woods Hole
7 Oceanographic Institution, Woods Hole, Massachusetts 02543, USA ³Geological Sciences,
8 Stanford University, Stanford, CA, USA ⁴Institut des Sciences de la Terre d'Orléans (ISTO),
9 UO/CNRS/BRGM, 1A rue de la Férellerie, 45071, Orléans, France

10 *Corresponding author: Olivia E. Anderson (anderson03@ucsb.edu)
11

12 **Highlights:**

- 13
- 14 ● Samoan melt inclusions have higher H₂O/Ce—indicating less degassing—compared to
15 Samoan pillow glasses.
 - 16
 - 17 ● High ⁸⁷Sr/⁸⁶Sr melt inclusions have high H₂O/Ce, contrary to prior observations using
18 pillow glasses.
 - 19
 - 20 ● Low H₂O/Ce in high ⁸⁷Sr/⁸⁶Sr glasses indicates extensive degassing has occurred, so
21 cannot be used to infer mantle H₂O/Ce.
 - 22
 - 23 ● Melt inclusions show that enriched mantle (EM) lavas have H₂O/Ce similar to non-EM
24 lavas.
 - 25
 - 26 ● Elevated CO₂ in EM melts leads to greater degassing and lower H₂O/Ce in erupted
27 glasses compared to depleted mantle.
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36 Anderson, O.E., Jackson, M.G., Pamukçu, A.S., Rose-Koga, E.F., Le Roux, V., Klein, F., Koga,
37 K.T., Gaetani, G.A. and Price, A.A. (2024). Extensive H₂O degassing in deeply erupted
38 submarine glasses inferred from Samoan melt inclusions: The EM2 mantle source is damp, not
39 dry. *Chemical Geology*, 651, 121979. <https://doi.org/10.1016/j.chemgeo.2024.121979>

40 **Abstract**

41 Submarine glasses erupted at intraplate volcanic hotspot settings sampling enriched mantle
42 (EM)—characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ —exhibit lower $\text{H}_2\text{O}/\text{Ce}$ than glasses representing less
43 enriched mantle domains, leading to the interpretation that the EM mantle is H_2O -poor (“dry”).
44 We test whether low $\text{H}_2\text{O}/\text{Ce}$ observed in pillow glasses of EM lavas resulted from degassing of
45 higher $\text{H}_2\text{O}/\text{Ce}$ primary melts by measuring $\text{H}_2\text{O}/\text{Ce}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in olivine-hosted melt
46 inclusions from two deeply-erupted (3950 and 2190 meters below sea level (mbsl)) Samoan
47 submarine lavas from Vailulu‘u and Malumalu seamounts. Vailulu‘u ($\text{H}_2\text{O}/\text{Ce}=161\text{--}275$) and
48 Malumalu (149–232) melt inclusions have an average $\text{H}_2\text{O}/\text{Ce}$ (197 ± 58 2SD, $N=15$) that is
49 nearly twice as high as $\text{H}_2\text{O}/\text{Ce}$ in pillow glasses from these two seamounts (average
50 $\text{H}_2\text{O}/\text{Ce}=106\pm 51$, $N=65$). Notably, the average $\text{H}_2\text{O}/\text{Ce}$ of Samoan melt inclusions (197 ± 58) is
51 comparable to pillow glasses from non-EM hotspots. We show that lower $\text{H}_2\text{O}/\text{Ce}$ in submarine
52 Samoan glasses compared to melt inclusions results from greater closed-system degassing, and
53 concomitant loss of H_2O , because EM melts have higher initial concentrations of CO_2 . We show
54 that the lower $\text{H}_2\text{O}/\text{Ce}$ in global EM pillow glasses compared to non-EM pillow glasses can be
55 modeled to be the result of more extensive degassing of H_2O in EM melts, which owes to higher
56 CO_2 in primary melts (20,000–90,000 ppm) of EM sources compared to non-EM melts (300–
57 50,000 ppm CO_2). Instead of originating from a dry mantle, we conclude that EM lavas derive
58 from a damp mantle, but EM melts lose more H_2O by degassing than non-EM melts.

59 **Keywords:** melt inclusion, Samoa, hotspot, degassing, enriched mantle, H_2O

60

61

62 **1. Introduction**

63 Although volatiles are a minor component in silicate melts, they play an outsize role on
64 the properties and behavior of magmatic systems. Hydrogen and carbon affect the rheology of
65 the mantle, the depth and extent of melting, the composition of melts, and how melts evolve
66 (e.g., Asimow & Langmuir, 2003; Gaetani & Grove, 1998; Hirschmann, 2006; Hirth &
67 Kohlstedt, 1996, 2003; Portnyagin et al., 2007). Therefore, connecting volatile element
68 compositions to mantle domains characterized by particular isotopic compositions, such as
69 enriched mantle (EM), can provide additional insights into mantle heterogeneities. A variety of
70 geochemical “flavors” have been identified in the mantle via geochemical taxonomy of ocean
71 island basalts (OIB), and the various mantle species are broadly encompassed by several
72 canonical mantle endmembers that include HIMU (high $\mu=^{238}\text{U}/^{204}\text{Pb}$), EM1 (enriched mantle 1),
73 EM2 (enriched mantle 2), and DM (depleted mantle). Samoan lavas have unique geochemical
74 signatures that extend to Enriched Mantle 2 (EM2) isotopic compositions (e.g., high $^{87}\text{Sr}/^{86}\text{Sr}$,
75 intermediate $^{206}\text{Pb}/^{204}\text{Pb}$, and low $^{143}\text{Nd}/^{144}\text{Nd}$). The EM2 mantle source has been suggested to be
76 derived from recycled continental materials (e.g., White & Hofmann, 1982; White & Duncan,
77 1996; Jackson & Macdonald, 2022). Therefore, characterization of Samoan EM2 lavas can
78 provide insights into the role that deep continental crust subduction plays in controlling the
79 volatile budgets of the mantle.

80 The ratios $\text{H}_2\text{O}/\text{La}$ or $\text{H}_2\text{O}/\text{Ce}$ measured in submarine glasses are commonly used to
81 evaluate H_2O enrichment or depletion in the mantle because H_2O , La, and Ce have similar
82 degrees of incompatibility (e.g., Michael, 1995). Thus, their ratios are not significantly affected
83 by partial melting and crystal fractionation. The EM2 mantle source has been interpreted to be
84 ‘dry’ because the $\text{H}_2\text{O}/\text{Ce}$ (or $\text{H}_2\text{O}/\text{La}$) is lower at higher $^{87}\text{Sr}/^{86}\text{Sr}$ for Samoan glasses (Workman

85 et al., 2006). Workman et al. (2006) found that H_2O/La anticorrelates with $^{87}Sr/^{86}Sr$: the more
86 geochemically enriched (higher $^{87}Sr/^{86}Sr$) Samoan glasses have lower H_2O/La than more
87 geochemically depleted Samoan glasses; the high H_2O/La MORB mantle endmember anchors
88 the low $^{87}Sr/^{86}Sr$ portion of the array. Workman et al. (2006) explained this relationship between
89 $^{87}Sr/^{86}Sr$ and H_2O/La as the result of diffusive H_2O loss from EM2 reservoirs during long-term
90 storage in a dry and depleted mantle, resulting in a “dry” EM2 mantle domain that has low
91 H_2O/La and low H_2O . Similarly, Dixon et al. (2002) found that high $^{87}Sr/^{86}Sr$ basalts erupted in
92 MOR settings had low H_2O/Ce . However, unlike Workman et al. (2006), Dixon et al. (2002)
93 suggested that the dry nature of the EM reservoir was due to dehydration of sediments during
94 subduction, resulting in low H_2O/Ce signatures in subducted, dehydrated sediments, which
95 ultimately contribute to enriched mantle domains. Bizimis and Peslier (2015) offered further
96 discussion regarding the origin of apparently dry EM2 domains and argued that the low H_2O/Ce
97 in EM lavas is the result of recycling of pyroxenite-bearing oceanic lithosphere. The pyroxenites
98 they examined have low H_2O/Ce and high H_2O , a result of preferential partitioning of Ce into
99 clinopyroxene compared to H_2O .

100 Additional work highlights the low H_2O/Ce in enriched mantle domains (Kendrick et al.,
101 2017). In particular, classical EM1 and EM2 oceanic hotspots—Pitcairn and Societies,
102 respectively—exhibit negative correlations between $^{87}Sr/^{86}Sr$ and H_2O/Ce in submarine glasses
103 (Kendrick et al., 2014). Thus, low H_2O/Ce appears to be a defining feature of EM lavas, and
104 constraining the origin of this geochemical signature is critical for understanding the origin of the
105 EM mantle and/or the petrogenesis of EM lavas.

106 Existing models for the origin of low H_2O/La and H_2O/Ce in EM-flavored OIB pillow
107 glasses quenched in deep submarine environments are predicated on the assumption that the low

108 H₂O/Ce is a source feature and the EM primary melts have low H₂O/Ce inherited from the
109 mantle source (Dixon et al., 2002; Dixon & Clague, 2001; Wallace, 2002; Workman et al., 2006;
110 Kendrick et al., 2014). This interpretation assumes that magmatic degassing follows open system
111 behavior, a mechanism that results in significant loss of CO₂, but not H₂O, from the melt by
112 degassing: the H₂O/Ce in deeply erupted glasses (i.e., ≥ 0.1 kbar; Workman et al., 2006) resulting
113 from this process are similar to the mantle source despite having degassed most of their
114 magmatic CO₂.

115 In this study, we test this assumption using combined H₂O/Ce and ⁸⁷Sr/⁸⁶Sr
116 measurements in individual olivine-hosted melt inclusions isolated from two well-characterized
117 submarine Samoan basalts that were characterized by Workman et al. (2006). We present
118 volatile (H₂O, CO₂, Cl, F, S), major, and trace element concentrations and ⁸⁷Sr/⁸⁶Sr on Samoan
119 melt inclusions from both samples—AVON3-78-1 and AVON3-71-2—which were obtained
120 from Malumalu and Vailulu‘u seamounts, respectively. Malumalu lavas reach ⁸⁷Sr/⁸⁶Sr of up to
121 0.708901, which is the most extreme EM2 composition that we explore in this study. In contrast,
122 Vailulu‘u lavas have ⁸⁷Sr/⁸⁶Sr that range from 0.705352 to 0.706720, and thus represent a less
123 enriched composition at the Samoan hotspot. Previous ⁸⁷Sr/⁸⁶Sr analyses of Samoan melt
124 inclusions demonstrated extreme heterogeneity (0.70434 to 0.70926) that has been verified using
125 both *in situ* LA-ICP-MS approach (laser-ablation inductively coupled plasma mass spectrometry;
126 Jackson & Hart, 2006) and an approach involving wet chemistry followed by TIMS (thermal
127 ionization mass spectrometry; Reinhard et al., 2018). Critically for this study, the melt inclusions
128 from the two lavas examined here span nearly the same range of ⁸⁷Sr/⁸⁶Sr (0.704858–0.709225)
129 as identified in prior melt inclusion studies (Jackson & Hart, 2006; Reinhard et al., 2018) and
130 have similar trace element characteristics as the Samoan glasses examined for H₂O/La and

131 $^{87}\text{Sr}/^{86}\text{Sr}$ by Workman et al. (2006) (0.704521–0.708901). We interpret this to indicate that the
132 melt inclusions thus sample the same mantle sources as the pillow glasses studied by Workman
133 et al. (2006).

134 However, Samoan melt inclusions in this study exhibit two key differences with the
135 Samoan submarine glasses reported in Workman et al. (2006): 1) the melt inclusions have higher
136 $\text{H}_2\text{O}/\text{Ce}$ than Samoan submarine glasses and 2) the inclusions exhibit no relationship between
137 $\text{H}_2\text{O}/\text{Ce}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, which contrasts with the negative correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and
138 $\text{H}_2\text{O}/\text{Ce}$ observed in Samoan pillow glasses. We model the difference in $\text{H}_2\text{O}/\text{Ce}$ between melt
139 inclusions and pillow glasses as being a result of closed-system degassing, a mechanism that
140 results in greatly diminished CO_2 and H_2O concentrations in the melt (in contrast to open-system
141 degassing, which results in greatly diminished CO_2 , but not H_2O , melt concentrations). In this
142 model, the melt inclusions experience less closed-system degassing compared to submarine
143 glasses because of deep entrapment of the melt inclusions in growing olivine crystals within
144 magma chambers. Melts that were not trapped continued to degas both CO_2 and H_2O up until
145 eruption and quenching on the seafloor, resulting in lower $\text{H}_2\text{O}/\text{Ce}$ in the submarine glasses
146 compared to the deeply entrapped melt inclusions.

147 We also present a model suggesting that, across global oceanic hotspots, primary melts
148 with higher $^{87}\text{Sr}/^{86}\text{Sr}$ (e.g., Samoan and Societies EM2 glasses, Pitcairn EM1 glasses) have
149 higher primary melt CO_2 than lower $^{87}\text{Sr}/^{86}\text{Sr}$ melts (e.g., Foundation, Hawai‘i (Lō‘ihi), and
150 Easter hotspots). Higher CO_2 in high $^{87}\text{Sr}/^{86}\text{Sr}$ (EM) melts results in greater degassing of both
151 CO_2 and H_2O (and a greater reduction in the $\text{H}_2\text{O}/\text{Ce}$ ratio) compared to low $^{87}\text{Sr}/^{86}\text{Sr}$ melts,
152 which explains the negative global correlation between $\text{H}_2\text{O}/\text{Ce}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in OIB glasses.
153 This new result suggests that submarine glasses sourcing EM domains do not provide reliable

154 records for evaluating the H₂O and H₂O/Ce in the mantle source. In melt inclusions, degassing is
155 arrested at great depth, making it possible to identify H₂O/Ce ratios that are closer to values in
156 the primary melt.

157 **2. Methods**

158 Submarine pillow basalt samples in this study are from two Samoan seamounts (Figure 1)
159 that are young (<8 ka; Sims et al., 2008) and associated with visually fresh lavas: Malumalu
160 (sample AVON3-78-1; 2260–2190 mbsl) and Vailulu‘u (sample AVON3-71-2; 4420–3950
161 mbsl) are olivine-rich lavas with glassy chill margins on the pillow rims. Olivine-hosted melt
162 inclusions from Vailulu‘u and Malumalu seamounts in this study were rehomogenized on a
163 heating stage (see supplement for methods), and these rehomogenized inclusions were then
164 characterized for ⁸⁷Sr/⁸⁶Sr (15 melt inclusions total), ¹⁴³Nd/¹⁴⁴Nd (only three melt inclusions),
165 stable hydrogen isotope ratios (δD), and major, trace and volatile element concentrations (Table
166 S1). This supplement also includes methodological details for the glass major element (electron
167 microprobe), volatile (ion probe), hydrogen isotope (ion probe), and trace element (LA-ICP-MS)
168 analyses and the host olivine major element (electron microprobe) analyses. Strontium separation
169 chemistry and ⁸⁷Sr/⁸⁶Sr analyses by TIMS used in this study follow the same procedure as
170 described in Anderson et al. (2021). The supplement includes details of Nd separation chemistry
171 for melt inclusions, and ¹⁴³Nd/¹⁴⁴Nd analyses by TIMS at the University of California, Santa
172 Barbara Isotope Geochemistry Facility. Only three melt inclusions (all from the Vailulu‘u
173 Seamount sample) in this study had sufficient Nd for the isotopic analysis.

174 The results of *in situ* analyses (of δD, and major, trace and volatile element concentrations)
175 of geologic reference materials (ALV519-4-1, ALV1833-1, GL07 D52-5, and BCR-2) can be

176 found in Table S2, and $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ analyses of BCR-2 can be found in Tables S6
177 and S8.

178 Melt inclusion major, trace, and volatile element concentrations were corrected for post-
179 entrapment crystallization (PEC) by addition or subtraction of equilibrium olivine in 0.1%
180 increments until the major element composition of the inclusion is in equilibrium with the host
181 olivine forsterite (Fo) content. In the calculation, two assumptions are made: (i) the olivine-melt
182 Fe-Mg $K_d = 0.30$ (Roeder & Emslie, 1970; Ford et al., 1983; $K_d = (\text{Fe}^{2+}/\text{Mg})_{\text{olivine}}/(\text{Fe}^{2+}/\text{Mg})_{\text{melt}}$)
183 and (ii) Fe^{3+} comprises 10% of the total moles of iron in the melt (following Hauri, 1996).
184 Unless stated otherwise, all major, trace, and volatile element concentrations reported below
185 have been corrected for equilibrium olivine addition/subtraction so that the inclusion is in
186 equilibrium with the host olivine.

187 The supplement also details the method of accounting for all CO_2 within a melt inclusion,
188 including both the CO_2 in the glass analyzed by ion probe, the CO_2 contained within the vapor
189 bubble obtained by Raman spectroscopy, and the volumes of bubble and glass for each melt
190 inclusion obtained by X-ray computed microtomography (see Table S3 for the method of
191 reconstructing the total CO_2 content of each melt inclusion).

192

193 **3. Methods for data treatment**

194 We use a series of criteria to identify inclusions where the volatile contents have been
195 compromised. This way the results and discussion can focus on primary magmatic signatures.
196 Figure 2 shows all melt inclusions from which we collected volatile data. Inclusions whose
197 volatile contents were likely compromised are designated with a black “x” in Figure 2. We do

198 not consider these inclusions further in our data analysis and interpretation so as to focus on
199 primary magmatic signatures. However, one inclusion with exceptionally high Cl concentration
200 (1.90 wt.% Cl) is included in subsequent analysis, but it is identified in all plots where it is
201 shown.

202 Inclusions are excluded if they show evidence of being affected by one or more of the following:

203 i) *Diffusive proton loss.* Hydrogen isotopes can indicate whether H₂O loss from the melt
204 inclusion has occurred by proton diffusion through the host olivine. Melt inclusions
205 that have been affected by proton diffusion will have low H₂O contents and high δD
206 values due to faster diffusion of hydrogen over deuterium (Hauri, 2002; Gaetani et al.,
207 2012; Bucholz et al., 2013; Hartley et al., 2015). Therefore, we measured δD on all
208 melt inclusions reported in this study. Melt inclusions in the Malumalu sample
209 (AVON3-78-1) have a δD range of -51.8‰ to +127.6‰, and melt inclusions in the
210 Vailulu‘u sample (AVON3-71-2) have a δD range of -52.4‰ to -22.0‰ (Figure 2).
211 Diffusive H₂O loss from melt inclusions should produce a systematic relationship
212 between melt inclusion δD and volume. Melt inclusions from both lavas with
213 volumes $>10^5 \mu\text{m}^3$ exhibit no systematic relationship between δD and melt inclusion
214 volume, and they exhibit a relatively narrow range in δD of $-35.8 \pm 17.0\%$ (2SD,
215 $N=19$). However, the two melt inclusions with positive δD values, both from
216 Malumalu (samples AVON3-78-1#13 and AVON3-78-1#32), have the smallest
217 volumes ($\sim 8.8 \times 10^4 \mu\text{m}^3$ and $4.3 \times 10^4 \mu\text{m}^3$). Prior work has shown that smaller
218 volume melt inclusions are more susceptible to diffusive proton loss that results in
219 elevated δD (Hauri, 2002; Gaetani et al., 2012; Bucholz et al., 2013; Hartley et al.,
220 2015). Therefore, the two small-volume inclusions are excluded.

- 221 ii) *Breaching*. Two melt inclusions have likely suffered breaching because CO₂ is <200
222 ppm and H₂O is <1 wt. % (see Figure S4; AVON3-78-1#25, AVON3-78-1#37). Both
223 melt inclusions exhibit melt-filled cracks that intersect the melt inclusions, which is
224 strong physical evidence that supports the breaching interpretation.
- 225 iii) *Extremely large vapor bubbles*. Three melt inclusions (AVON3-78-1#10, AVON3-
226 78-1#28, AVON3-71-2#20) have vapor bubbles that make up >10 vol. % of the melt
227 inclusion and are excluded. Prior work suggested that large vapor bubbles result from
228 simultaneous entrapment of a mix of melt and CO₂ fluid (e.g. Anderson, 1974;
229 Frezzotti, 2001; Hanyu et al., 2020; Moore et al., 2015), which is not representative of
230 melt-only compositions.
- 231 iv) *No CO₂ detected by Raman*. No Fermi doublets were observed by Raman
232 spectroscopy for two melt inclusions (AVON3-71-2#14, AVON3-71-2#18), thus the
233 CO₂ densities may have been too low for detection. To err on the side of caution, we
234 are excluding these two melt inclusions from the interpretations of this study. For
235 other excluded melt inclusions, CO₂ densities in the vapor bubbles were highly
236 uncertain (AVON3-71-2#20; ±0.092) or so low that negative values resulted from the
237 calibration (AVON3-78-1#25, AVON3-78-1#37, AVON3-71-2#14), and the volatile
238 data for these four melt inclusions are excluded from the discussion (except for
239 AVON3-71-2#14, which has an unusually high Cl concentration and is identified in
240 each plot where it is shown).
- 241 v) *Carbonate detected by Raman*. If carbon exists as carbonate in a melt inclusion, the
242 CO₂ budget of the melt inclusion may be underestimated. In this study, carbonates

243 were detected by Raman in two Malumalu melt inclusions (AVON3-78-1#15 and
244 AVON3-78-1#32), and volatile data for these inclusions are excluded.

245

246 4. Results

247 4.1 Hydrogen and strontium isotopes

248 After filtering the data for the compromised melt inclusions, the Samoan melt inclusions
249 from Malumalu ($-37.8 \pm 13.2\%$, $N=9$) and Vailulu'u ($-33.9 \pm 19.7\%$, $N=10$) are relatively
250 homogenous in δD with an average δD value of -35.8% ($\pm 17.0\%$, 2SD, $N=19$). The Samoan
251 inclusions have heavier δD than most MORB and Lō'ihī (now known as Kama'ehuakanaloa)
252 values, consistent with heavy δD values (ca. -40%) found in OIBs with recycled components
253 (Loewen et al., 2019).

254 Critically, $^{87}\text{Sr}/^{86}\text{Sr}$ measurements in melt inclusions provide a test for whether the Samoan
255 melt inclusions of this study represent the Samoan mantle sources sampled by Vailulu'u and
256 Malumalu glasses. If they do represent the same sources, then the volatile and trace element
257 concentrations of the melt inclusions can be directly compared to concentration measurements in
258 Samoan pillow lava glasses. The $^{87}\text{Sr}/^{86}\text{Sr}$ range for all of the Malumalu (sample AVON3-78-1)
259 melt inclusions reported here is large, from 0.706594 to 0.709225 (Figure 3, 4). The inclusions
260 largely fall within the range reported for Malumalu pillow glasses and whole rocks (0.706374–
261 0.708901; Workman et al., 2006). The $^{87}\text{Sr}/^{86}\text{Sr}$ range for all of the Vailulu'u (sample AVON3-
262 71-2) melt inclusions reported here is smaller compared to AVON3-78-1 melt inclusions, from
263 0.704858 to 0.705718. The range of Vailulu'u melt inclusion $^{87}\text{Sr}/^{86}\text{Sr}$ overlaps with the range
264 reported for Vailulu'u pillow glasses (0.705352–0.706720; Workman et al., 2006) but, relative to

265 Vailulu‘u pillow glasses and whole rocks, the Vailulu‘u melt inclusions are shifted to less
266 radiogenic (lower) $^{87}\text{Sr}/^{86}\text{Sr}$ values. Taken together, the $^{87}\text{Sr}/^{86}\text{Sr}$ for the Malumalu and Vailulu‘u
267 melt inclusions in this study bracket the $^{87}\text{Sr}/^{86}\text{Sr}$ obtained pillow glasses from each volcano: the
268 lowest $^{87}\text{Sr}/^{86}\text{Sr}$ in the melt inclusions (0.704858) is somewhat lower than the lowest value
269 measured in whole rocks and pillow glasses (0.705352) from these two seamounts, and the
270 highest $^{87}\text{Sr}/^{86}\text{Sr}$ in the melt inclusions (0.709225) is slightly higher than the highest value
271 measured in pillow glasses (0.708901). This statement is also true for the $(\text{La}/\text{Sm})_{\text{N}}$ and
272 $\text{K}_2\text{O}/\text{TiO}_2$ for the melt inclusions compared to the whole rocks and pillow glasses (Figure 4).
273 Therefore, the Malumalu and Vailulu‘u melt inclusions from these two hand samples represent
274 the full compositional range previously identified in these volcanoes and, in fact, span nearly the
275 entire range encountered in $^{87}\text{Sr}/^{86}\text{Sr}$ (i.e., 0.7045 to 0.7089) for the eastern Samoan volcanic
276 province—including Ta‘u, Vailulu‘u, and Malumalu volcanoes—examined by Workman et al.
277 (2006). Thus, the melt inclusions can be used to interpret mantle source geochemical
278 characteristics, including volatile budgets, of the volcanoes examined in Workman et al. (2006).

279 *4.2 Volatiles*

280 After omitting melt inclusions that have been contaminated, breached, affected by hydrogen
281 diffusion, and have unreliable CO_2 analyses by Raman, the magmatic volatile content of the
282 Samoan melt inclusions can be explored. Figure 5 provides ratios ($\text{H}_2\text{O}/\text{Ce}$, CO_2/Nb , Cl/Nb ,
283 S/Gd , and F/Nd) of volatile (H_2O , CO_2 , Cl , S , and F) to nonvolatile (Ce , Nb , Gd , and Nd)
284 incompatible trace elements (ITEs) that have similar mineral-melt partition coefficients during
285 mantle melting and magmatic differentiation processes. Below we examine the volatile
286 concentrations and their ratios to nonvolatile ITEs.

287

288 4.2.1. CO₂ in Samoan melt inclusions.

289 We use the CO₂ concentration in the melt inclusion glass analyzed by SIMS and the CO₂
290 density in the vapor bubble from Raman spectroscopy to reconstruct the total CO₂ concentration
291 of the melt inclusion. When comparing melt inclusion and vapor bubble CO₂, 3 to 94 mass
292 percent (average ~59 mass percent) of the total CO₂ (i.e., melt inclusion CO₂+vapor bubble CO₂)
293 resides in the vapor bubble, consistent with prior findings of large CO₂ fractions residing in melt
294 inclusion vapor bubbles (e.g., DeVitre et al., 2021; Aster et al., 2016; Moore et al., 2015).
295 Malumalu and Vailulu‘u melt inclusions have relatively similar total CO₂ contents of 1506–5746
296 ppm and 658–4771 ppm, respectively. The associated host pillow glasses for the Malumalu and
297 Vailulu‘u samples have total CO₂ contents of 70 ppm and 179 ppm, respectively (Workman et
298 al., 2006), which is far lower than the melt inclusions from these two volcanoes. These
299 observations are consistent with greater CO₂-H₂O saturation pressures for the melt inclusions
300 than the pillow glasses.

301 During melting and crystallization, the incompatibility (i.e., the bulk partition coefficient) of
302 CO₂ is similar to Nb and Ba, thus the ratios of CO₂/Nb or CO₂/Ba have been used to estimate
303 upper mantle carbon content (Hirschmann, 2018; Michael & Graham, 2015; Saal et al., 2002;
304 Cartigny et al., 2008; Le Voyer et al., 2017). However, only undegassed, CO₂-undersaturated
305 melts will have CO₂/Nb or CO₂/Ba that are representative of the mantle source, but such melts
306 are rare (Hauri et al., 2018; Graham & Michael, 2021; Le Voyer et al., 2017; Michael & Graham,
307 2015; Saal et al., 2002). These CO₂-undersaturated melts tend to be geochemically depleted
308 (Hauri et al., 2018; Shimizu et al., 2023) and have higher CO₂/Nb than most submarine volcanic
309 glasses, which are CO₂-saturated and thus degassed (e.g., the Samoan pillow glasses and melt
310 inclusions examined here). The Samoan melt inclusions in this study have a measured CO₂/Nb

311 range of 19 to 125 for Vailulu‘u melt inclusions and 27 to 133 for Malumalu melt inclusions, and
312 such ratios are lower than inferred for mantle sources of oceanic hotspot lavas (e.g., >1000 for
313 Iceland; Matthews et al., 2021) and MORB ($\text{CO}_2/\text{Nb} > 283$; Michael & Graham, 2015). Thus,
314 we suggest the Samoan samples are CO_2 -saturated and degassed, which is consistent with highly
315 variable total CO_2 contents (658 to 5746 ppm) relative to the narrow range of Nb concentrations
316 in our Samoan melt inclusions (Figure S6b,d). The Samoan pillow glasses from these two
317 volcanoes have even lower (more degassed) CO_2 concentrations while exhibiting similar Nb
318 concentrations to the melt inclusions (Figure S6b,d).

319

320 4.2.2. Cl in Samoan melt inclusions versus Samoa pillow glasses.

321 Malumalu melt inclusions have 651–1198 ppm Cl, and Vailulu‘u melt inclusions have 412–
322 765 ppm Cl (excluding the high Cl inclusion AVON3-71-2#14, which has a Cl concentration of
323 1.9 wt.% Cl). The associated pillow glasses from the two samples hosting the melt inclusions—
324 AVON3-78-1 and AVON3-71-2—have 1004 ppm Cl and 1490 ppm Cl, respectively. The suite
325 of pillow glasses from all Malumalu and Vailulu‘u samples have Cl contents that vary from 886
326 to 1725 ppm and 547 to 1818 ppm, respectively.

327 To determine if any melt inclusions are influenced by the assimilation of seawater-derived
328 materials, we use Cl/Nb as an indicator of assimilation of seawater-derived materials (e.g.,
329 Kendrick et al., 2013, 2015; Kent et al., 1999a, 1999b, 2002). This is a useful ratio because Cl
330 and Nb behave similarly during crystal fractionation and melting due to their similar
331 incompatibility in basalt melts (Rowe & Lassiter, 2009). Malumalu melt inclusions have a Cl/Nb
332 range of 14–25 and Vailulu‘u melt inclusions have a Cl/Nb range of 14–22 (excluding melt

333 inclusion sample AVON3-71-2#14, which has with $Cl/Nb = 840$) (Figure 5). The Samoan melt
334 inclusions have Cl/Nb that overlap with mid-ocean ridge basalts (MORB), where Cl/Nb_{MORB} is 5
335 to 17 (Lassiter et al., 2002; Le Roux et al., 2006), but the Samoan inclusions tend to be shifted to
336 higher Cl/Nb .

337 The pillow glasses for the Malumalu (AVON3-78-1) and Vailulu'u (AVON3-71-2) samples
338 hosting the Samoan melt inclusions have Cl/Nb of 13 and 27, respectively (Kendrick et al.,
339 2015). Both lavas have been previously suggested to have assimilated seawater-derived materials
340 (Kendrick et al., 2014; Reinhard et al., 2018). We find some evidence for assimilation in a single
341 melt inclusion from Vailulu'u (AVON3-71-2#14), which has a high Cl/Nb ratio of 840,
342 suggesting contamination by seawater-derived materials; however, any such assimilation does
343 not appear to have impacted $^{87}Sr/^{86}Sr$ (0.705471 ± 0.000022) as it is at the lower end of the range
344 observed here (Figure 5).

345 4.2.3 S in Samoan melt inclusions versus Samoa pillow glasses.

346 Malumalu melt inclusions have 1786–3163 ppm S, and Vailulu'u melt inclusions have 1582–
347 2090 ppm S. The associated host pillow glasses (AVON3-78-1 and AVON3-71-2) have 831 ppm
348 S and 2337 ppm S, respectively. The suite of pillow glasses from all Malumalu and Vailulu'u
349 samples have S contents varying from 781 to 2391 ppm and 1010 to 4834 ppm, respectively
350 (Workman et al., 2006).

351 Sulfur and Gd and Dy have similar incompatibility during melting and crystal fractionation
352 (Saal et al., 2002) when sulfide is not present, except at lower pressures when sulfur degasses.
353 However, Samoan basalts are known to host both sulfates and sulfides (Labidi et al., 2015). The
354 melt inclusions in this study are sulfide supersaturated (Figure S5; using the model of Fortin et

355 al., 2015 and Smythe et al., 2017)—and sulfides are in fact, observed in some of the inclusions
356 from the two samples examined here —thus S/Gd (Figure 5) of Samoan melt inclusions in this
357 study may have been influenced by sulfide saturation and are likely not representative of the
358 Samoan primary melts.

359

360 4.2.4. F in Samoan melt inclusions versus Samoa pillow glasses.

361 Malumalu melt inclusions have 1161–1293 ppm F, and Vailulu‘u melt inclusions have 777–
362 1145 ppm F. The associated host pillow glasses (AVON3-78-1 and AVON3-71-2) have 1254
363 ppm F and 903 ppm F, respectively. The suite of pillow glasses from all Malumalu and Vailulu‘u
364 samples have F contents varying from 1173 to 1409 ppm, and 843 to 1188 ppm F, respectively
365 (Workman et al., 2006).

366 F/Nd in melt inclusions and glasses from global datasets of MORB and OIB are suggested to
367 be relatively constant because there is no significant F/Nd fractionation during crystallization and
368 melting. The F/Nd values of global OIB and MORB have been estimated to be 20.1 ± 5.8
369 (Workman et al., 2006), but there is evidence for greater F/Nd variability (Koleszar et al., 2009;
370 Shimizu et al., 2016; Jackson et al., 2015; Lassiter et al., 2002; Métrich et al., 2014; Cabral et al.,
371 2014; Rose-Koga et al., 2012). The average F/Nd for Malumalu melt inclusions (30 ± 6 2SD,
372 $N=9$) is similar to the average F/Nd for Vailulu‘u melt inclusions (29 ± 14 2SD, $N=10$), but
373 Vailulu‘u melt inclusions have more variability in F/Nd (Figure 5). Three Vailulu‘u melt
374 inclusions (AVON3-71-2#7, #17, #22) have ~200 ppm lower F contents than the other Samoan
375 melt inclusions, but similar Nd contents, resulting in lower F/Nd (21–23). The Samoan melt
376 inclusion have F/Nd (29 ± 11 , 2SD, $N=19$) tends to be higher than the canonical F/Nd (~21) for

377 fresh global OIB and MORB, and higher than the average pillow glass F/Nd from Malumalu
378 (22 ± 2 , 2SD, N=17; Workman et al., 2006) and Vailulu'u (22 ± 3 , 2SD, N=48; Workman et al.,
379 2006). However, the average F/Nd of Samoan melt inclusions overlaps within two standard
380 deviations of the canonical F/Nd value and the F/Nd of Samoan pillow glasses. Nonetheless, the
381 Vailulu'u melt inclusions tend to very high F/Nd up to 41. Elevated F may be characteristic of
382 the HIMU mantle source (Hauri & Hart, 1993; Rose-Koga et al., 2017; Jackson et al., 2015), and
383 Vailulu'u is thought to contain a small contribution from a HIMU component (Workman et al.,
384 2004; Jackson et al., 2014). However, we do not have an explanation for the higher F/Nd in the
385 Vailulu'u melt inclusions relative to the glasses from this seamount.

386

387 4.2.5. H₂O in Samoan melt inclusions versus Samoa pillow glasses.

388 Malumalu melt inclusions have 1.56–1.95 wt.% H₂O, and Vailulu'u melt inclusions have 1.13–
389 1.39 wt.% H₂O. The associated host glasses from these two submarine samples tend to have
390 lower H₂O contents than the melt inclusions with 0.91 wt.% H₂O (AVON3-78-1) and 1.18 wt.%
391 H₂O (AVON3-71-2), respectively. The low H₂O in the AVON3-78-1 Malumalu glass sample
392 lies within the range of H₂O for pillow glass samples from Malumalu (0.89 to 1.43 wt.%), and
393 the same applies for the AVON3-71-2 Vailulu'u glass sample as it also lies in the range of pillow
394 glasses from this seamount (0.63 to 1.50 wt.%) (Figure 6). When the melt inclusions and pillow
395 glasses are corrected for olivine fractionation to be in equilibrium with mantle olivine (F_{0.90}), a
396 figure of H₂O_{F_{0.90}} (wt.%) versus Ce_{F_{0.90}} (ppm) shows that the melt inclusions and pillow glasses
397 from Malumalu and Vailulu'u seamounts have similar Ce_{F_{0.90}}, but the inclusions have H₂O that is
398 higher than the pillow glasses (Figure S6c). We also show the same plot but instead provide the

399 *measured* H₂O and Ce in the glass glasses—due to uncertainties associated with the olivine
400 correction—and find that it does not change our conclusions.

401 Consistent with this observation, the H₂O/Ce range of the Malumalu AVON3-78-1 melt
402 inclusions (149–232, average 193±47, 2SD, N=10) and the Vailulu‘u AVON3-71-2 melt
403 inclusions (161–275, average 190±78, 2SD, N=10) are higher than the host pillow glasses, 59
404 (for pillow glass from sample AVON3-78-1) and 123 (for pillow glass from sample AVON3-71-
405 2), respectively. Critically, the average H₂O/Ce (197±58 2SD, N=15) in the melt inclusion
406 dataset from Malumalu and Vailulu‘u seamounts is nearly twice as high as the same ratio in the
407 Samoan pillow glasses from these two seamounts (106±51, 2SD, N=65). This is notable because
408 the inclusions and pillow glasses are from the same two volcanoes, span the same range of
409 ⁸⁷Sr/⁸⁶Sr (Figure 3), and have similar ITE ratios (Figure 4), suggesting they sample the same
410 mantle sources. This observation that melt inclusions have higher H₂O/Ce than submarine pillow
411 glasses may relate to the fact that the Samoan melt inclusions from Malumalu and Vailulu‘u
412 have universally higher calculated MagmaSat CO₂-H₂O vapor saturation pressures (Figure 3)
413 than the submarine pillow glasses, reflective of higher entrapment pressures for the melt
414 inclusions (>0.870 kbar) than the eruption pressures experienced by the glasses (<0.53 kbar) (see
415 Figure 3).

416 While Workman et al. (2006) found a negative correlation between H₂O/La and ⁸⁷Sr/⁸⁶Sr for
417 Samoan glasses, we find that the Samoan melt inclusions in this study exhibit *no correlation*
418 between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr (Figure 3, 5a, 7a), even though the melt inclusions are from two of
419 the three volcanoes studied by Workman et al. (2006) and span the same range of ⁸⁷Sr/⁸⁶Sr as
420 their pillow glasses. In contrast to Workman et al. (2006), the H₂O/Ce of the melt inclusions is
421 quite constant (i.e., 197±58 2SD, N=15) over a range of ⁸⁷Sr/⁸⁶Sr from 0.704858 to 0.709225,

422 and the melt inclusions with the strongest EM2 mantle signatures (i.e., $^{87}\text{Sr}/^{86}\text{Sr} > 0.7080$, N=4)
423 have elevated $\text{H}_2\text{O}/\text{Ce}$ (193 ± 19 2SD) that is indistinguishable from the $\text{H}_2\text{O}/\text{Ce}$ (202 ± 31) in melt
424 inclusions with weaker EM2 signatures ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7080$, N=3).

425 While the Samoan pillow glasses and melt inclusions exhibit some overlap with each other in
426 $\text{H}_2\text{O}/\text{Ce}$ at the lowest $^{87}\text{Sr}/^{86}\text{Sr}$, they exhibit diverging trends in $\text{H}_2\text{O}/\text{Ce}$ with increasing $^{87}\text{Sr}/^{86}\text{Sr}$:
427 melt inclusions exhibit unchanging $\text{H}_2\text{O}/\text{Ce}$ with increasing $^{87}\text{Sr}/^{86}\text{Sr}$, and glass exhibit
428 decreasing $\text{H}_2\text{O}/\text{Ce}$ with increasing $^{87}\text{Sr}/^{86}\text{Sr}$. Thus, the difference in $\text{H}_2\text{O}/\text{Ce}$ between melt
429 inclusions and glasses is largest at the highest $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 7). To illustrate this, we note that
430 all four pillow glasses with the strongest EM2 signatures ($^{87}\text{Sr}/^{86}\text{Sr} > 0.7080$) have $\text{H}_2\text{O}/\text{Ce} < 90$
431 ($\text{H}_2\text{O}/\text{Ce}$ average of 75 ± 30 , 2SD) while the $\text{H}_2\text{O}/\text{Ce}$ of the four melt inclusions with the highest
432 $^{87}\text{Sr}/^{86}\text{Sr}$ (> 0.7080) have $\text{H}_2\text{O}/\text{Ce}$ that is more than twice as high as that in the pillow glasses
433 ($\text{H}_2\text{O}/\text{Ce}$ average of 193 ± 19 , 2SD). Prior studies (e.g., Workman et al., 2006) often cite that
434 pillow glasses erupted at depths > 1000 mbsl retain volatile/ITE ratios of the mantle source. All
435 pillow glasses shown in Figure 7 have $\text{H}_2\text{O}-\text{CO}_2$ saturation pressures ≥ 0.1 kbar. Given that the
436 melt inclusions and glasses in Figure 7 exhibit deep saturation pressures and appear to sample
437 the same mantle source (Figure 4), we might expect the deeply-erupted pillow glasses should
438 have the same $\text{H}_2\text{O}/\text{Ce}$ as melt inclusions. These observations raise a key question that we will
439 address in the discussion: why do melt inclusions and pillow glasses erupted at depths > 1000
440 mbsl from the same volcanoes and with the same $^{87}\text{Sr}/^{86}\text{Sr}$ (i.e., sampling the same mantle
441 sources) have $\text{H}_2\text{O}/\text{Ce}$ that differ, on average, by nearly a factor of two?

442

443 **5. Modeling degassing processes for Samoan melts**

444 We find that melt inclusions from the Vailulu‘u and Malumalu seamounts have higher
445 CO₂ concentrations than their corresponding pillow glasses (Figure 6), indicating that the deeply-
446 erupted submarine pillow glasses are more degassed than the melt inclusions. An outstanding
447 question is whether the lower H₂O/Ce in the pillow glasses reflects this higher degree of
448 degassing via concomitant degassing of both CO₂ and H₂O.

449 We show that the data are consistent with Samoan pillow glasses being related to the
450 Samoan melt inclusions through closed-system degassing; the new insight gained here is that,
451 when compared with genetically-related melt inclusions, it is clear that even deeply erupted
452 glasses (with CO₂-H₂O saturation pressures ≥ 0.1 kbar) have lost significant H₂O and have lower
453 H₂O/Ce compared to their primary melt (Figure 3). This is evident in models we have run using a
454 set of open- and closed-system degassing paths while also varying the fraction of CO₂+H₂O fluid
455 in equilibrium with the initial melt (Figure 6). In the models, we define the variable M as the
456 percentage of fluid in equilibrium with the melt, where M = 0% means that no initial fluid is in
457 equilibrium with the melt (i.e., all volatiles are dissolved in the melt, no fluid is present), and
458 where M = 100% means that all volatiles are in the fluid (i.e., no melt is present). The higher the
459 M value, the deeper degassing starts. We generate degassing paths assuming a starting H₂O and
460 CO₂ composition equivalent to the melt inclusion with the highest H₂O content from Malumalu
461 seamount (sample AVON3-78-1#3) to model Malumalu data, and the equivalent high-H₂O melt
462 inclusion from Vailulu‘u (sample AVON3-71-2#10) to model Vailulu‘u data. We use MagmaSat
463 (Ghiorso & Gualda, 2015) to calculate the fluid composition (i.e., X_{CO_2} and $X_{\text{H}_2\text{O}}$) in
464 equilibrium with the two melt inclusions (see Table S9 for model melt inclusion compositions).
465 Additionally, we use rhyolite-MELTS v.1.2 (which incorporates the same fluid solubility model
466 as MagmaSat) to simulate degassing because this model is well-suited for high CO₂ contents in

467 the initial melt composition (Ghiorso & Gualda, 2015; Gualda et al., 2012). The models are run
468 at 1200 °C, and start at 7–15 kbar (for Malumalu degassing paths, due to higher initial CO₂
469 contents), or 7 kbar (for Vailulu‘u, which has lower initial CO₂), and run to 1 bar. The influence
470 of oxygen fugacity on the model degassing path is negligible, so we assume QFM for all models.
471 The compositional and physical parameters used in the MagmaSat and rhyolite-MELTS models
472 are given in Table S9.

473 The degassing model results are presented in Figure 6. While there is no single degassing
474 path that explains the difference in pillow glass and melt inclusion CO₂ and H₂O concentrations,
475 closed-system degassing paths with M values ranging from 0% to 10% describe most of the
476 pillow glasses from both seamounts. However, there are some Vailulu‘u pillow glasses that have
477 H₂O that is higher than the range described by the calculated degassing paths. For example, three
478 Vailulu‘u pillow glasses have higher H₂O concentrations than the highest-H₂O melt inclusion.
479 This could be because the melt inclusion suite in this study does not represent the full range of
480 H₂O contents possible at the seamount, and higher initial H₂O concentrations may be more
481 reflective of the primary melts.

482 A primary observation from this modeling exercise is that closed-system degassing from
483 melt inclusion entrapment pressures (i.e., >0.87 kbar) to eruption on the seafloor (pillow glasses
484 have equilibrium pressures of 0.08 to 0.53 kbar) results in significant loss of both CO₂ and H₂O,
485 even for glasses with CO₂-H₂O saturation depths near 0.4 kbar (see closed-system degassing
486 paths in Figure 6). Furthermore, the presence of equilibrium fluid (M) indicates that the
487 magmatic system is richer in CO₂, and thus starts to degas at greater depths. Below we show that
488 loss of H₂O during closed-system degassing to shallow levels (i.e., <0.53 kbar) explains the
489 lower H₂O/Ce in pillow glasses compared to the melt inclusions.

490 **6. Discussion**

491 H₂O has incompatibility during mantle melting similar Ce (Michael, 1995), thus H₂O/Ce
492 of the melt inclusions and glasses should reflect the mantle source unless the samples have
493 degassed. Clear negative correlations between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr in pillow glasses have been
494 used to infer the H₂O/LREE (light rare earth element) ratios of the mantle source, assuming the
495 H₂O has not been degassed. The primary observation in this study that we seek to explain is that
496 Samoan pillow glasses and olivine-hosted melt inclusions span the same range of ⁸⁷Sr/⁸⁶Sr and
497 trace element ratios—and thus sample the same mantle sources, yet the melt inclusions have
498 H₂O/Ce ratios that are approximately twice as high as the pillow glasses. The second key
499 observation is that the melt inclusion H₂O/Ce ratios are relatively constant over a wide range of
500 ⁸⁷Sr/⁸⁶Sr, in contrast to the pillow glasses whose H₂O/Ce ratios anticorrelate with ⁸⁷Sr/⁸⁶Sr. This
501 raises two key questions: Why do Samoan EM2 pillow glasses exhibit H₂O/Ce that are
502 approximately half the values in Samoan EM2 melt inclusions at the same seamounts, and what
503 does this mean for the H₂O content of the EM2 mantle?

504

505 **6.1. Higher H₂O/Ce in melt inclusions relative to pillow glasses: Diffusive H₂O gain through**
506 **host olivine and/or assimilation of seawater-derived materials?**

507 In order to compare the volatile contents of the Samoan melt inclusions and pillow
508 glasses in this study, it is important to assess whether the higher H₂O/Ce in the inclusions reflects
509 processes operating in the magma during ascent, such as diffusive proton gain (i.e., addition of
510 H) or assimilation of seawater-derived materials. Prior work has shown that, compared to large
511 melt inclusions, small inclusions are more susceptible to diffusive loss or addition of protons,

512 and this results in modified δD (Hauri, 2002; Portnyagin et al., 2008; Gaetani et al., 2012;
513 Bucholz et al., 2013; Hartley et al., 2015). Given enough time, the δD of all inclusions will
514 eventually equilibrate with the external melt. Diffusive proton loss from the inclusion can be
515 identified by an increase in δD , which is associated with decreasing melt inclusion volume.
516 Conversely, diffusive gain of protons by the inclusion is identified by a decrease in δD , where
517 the magnitude of the δD reduction is greater in the smaller volume melt inclusions. The new δD
518 analyses on melt inclusions show a lack of variation in δD ($-35.8 \pm 17.0\%$, 2SD, N=19) with melt
519 inclusion size for melt inclusions with volumes $>10^5 \mu\text{m}^3$, which indicates no water loss or gain
520 in the larger inclusions (Figure 2). However, the two smallest melt inclusions (AVON3-78-1#13
521 and AVON3-78-1#32), both with melt inclusion volume $<10^5 \mu\text{m}^3$, have significantly higher δD
522 ($+128\%$ and $+6\%$, respectively) than the other melt inclusions from this lava, which indicates
523 that the small volume melt inclusions have experienced diffusive H_2O loss, not H_2O addition
524 (Figure 2). These two small volume inclusions are excluded from the discussion below.

525 Assimilation of seawater-derived materials can increase H_2O in magmas (except if the
526 magma is saturated in H_2O), and this process can be traced by monitoring Cl/Nb, a ratio that is
527 elevated in seawater-derived materials. One hypothesis for the higher $\text{H}_2\text{O}/\text{Ce}$ in melt inclusions
528 is that they have experienced more assimilation of seawater-derived materials compared to
529 Samoan pillow glasses, and this hypothesis can be tested by measurement of $^{87}\text{Sr}/^{86}\text{Sr}$. A plot of
530 Cl/Nb versus $^{87}\text{Sr}/^{86}\text{Sr}$ shows that Samoan pillow glasses and melt inclusions have an
531 overlapping range of Cl/Nb at any given $^{87}\text{Sr}/^{86}\text{Sr}$, so the offset to higher $\text{H}_2\text{O}/\text{Ce}$ in the melt
532 inclusions is not explained by greater assimilation experienced by melt inclusions (Figure 5). We
533 do acknowledge that one melt inclusion with exceptionally high Cl/Nb (840)—a ratio consistent
534 with assimilation of seawater-derived materials (Table S1)—also has elevated $\text{H}_2\text{O}/\text{Ce}$ (366),

535 suggesting a role for assimilation in increasing the H₂O/Ce in this particular inclusion. However,
536 this single inclusion has been excluded from the discussion below owing to its very high Cl/Nb.

537 In short, diffusive gain of H₂O and preferential assimilation of seawater-derived materials
538 by the melt inclusions relative to the pillow glasses do not explain the higher H₂O/Ce in the melt
539 inclusions relative to the pillow glasses. Instead, we argue in the following section that closed-
540 system degassing plays a key role in lowering the H₂O and the H₂O/Ce of pillow glasses. In
541 contrast, limited H₂O degassing has occurred in the melt inclusions in this study, leaving the melt
542 inclusion H₂O/Ce relatively unchanged, thereby explaining why melt inclusions have higher
543 H₂O/Ce than pillow glasses. This contrasts with prior studies (e.g., Workman et al., 2006)
544 suggesting that pillow glasses erupted at depths >1000 mbsl retain H₂O/LREE ratios of the
545 mantle source.

546 **6.2 Higher H₂O/Ce in melt inclusions relative to pillow glasses: H₂O loss in Samoan glasses**
547 **caused by degassing**

548 We argue that the difference in H₂O/Ce between Samoan EM2-flavored melt inclusions
549 and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses
550 relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from
551 great depth all the way to eruption and quenching on the seafloor, melt inclusions trap melts at
552 magma chamber depths and act as pressure vessels, which inhibits degassing at shallower levels
553 during magma ascent. To evaluate this hypothesis, we build on the indistinguishable ⁸⁷Sr/⁸⁶Sr
554 and nonvolatile incompatible trace element ratios between pillow glasses and melt inclusions and
555 argue that, at the depth of melt inclusion entrapment, the H₂O/Ce of the melts that later erupted
556 as Samoan pillow glasses was *also* the same as the Samoan melt inclusions (i.e., nonvolatile ITE
557 ratios—which remain unmodified from primary melt compositions during fractional

558 crystallization of magmas with MgO as high as identified in the data reported here (Figure S1)—
559 and $^{87}\text{Sr}/^{86}\text{Sr}$ data obtained on the melt inclusions indicate that they derive from the same
560 parental melts as the pillow glasses and thus should have started with the same $\text{H}_2\text{O}/\text{Ce}$. The
561 $\text{H}_2\text{O}/\text{Ce}$ of the pillow glasses, but not the melt inclusions, was then lowered by H_2O degassing
562 during ascent.

563 The hypothesis of H_2O loss from the matrix melts by degassing is supported by closed-
564 system degassing models in Figure 6. For example, the degassing model for Malumalu AVON3-
565 78-1 starts with a melt inclusion composition like AVON3-78-1#3 which has an elevated CO_2
566 concentration of 2810 ppm, the highest H_2O concentration from this lava (1.95 wt.%), and a high
567 entrapment pressure of 2.63 kbar (i.e., the CO_2 - H_2O saturation pressure calculated for the melt
568 inclusion using MagmaSat). Closed-system degassing of this melt composition from 2.63 kbar to
569 0.2 kbar—the approximate CO_2 - H_2O saturation pressure for the pillow glass from this lava,
570 sample AVON3-78-1—at $M=1.6$ lowers the water content by a factor of ~ 2.1 to 0.90 wt.%, and
571 the CO_2 content by a factor of ~ 40 to 69 ppm. The red “x” in Figure 6a defines the CO_2 and H_2O
572 composition of the model melt following degassing, and the degassed model melt is very similar
573 in composition to the pillow glass sample AVON3-78-1 and helps explain the low H_2O (0.91
574 wt.%) and CO_2 (70 ppm) of AVON3-78-1. This is important because this particular pillow glass
575 sample anchors the highest $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7089) and lowest $\text{H}_2\text{O}/\text{Ce}$ (59) portion of the $^{87}\text{Sr}/^{86}\text{Sr}$
576 versus $\text{H}_2\text{O}/\text{Ce}$ array produced by Workman et al. (2006) who interpreted that the low $\text{H}_2\text{O}/\text{Ce}$ in
577 this EM2 glass reflects melting of a water-poor (“dry”) EM2 mantle. In contrast, we show that
578 dramatic H_2O -loss during closed-system degassing of an ascending EM2 melt with an initially
579 high $\text{H}_2\text{O}/\text{Ce}$ ratio ($\text{H}_2\text{O}/\text{Ce} = 200$) is responsible for the low $\text{H}_2\text{O}/\text{Ce}$ (59) in the AVON3-78-1
580 glass. This model contrasts with prior studies (e.g., Workman et al., 2006) suggesting that pillow

581 glasses erupted at depths >1000 mbsl (≥ 0.1 kbar) retain the H₂O/LREE ratios of the mantle
582 source.

583 We observe a relatively constant and elevated H₂O/Ce ratio in melt inclusions over a
584 wide range of ⁸⁷Sr/⁸⁶Sr—melt inclusions with strong EM2 mantle signatures (i.e., ⁸⁷Sr/⁸⁶Sr >
585 0.7080) have elevated H₂O/Ce (193±19 2SD, N=4) that is indistinguishable from H₂O/Ce
586 (202±31, N=3) in melt inclusions with weaker EM2 signatures (⁸⁷Sr/⁸⁶Sr < 0.7080). This also
587 contrasts with Workman et al.'s (2006) observation that H₂O/LREE is lower in the Samoan EM2
588 pillow glasses with higher ⁸⁷Sr/⁸⁶Sr. Unlike Workman et al. (2006), who argued that the low
589 H₂O/LREE in Samoan EM2 glasses is a source feature, we show that the low ratio in these
590 pillow glasses relative to that of the melt inclusions can be explained by closed-system degassing
591 of magmas during ascent to the seafloor. If this degassing model is correct, and if Samoan high
592 ⁸⁷Sr/⁸⁶Sr and low ⁸⁷Sr/⁸⁶Sr melts have the same initial H₂O/Ce—as supported by observations
593 from melt inclusions in Figure 5a—then the negative correlation between ⁸⁷Sr/⁸⁶Sr in H₂O/Ce in
594 the pillow glasses in Workman et al. (2006) (Figure 7) leads us to an important conclusion: the
595 Samoan EM2 pillow glasses have degassed more H₂O (to achieve lower H₂O/Ce) than Samoan
596 pillow glasses with weaker EM2 signatures (which have higher H₂O/Ce). Therefore, we next
597 focus on identifying the mechanism that results in greater H₂O degassing in more extreme EM
598 melts relative to non-EM melts.

599

600 **6.3 Explaining the inverse relationship between ⁸⁷Sr/⁸⁶Sr and H₂O/Ce in global pillow**
601 **glasses by degassing.**

602 The global OIB dataset on submarine pillow glasses exhibits an inverse relationship
603 between ⁸⁷Sr/⁸⁶Sr and H₂O/Ce (Figure 7) that is similar to the inverse correlation observed in

604 Samoan submarine glasses, and it has long been known that submarine glasses with low $^{87}\text{Sr}/^{86}\text{Sr}$
605 tend to have higher $\text{H}_2\text{O}/\text{Ce}$ than glasses with high $^{87}\text{Sr}/^{86}\text{Sr}$ (e.g., Dixon et al., 2002; Workman
606 et al., 2006; Kendrick et al., 2014). The Samoan melt inclusions noticeably stray from this trend.
607 The Samoan melt inclusions with high $^{87}\text{Sr}/^{86}\text{Sr}$ are shifted to higher, relatively constant $\text{H}_2\text{O}/\text{Ce}$
608 (197 ± 58 2SD, $N=15$) compared to the $\text{H}_2\text{O}/\text{Ce}$ (108 ± 58 , 2SD, $N=41$) in a global database of OIB
609 glasses (including Samoa) that have similarly high $^{87}\text{Sr}/^{86}\text{Sr}$ (i.e., >0.7037) (Figure 7). In fact, the
610 high $\text{H}_2\text{O}/\text{Ce}$ of Samoan inclusions (197 ± 58 2SD, $N=15$) is similar to the $\text{H}_2\text{O}/\text{Ce}$ (209 ± 92 , 2SD,
611 $N=32$) of pillow glasses characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ (<0.7037 , the threshold value used to
612 distinguish between EM and non-EM melts). If the Samoan melt inclusions represent less
613 degassed versions of the melts sampled by Samoan submarine glasses, then the similarity in
614 $\text{H}_2\text{O}/\text{Ce}$ between low $^{87}\text{Sr}/^{86}\text{Sr}$ (<0.7037) OIB pillow glasses and Samoan melt inclusions
615 (>0.7037) raises the possibility that non-EM OIB melts and EM OIB melts initially have the
616 same $\text{H}_2\text{O}/\text{Ce}$, but the latter suffer more degassing of H_2O than the former during magma ascent.
617 If the inverse correlation between $\text{H}_2\text{O}/\text{Ce}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in Samoan, and global, OIB glasses is
618 driven by greater degassing of the most geochemically enriched lavas compared to
619 geochemically depleted lavas, what mechanism causes geochemically enriched glasses from OIB
620 mantle sources to have suffered more H_2O degassing than geochemically depleted glasses?

621 Previous work suggests that EM mantle sources have higher CO_2 , and generate primary
622 melts with higher CO_2 , than non-EM mantle sources (Burnard et al., 2014; Cartigny et al., 2008;
623 Taracsák et al., 2019; Hauri et al., 2018; Miller et al 2019; Matthews et al. 2021; Michael &
624 Graham, 2015; Shimizu et al., 2023). We show that primary melts with higher CO_2 degas more
625 CO_2 and more H_2O by closed-system degassing during ascent than primary melts with the same
626 H_2O but lower CO_2 concentrations. As a result, EM lavas that were initially more CO_2 -rich erupt

627 on the seafloor with lower H₂O/Ce than their geochemically-depleted non-EM counterparts that
628 started with lower primary melt CO₂, even though both EM and non-EM primary melts started
629 with the same H₂O concentrations and H₂O/Ce. At the extreme end, non-EM (i.e., geochemically
630 depleted) melts erupted at, for example, MORB settings, can have such low primary melt CO₂
631 that they never saturate and neither CO₂ nor H₂O are lost by degassing (Saal et al., 2002;
632 Michael & Graham, 2015; Hauri et al., 2018).

633 By contrast, we argue that CO₂-rich primary melts, typical of geochemically-enriched
634 OIB settings, saturate CO₂ at great depths and lose significant CO₂ and H₂O by closed-system
635 degassing. In order to show this, we first estimate primary melt CO₂ for a suite of global OIB
636 glasses using a set of relationships shown in Figures 8 and 9. Because OIB glasses are degassed
637 in CO₂ to variable degrees, we estimate primary melt (undegassed) CO₂ for OIB glasses in the
638 following way. First, using a new correlation between undegassed CO₂/Nb and (La/Sm)_N in
639 MORB and OIB (see equation in Figure 9a and discussion in Supplementary Information section
640 S1.8), together with the measured (La/Sm)_N available in the suite of OIB glasses examined here,
641 we can calculate the primary melt CO₂/Nb in the OIB glasses (Figure 8c). (It is worth noting that
642 the correlation between CO₂/Nb and (La/Sm)_N in Figure 9a is similar to a relationship previously
643 suggested for MORB by Cartigny et al. (2008) (Figure 9b).) We then calculate the primary melt
644 Nb concentrations for each of the OIB glasses by correcting for olivine addition or subtraction so
645 the melts are in equilibrium with mantle (F₀₉₀) olivine (Figure 8d). By multiplying calculated
646 primary melt CO₂/Nb (Figure 8c) by the calculated primary melt Nb concentrations (Figure 8d),
647 we obtain primary melt CO₂ concentrations for the OIB glasses (Figure 8e). These calculations
648 suggest that the most extreme EM OIB glasses (which have the lowest H₂O/Ce)—all from the
649 Samoa, Societies, and Pitcairn hotspots—tend to have the highest primary melt CO₂ (Figure 8e),

650 with CO₂ concentrations commonly as high as 5 to 6 wt.% in Samoa and Societies lavas (and
651 higher than 80,000 ppm CO₂ in two Samoan lavas). These high OIB primary melt CO₂
652 concentrations calculated with our new model are in broad agreement with CO₂ concentrations
653 calculated using the petrologic model of Sun and Dasgupta (2020) (see supplementary Figure S9
654 for direct comparison).

655 Based on these calculations, Samoan primary melts inferred from the pillow rim glass
656 data have CO₂ concentrations between ~28,000 ppm and ~94,000 ppm, with most values
657 clustering near ~60,000 ppm CO₂ (Figure 8e). With few exceptions, the non-EM OIB (which
658 have the highest erupted H₂O/Ce)—Lō‘ihi, Easter, and Foundation—have lower calculated
659 primary melt CO₂ than the EM OIB—Samoa, Societies, Pitcairn, and Réunion (Figure 8e). This
660 is consistent with prior suggestions that geochemically enriched mantle domains with higher
661 ⁸⁷Sr/⁸⁶Sr generate primary melts with higher CO₂ than geochemically depleted mantle domains
662 (Burnard et al., 2014; Cartigny et al., 2008). Like Burnard et al. (2014), we argue that melts with
663 higher initial CO₂—characteristic of EM melts (Figure 8e)—undergo greater degrees of
664 degassing than melts with lower initial CO₂. We then show that, everything else being the same,
665 higher initial CO₂ melts experience greater degassing of H₂O (and thus have lower erupted
666 H₂O/Ce) than melts with lower initial CO₂ (Figure 8).

667 In order to demonstrate this quantitatively, we use the calculated primary melt CO₂ of the
668 OIB glasses in Figure 8e, as well as estimated primary melt H₂O (see below), as inputs to a
669 closed-system degassing model. We then show that the CO₂-rich (60,000 ppm) model primary
670 melt degasses by closed-system degassing to have H₂O concentration and H₂O/Ce similar to
671 values measured in Samoan EM pillow glasses. To test our hypothesis that high primary melt
672 CO₂ concentrations results in more degassing of H₂O, and thus, lower H₂O/Ce in the final

673 erupted and degassed melt, we examine how H₂O and CO₂ concentrations change with
674 decreasing pressure starting with two hypothetical primary melts that are identical in all respects
675 except for the initial CO₂ concentrations: the two melt endmembers are given the same starting
676 H₂O (2 wt.%), H₂O/Ce (200), and major and trace element chemistry (see compositions in Table
677 S9). The first model melt is assigned a higher CO₂ concentration of 60,000 ppm, meant to
678 approximate the elevated CO₂ concentration of EM glasses in Figure 8e (see previous
679 paragraph), and comes from our new model for calculating CO₂ in OIB primary melts (Figure
680 8c, 9a) for which calculated Samoan primary melt CO₂ concentrations tend to cluster near 60,000
681 ppm CO₂. The second model melt is assigned an initial CO₂ concentration of 5,000 ppm, and is
682 meant to approximate the CO₂ concentration of the non-EM glasses from Foundation, Easter,
683 and Lō‘ihi in Figure 8e. In order to illustrate the impact of H₂O loss during degassing as a
684 function of initial primary melt CO₂ concentration, we model the closed-system degassing paths
685 of the two melts using rhyolite-MELTS. Degassing of the high CO₂ (60,000 ppm) melt starts at
686 26 kbar (i.e., where CO₂ first saturates; see dark green line in Figure 10), which is higher than the
687 4 kbar pressure where the lower CO₂ melt saturates (see light green line in Figure 10). After both
688 the high- and low-CO₂ melts degas to the same low eruptive pressure (Figure 10)—0.5 kbar,
689 meant to represent pressure for eruption on the seafloor at ~5000 mbsl—the high CO₂ melt has a
690 significantly lower H₂O concentration and lower H₂O/Ce (~0.94 wt.% and 94, respectively)
691 compared to the low CO₂ melt (~1.56 wt.% wt.% and 156, respectively), even though both melts
692 started with the same H₂O (2 wt.%) and H₂O/Ce (200). In summary, a melt with initial CO₂ of
693 60,000 ppm degases nearly 53% of its H₂O (and 99.4% of its CO₂) during ascent to 0.5 kbar, but
694 the melt with 5000 ppm initial CO₂ degases just 22% of its H₂O (and 96.8% of its CO₂) during

695 ascent to 0.5 kbar. Thus, everything else being the same, high CO₂ melts degas more H₂O and
696 have lower H₂O/Ce than low CO₂ melts.

697 The simple degassing model in Figure 10 helps explain the observation that EM pillow
698 glasses erupted on the seafloor have lower H₂O/Ce compared to non-EM pillow glasses: EM
699 primary melts, which are associated with higher initial CO₂ (Figure 8e), saturate in volatiles
700 deeper in the crust/mantle and degas more CO₂ and H₂O prior to eruption than non-EM melts
701 with lower primary melt CO₂. The Samoan melt inclusions in this study exhibit high H₂O/Ce,
702 similar to non-EM melts, because CO₂ and H₂O degassing was arrested following melt inclusion
703 entrapment in olivine at high pressures (0.870 to 5.13 kbar). Although the Samoan melt
704 inclusions lost significant amounts of CO₂ prior to being entrapped by olivine, these melt
705 inclusions still preserve higher H₂O/Ce than the erupted pillow glasses due to having degassed
706 less CO₂ and, thus, less H₂O. However, we acknowledge that, prior to entrapment, even the melt
707 inclusions may have already lost some H₂O due to concomitant loss of both H₂O and CO₂ during
708 closed-system degassing. Nonetheless, melt inclusions preserve higher H₂O and H₂O/Ce than
709 pillow glasses, and thus preserve values closer to the primary melts.

710 **6.4 Comparison with prior models for the origin of low H₂O/Ce in EM lavas, and**
711 **implications for a “damp” EM mantle.**

712 Previous studies have suggested that the negative correlation between H₂O/Ce and
713 ⁸⁷Sr/⁸⁶Sr is the result of dehydration (H₂O depletion) in the EM source, which has low H₂O/Ce
714 that gives rise to EM primary melts with low H₂O/Ce. In these models, the EM mantle source
715 has low H₂O/Ce because subducted materials contributing to the EM mantle lose H₂O during
716 subduction (Dixon et al., 2002) or via diffusion during residence in the mantle (Workman et al.,
717 2006), or because the pyroxenite—which has low H₂O/Ce—contributes to the EM mantle

718 (Bizimis & Peslier et al., 2015). However, if these models explained the origin of the low
719 H₂O/Ce in high ⁸⁷Sr/⁸⁶Sr glasses from Samoa, then the Samoan melt inclusions with high
720 ⁸⁷Sr/⁸⁶Sr should also exhibit lower H₂O/Ce, but this is not the case.

721 Thus, an important implication is that submarine glasses cannot be reliably used to
722 estimate the H₂O/Ce content of OIB primary melts, particularly glasses for EM OIB that appear
723 to experience greater degassing (owing to higher initial CO₂) than non-EM OIB. Our data show
724 that, unlike Samoan submarine glasses, Samoan melt inclusions have similar H₂O/Ce (197±58,
725 2SD, N=15) that does not vary with ⁸⁷Sr/⁸⁶Sr. In fact, the H₂O/Ce ratio (193±19, 2SD, N=4) for
726 extreme Samoan EM2 (⁸⁷Sr/⁸⁶Sr > 0.708) melt inclusions overlaps with H₂O/Ce suggested for
727 depleted mantle domains that are sampled by non-EM OIB (⁸⁷Sr/⁸⁶Sr < 0.7037; H₂O/Ce =
728 209±92), average Pacific MORB (180±20; Dixon et al., 2017), average depleted N. Atlantic
729 MORB (230±20; Dixon et al., 2017), and PREMA (*Prevalent Mantle*) Pacific and Atlantic OIB
730 (215±30 and 220±30, respectively, where PREMA-type OIB do not bear EM or HIMU
731 signatures; Dixon et al., 2017). Thus, the major implication of this work is that, instead of being
732 “dry”, the EM2 mantle sampled by Samoa is just as “damp” as non-EM reservoirs, but this can
733 only be seen by examining deeply entrapped melt inclusions that preserve higher CO₂ and H₂O
734 than submarine pillow glasses. Due to pronounced CO₂ and concomitant H₂O degassing that
735 appears to impact enriched lavas more than depleted ones—owing to higher primary melt CO₂ in
736 the former relative to the latter—future melt inclusion studies will be important for determining
737 the initial H₂O/Ce in EM1 (Pitcairn) and other EM2 (Societies) lavas, where existing low
738 H₂O/Ce values measured in high ⁸⁷Sr/⁸⁶Sr Pitcairn and Societies submarine glasses (Kendrick et
739 al. 2014) may also be due to the same degassing mechanism that lowers H₂O/Ce in Samoan OIB.
740 If so, H₂O/Ce in the mantle is not likely to be as variable as previously supposed, and much of

741 the mantle sampled by MORB and OIB have very similar H₂O/Ce that is, on average, close to a
742 value of 200, and not as low as values found in pillow glasses of EM lavas (down to 59 in
743 Samoan pillow glasses, 86 in Societies glasses, and 95 in Pitcairn glasses). Thus, like the Pb/Ce
744 ratio, which is similar in OIB and MORB globally (Hofmann et al., 1986), the H₂O/Ce ratio may
745 also be similar in the sources of plume-derived lavas (Michael, 1995).

746 A second implication of “damp” H₂O/Ce in EM Samoan lavas is that, in spite of hosting
747 subducted continental materials which have presumably lost H₂O by degassing at an ancient
748 subduction zone (White & Hofmann, 1982; Farley et al., 1992; Jackson et al., 2007), Samoan
749 EM2 melt (as sampled by EM melt inclusions) do not have lower H₂O/Ce than non-EM OIBs.
750 This is a surprising result, and suggests that recycled continental materials may not play a large
751 role in governing the H₂O budgets of mantle domains. This could be because the amount of
752 recycled continental crust in the mantle sources of OIB is small, and thus has a diminished
753 impact on the overall H₂O and H₂O/Ce of the mantle source. For example, Samoan lava
754 AVON3-78-1 examined in this study, which has a strong EM2 signature (⁸⁷Sr/⁸⁶Sr of 0.7089), is
755 estimated to have only ~1% continental crust (Reinhard et al., 2018) that is added to a depleted
756 plume component that constitutes the rest (99%) of the mantle source. In this model, the H₂O and
757 Ce budgets of the EM2 mantle source is primarily controlled by the depleted plume component,
758 even if the recycled continental crust component has low H₂O/Ce. In this way, both depleted
759 mantle and EM OIB can have similar H₂O/Ce.

760

761 **Acknowledgements:** MGJ gratefully acknowledges being wrong (and that John Lassiter was
762 correct) in the debate about whether mantle source H₂O/Ce is preserved in deeply dredged
763 (>1000 mbsl) submarine pillow glasses. OEA thanks Marc Hirschmann for a discussion about

764 CO₂/Nb in oceanic lavas, Gareth Seward for his skillful assistance with UCSB's electron
765 microprobe, Jean-Luc Devidal for assisting EFR-K with LA-ICP-MS analyses, and Brian
766 Monteleone for his time and help with ion probe analyses. MGJ acknowledges NSF grants OCE-
767 1736984, EAR-1900652, OCE-1912931, and OCE-1929095 that supported this work.

768

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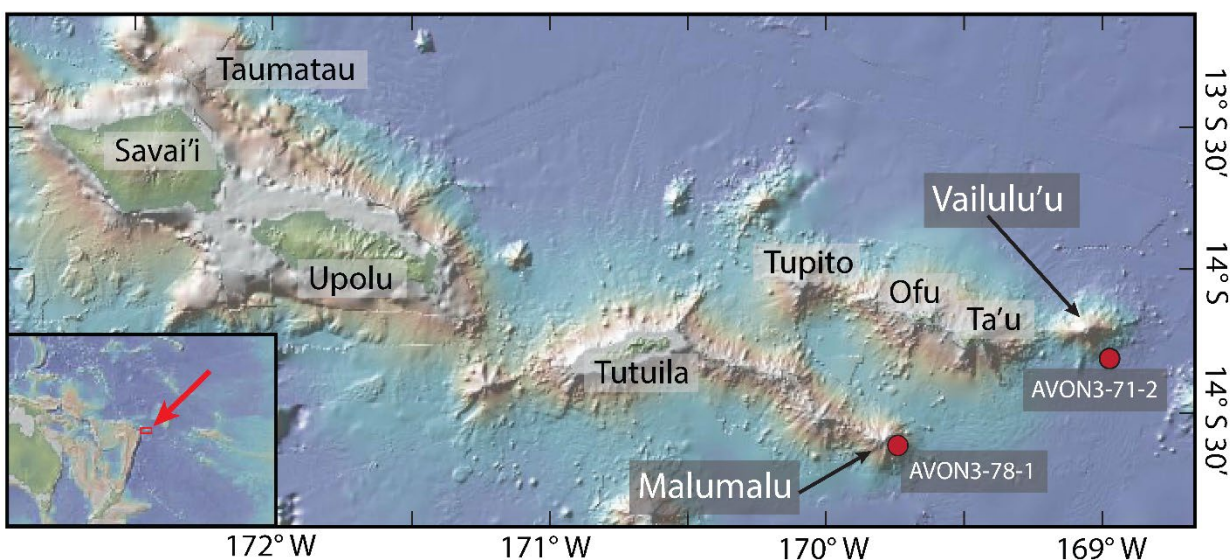
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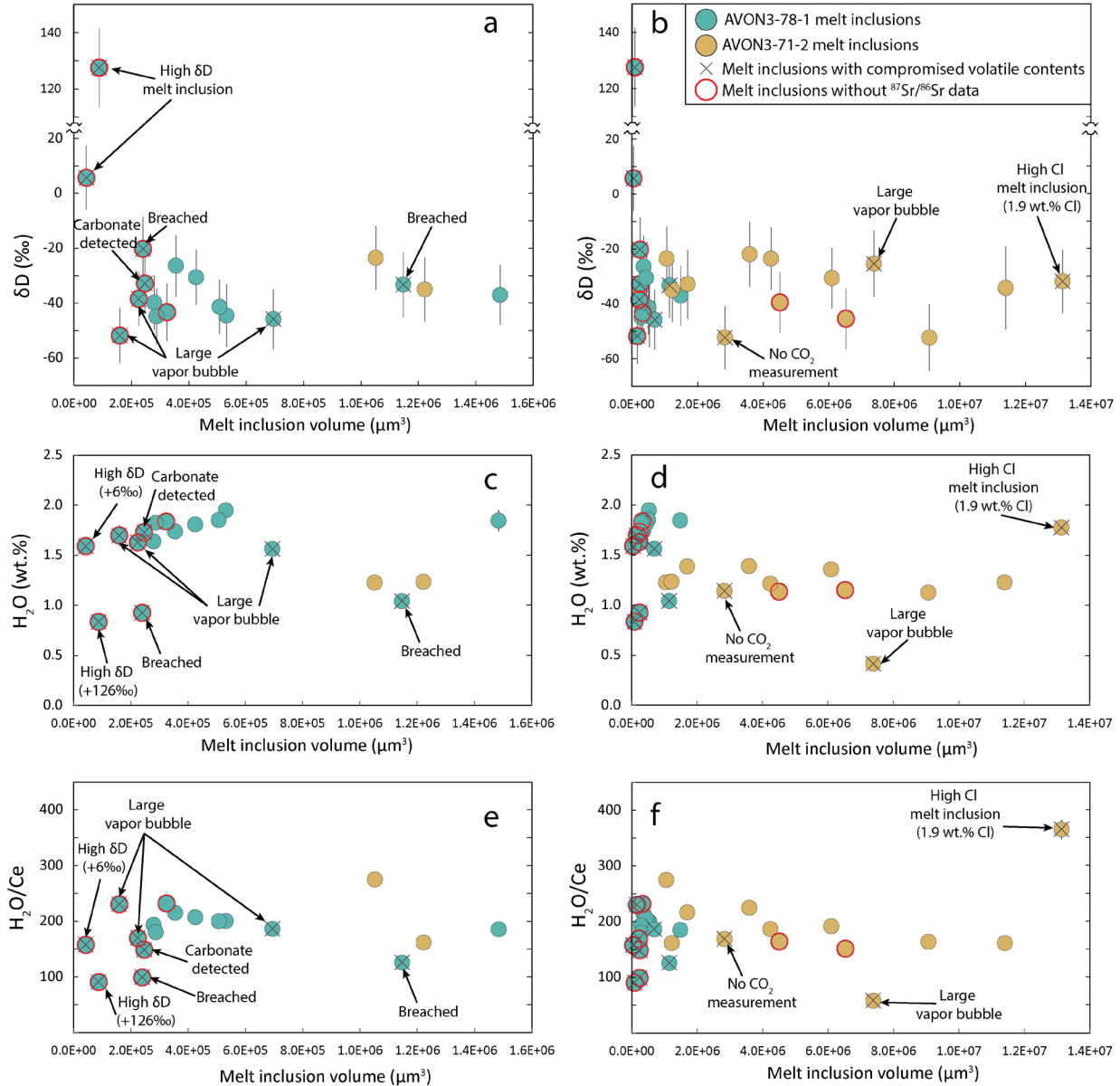
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1087

1088 **FIGURES**



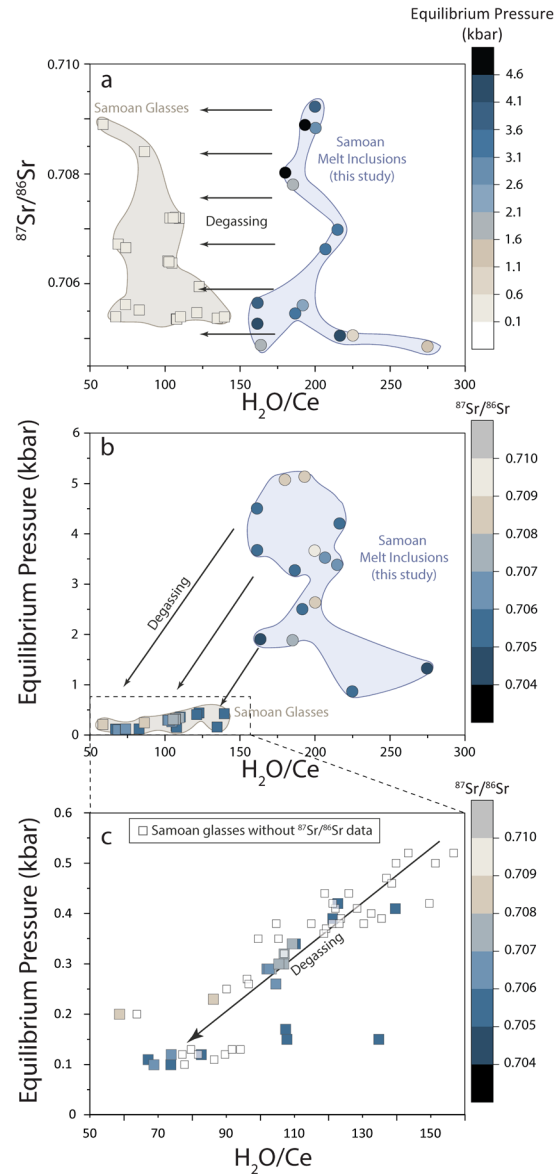
1089 **Figure 1.** Map of the Samoan Islands. Red dots indicate the location of AVON3 cruise dredge sites 71 and
1090 78, from the flanks of Vailulu'u and Malumalu, respectively. Map created using GeoMapApp
1091 (www.geomapapp.org).



1092

1093 **Figure 2. (a–b) δD (‰), (c–d) H_2O (wt.%), and (e–f) $\text{H}_2\text{O}/\text{Ce}$ versus melt inclusion volume (μm^3).** Left-
 1094 hand side panels focus (zoom in) on the Malumalu melt inclusions and right-hand side panels (zoom out)
 1095 to show the Vailulu’u melt inclusions. In panel (a) δD errors represent the 2σ in run measurement
 1096 precision of each analysis, which is generally slightly lower than the reproducibility of the secondary
 1097 standard ALV1833-1 (i.e., $\pm 16\%$, 2SD; see Table S2). Melt inclusion H_2O compositions are corrected for
 1098 olivine addition/subtraction to be in equilibrium with the host olivine (olivine correction is as in Section
 1099 2 of the main text). Measurement errors for H_2O , and reproducibility of H_2O analyses on ALV1833-1, are
 1100 smaller than the data symbol (see Table S2). As discussed in Section 3 of the text, we infer that the
 1101 volatile contents of eleven melt inclusions shown in this figure have been compromised in one of several
 1102 ways—hydrogen diffusion loss (and resultant elevated δD), breaching, large vapor bubbles, extremely
 1103 high Cl concentrations, presence of carbonate, and/or missing Raman-based CO_2 data—and are marked
 1104 with an “x” symbol. With the exception of the high Cl melt inclusion (which is individually identified in

1105 figures throughout the paper), the compromised melt inclusions are not shown in subsequent volatile
 1106 element figures.

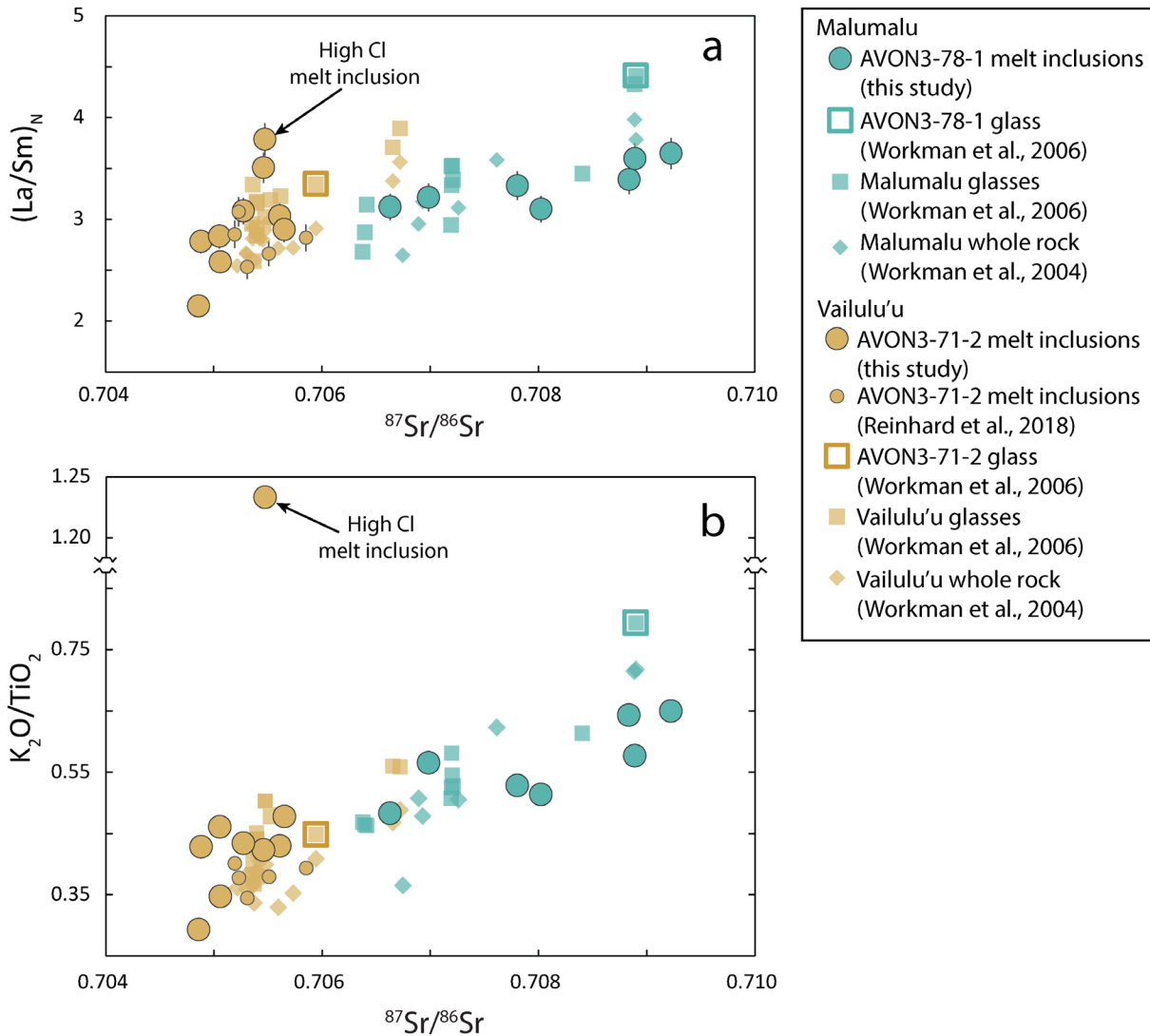


1107

1108 **Figure 3.** $^{87}\text{Sr}/^{86}\text{Sr}$, $\text{H}_2\text{O}/\text{Ce}$, and equilibrium pressure for submarine pillow glasses from Malumalu and
 1109 Vailulu'u seamounts are compared with melt inclusions from Malumalu sample AVON3-78-1 and
 1110 Vailulu'u sample AVON3-71-2. (a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\text{H}_2\text{O}/\text{Ce}$ for Samoan melt inclusions and glasses with
 1111 the color bar representing equilibrium pressure (kbar). The pillow glass data show separation in $\text{H}_2\text{O}/\text{Ce}$
 1112 from the melt inclusion data, even though both datasets span a similar range in $^{87}\text{Sr}/^{86}\text{Sr}$. Circles
 1113 represent melt inclusions and squares represent Samoan pillow glasses from Workman et al. (2006).
 1114 Melt inclusions in this figure do not include any volatile-compromised melt inclusions (as shown in
 1115 Figure 2). The equilibrium pressure of pillow glasses and melt inclusions was calculated using VESIcal's
 1116 MagmaSat model (Iacovino et al., 2021; Wieser et al., 2022) assuming oxygen fugacity (QFM) and
 1117 temperature (1200°C). Samoan pillow glass data are from Workman et al. (2006), except major elements
 1118 used to calculate equilibrium pressure for AVON3-71-2 and AVON3-78-1 (which are from Kendrick et al.,

1119 2015). (b) Equilibrium pressure versus H_2O/Ce for Samoan melt inclusions and pillow glasses with the
 1120 color bar representing $^{87}Sr/^{86}Sr$. (c) Expanded view of panel b that shows equilibrium pressure versus
 1121 H_2O/Ce for Samoan pillow glasses only. Smaller square data points with black outlines are pillow glasses
 1122 lacking $^{87}Sr/^{86}Sr$ data. Only samples with CO_2-H_2O saturation pressures ≥ 0.1 kbar are shown (just one
 1123 Samoan glass with $^{87}Sr/^{86}Sr$ data has a saturation pressure < 0.1 kbar, sample AVON3-68-03 Rpt, so its
 1124 removal does not significantly impact the dataset).

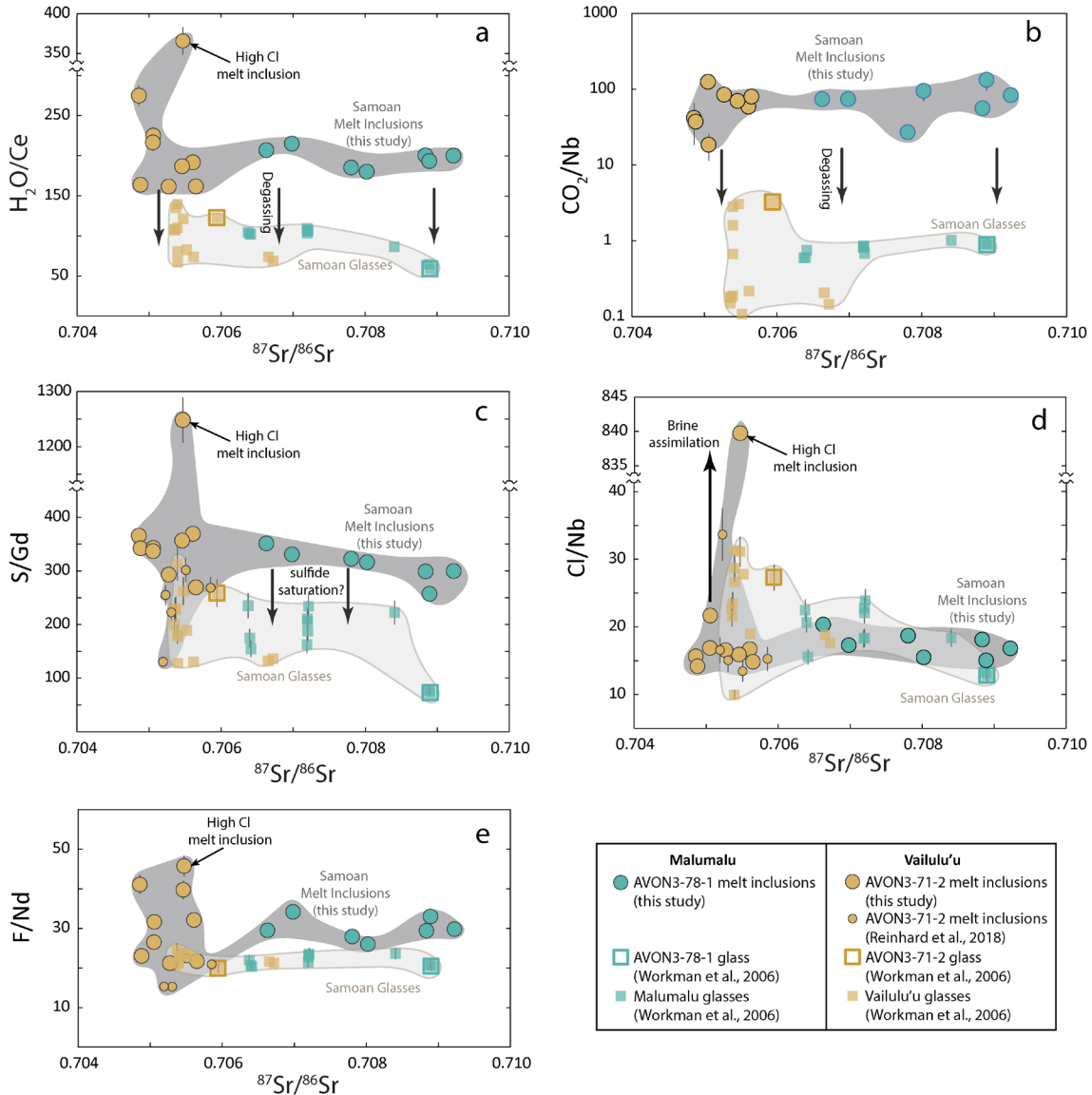
1125



1126

1127 **Figure 4.** Incompatible trace element ratios versus $^{87}Sr/^{86}Sr$ are shown for Samoan pillow glasses from
 1128 Malumalu and Vailulu'u seamounts and new melt inclusion data from Malumalu sample AVON3-78-1
 1129 and Vailulu'u sample AVON3-71-2. The melt inclusions have incompatible trace element ratios and
 1130 $^{87}Sr/^{86}Sr$ compositions that fall within the range identified in Samoan pillow glasses, indicating that the
 1131 Samoan melt inclusions sample melts represented by the pillow glass dataset. (a) $(La/Sm)_N$ versus
 1132 $^{87}Sr/^{86}Sr$, where N signifies normalization to primitive mantle (McDonough & Sun, 1995). (b) K_2O/TiO_2

1133 versus $^{87}\text{Sr}/^{86}\text{Sr}$. Data for Samoan pillow glasses are from Workman et al. (2006) and Kendrick et al.
 1134 (2015). Error bars for La/Sm (4.2%) are shown for the melt inclusions and are calculated as $((\text{La error})^2 + (\text{Sm error})^2)^{0.5}$, where the 2RSD of the secondary standard BCR-2 is used for La error (1.9%) and
 1135 Sm error (3.8%) (see Table S2). Error bars on $\text{K}_2\text{O}/\text{TiO}_2$ are smaller than the data symbols. Melt inclusions
 1137 that are compromised with respect to their volatile contents are not shown, except for the high Cl melt
 1138 inclusion.

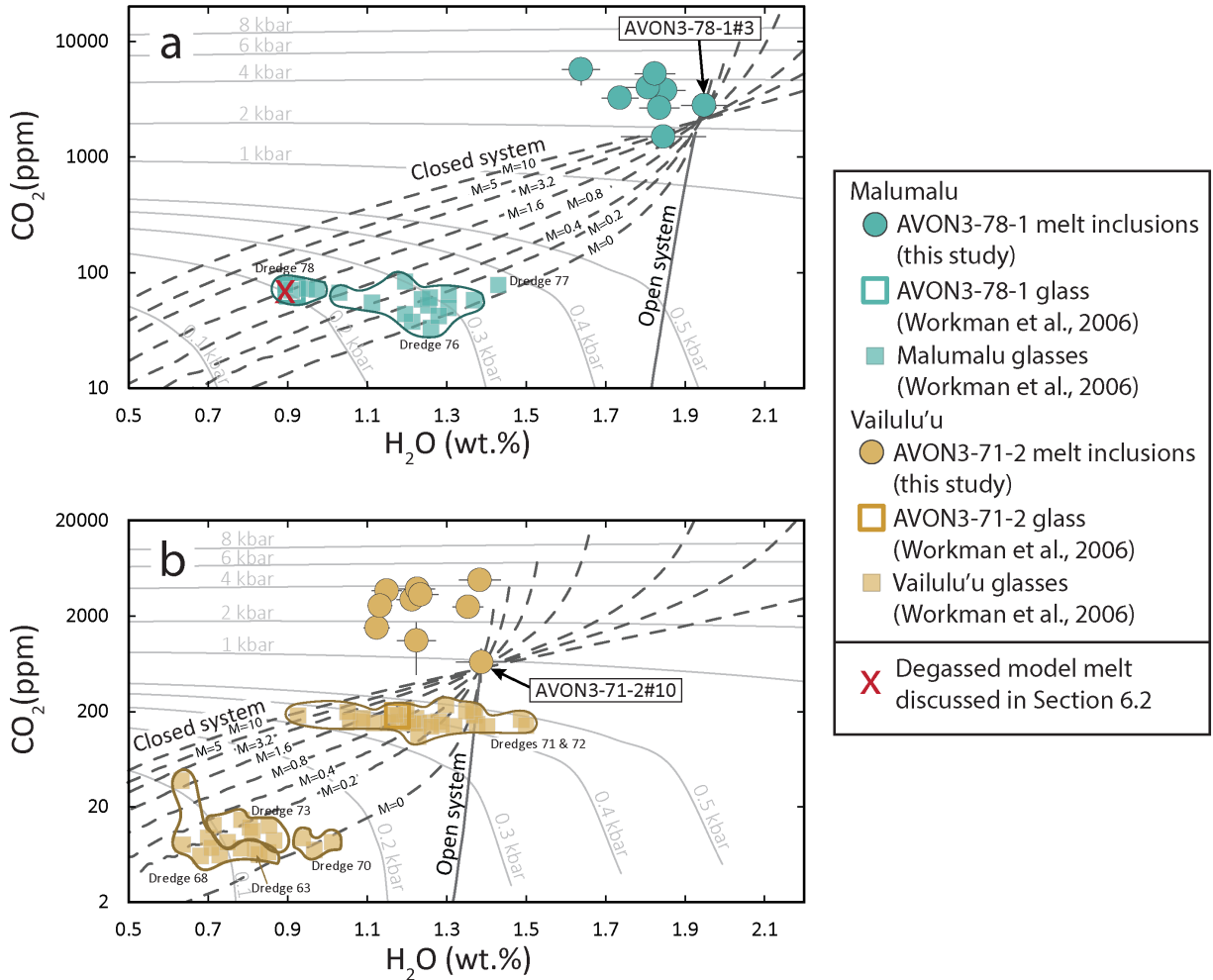


1139
 1140 **Figure 5.** Element ratios (volatile/incompatible trace element) are plotted against $^{87}\text{Sr}/^{86}\text{Sr}$ for Samoan
 1141 pillow glasses from Malumalu and Vailulu'u seamounts and the new melt inclusion data from Malumalu
 1142 sample AVON3-78-1 and Vailulu'u sample AVON3-71-2. See Supplementary Text section S1.6 for a
 1143 discussion on the calculation of the errors associated with the element ratios presented here; the error
 1144 bars for the $^{87}\text{Sr}/^{86}\text{Sr}$ of Samoan glasses and melt inclusions are smaller than the symbol size. Melt
 1145 inclusions that are compromised with respect to their volatile contents (as shown in Figure 2) are not

1146 shown. Only samples with CO₂-H₂O saturation pressures ≥0.1 kbar are shown (just one Samoan glass
 1147 with ⁸⁷Sr/⁸⁶Sr data has a saturation pressure <0.1 kbar, sample AVON3-68-03 Rpt, so its removal does
 1148 not significantly impact the dataset).

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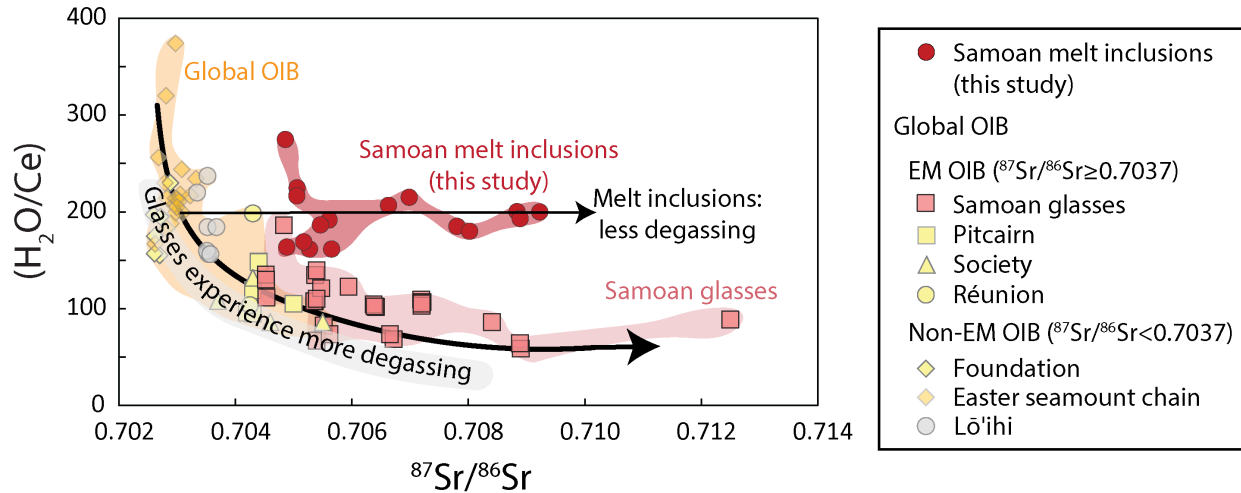
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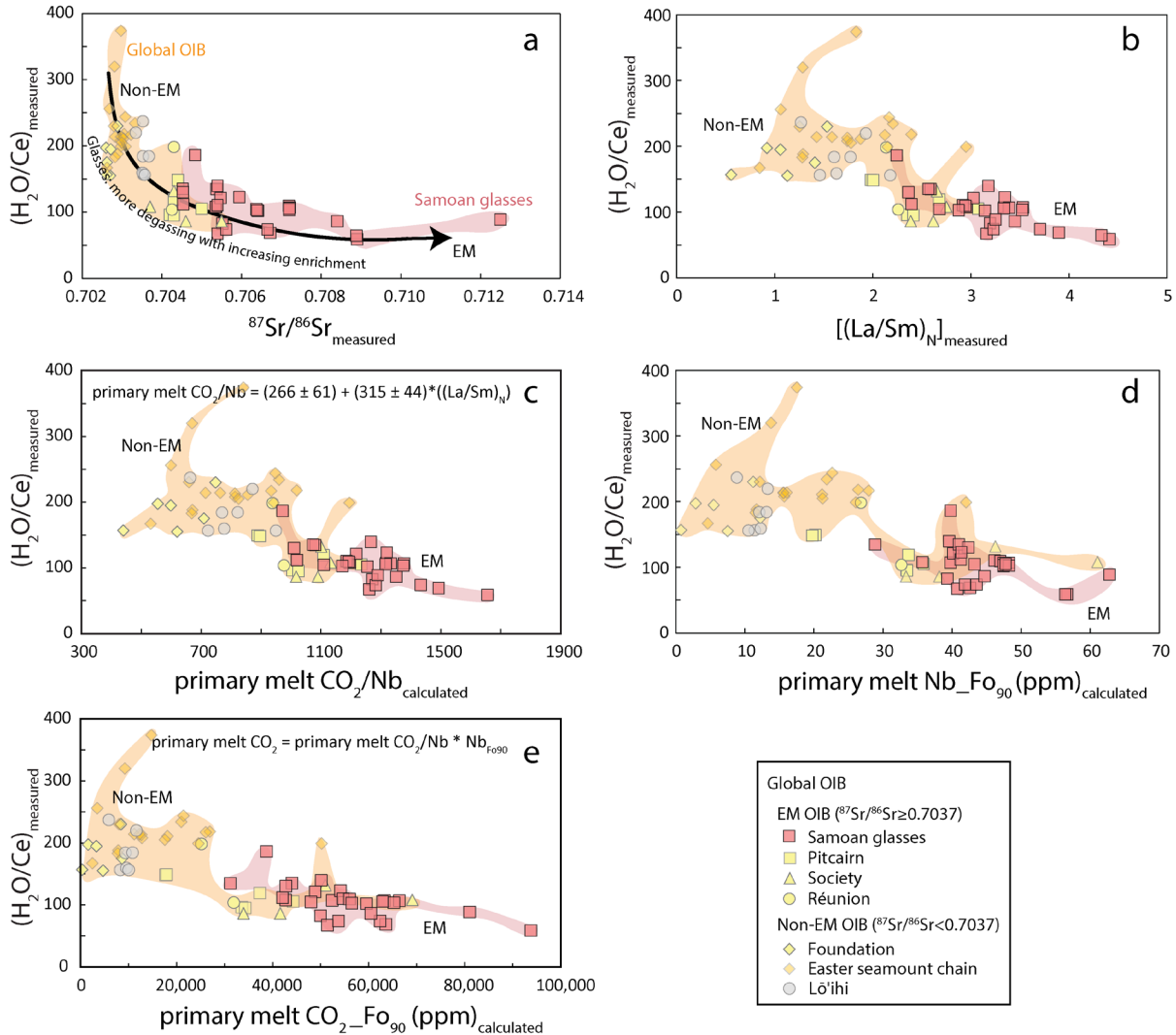
1152 **Figure 6.** CO₂ versus H₂O for (a) melt inclusions from Malumalu sample AVON3-78-1 and all glasses from
 1153 Malumalu seamount and (b) melt inclusions from Vailulu'u sample AVON3-71-2 and all glasses from
 1154 Vailulu'u seamount. Melt inclusion data are from this study and Samoan glass data are from Workman
 1155 et al. (2006) and the data are shown in fields separated by the dredge number (which is provided next to
 1156 the relevant field). Isobars are calculated using MagmaSat for an average melt inclusion composition of
 1157 each sample at 1200°C. Closed system degassing curves are calculated with varying values for M (where
 1158 "M" represents mass fraction of equilibrium fluid in the magma; e.g., M=1.6 means there was 1.6 wt.%
 1159 of fluid in the magma before degassing). Degassing trends assume an oxygen fugacity (QFM) and
 1160 temperature (1200°C) and are calculated in rhyolite-MELTS v1.2 using H₂O and CO₂ compositions that
 1161 match the highest H₂O melt inclusions in the respective panels (i.e., Malumalu melt inclusion AVON3-78-

1162 1#3 in the upper panel, and Vailulu'u melt inclusion AVON3-71-2#10 in the lower panel); other
 1163 compositions used in the degassing calculation are in Table S9. Melt inclusion CO₂ and H₂O
 1164 concentrations shown are values that have been corrected to be in equilibrium with the host olivine.
 1165 Volatile-compromised melt inclusions (as shown in Figure 2) are not included in this figure.



1166

1167 **Figure 7.** Samoan melt inclusions and pillow glasses compared to a global dataset of submarine OIB
 1168 glasses. Samoan melt inclusions—protected from the extensive degassing experienced by Samoan
 1169 glasses—have higher H₂O/Ce than Samoan pillow glasses, and thus fall off of the global submarine OIB
 1170 pillow glass trend that shows decreasing H₂O/Ce with increasing ⁸⁷Sr/⁸⁶Sr. Only OIB glasses with ⁸⁷Sr/⁸⁶Sr
 1171 (to establish the level of source enrichment) and MgO > 4.5 wt.% (to minimize the impact of fractional
 1172 crystallization) are shown. Sources of data (see Table S11): Pitcairn (Kendrick et al., 2014; Woodhead &
 1173 Devey, 1993), Society (Devey et al., 1990; Kendrick et al., 2014), Réunion (Kendrick et al., 2017; Fretzdorf
 1174 & Haase, 2002), Foundation (Kendrick et al., 2017), Easter seamount chain (Dixon et al., 2002), Lō'ihi
 1175 (Dixon & Clague, 2001; Staudigel et al., 1984). Samples from Pitcairn, Society, Réunion, and Foundation
 1176 can be found in a data compilation by Kendrick et al. (2017). Samples marked as having experienced
 1177 assimilation of seawater Cl in Kendrick et al. (2017) are excluded. However, unlike Dixon et al. (2002),
 1178 we do not use H₂O/Ce as a filter for assimilation. Samoan pillow glasses include submarine glasses
 1179 characterized for ⁸⁷Sr/⁸⁶Sr from Vailulu'u, Malumalu, Tupito (formerly known as Muli), Taumatau, and
 1180 Ta'u (Kendrick et al., 2015; Workman et al., 2006). Volatile-compromised melt inclusions (as shown in
 1181 Figure 2) are not shown. Melt inclusions from other OIB localities are not shown because there are no
 1182 other OIB melt inclusions characterized for both ⁸⁷Sr/⁸⁶Sr and H₂O/Ce. Only samples with CO₂-H₂O
 1183 saturation pressures ≥ 0.1 kbar are shown (just one Samoan glass with ⁸⁷Sr/⁸⁶Sr data has a saturation
 1184 pressure < 0.1 kbar, sample AVON3-68-03 Rpt, so its removal does not significantly impact the dataset).

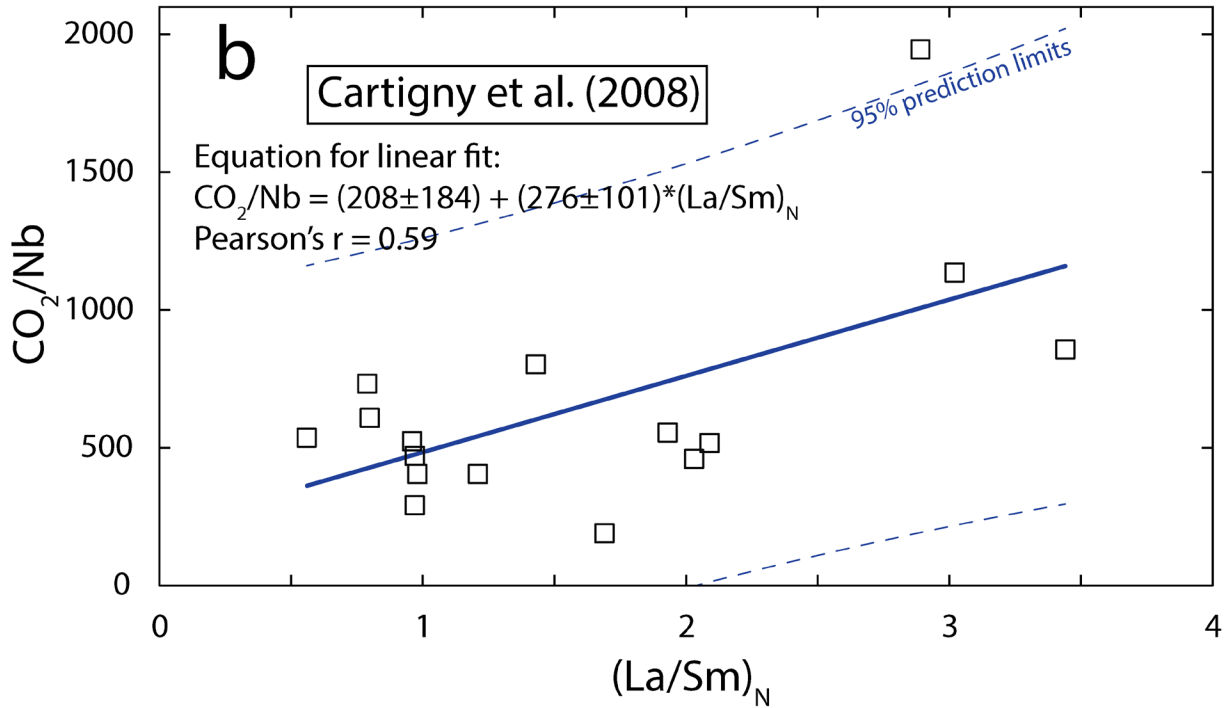
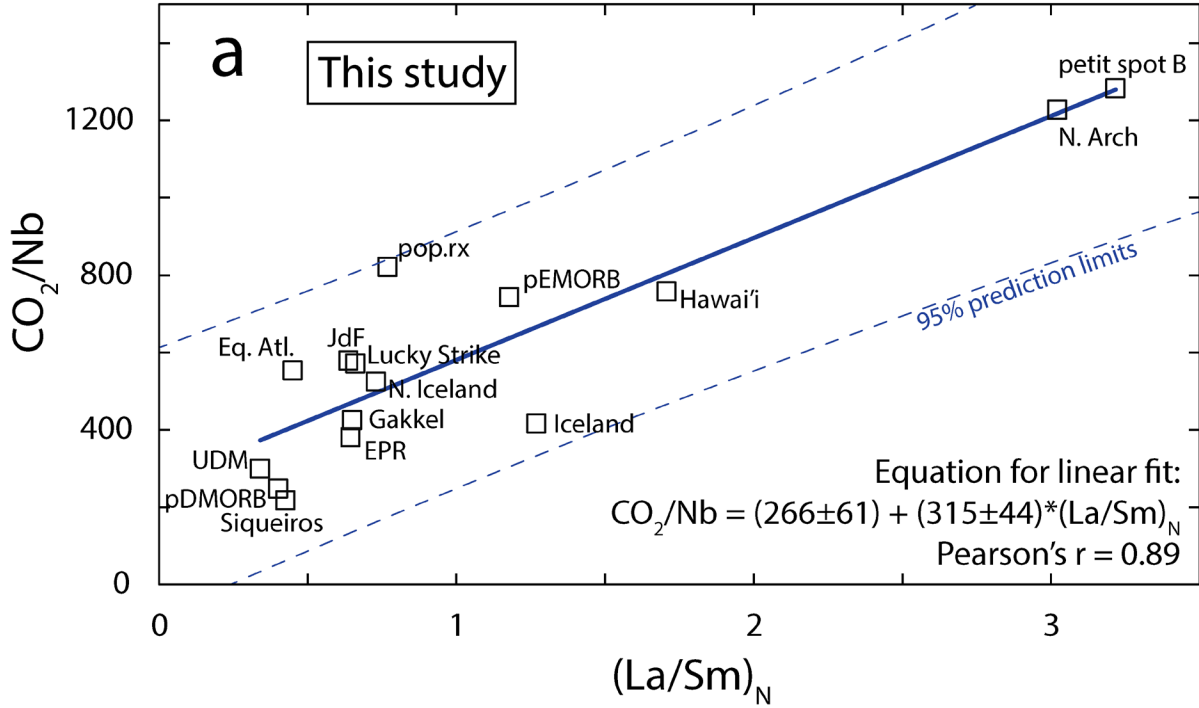


1185

1186 **Figure 8.** Samoan pillow glasses compared to a global dataset of submarine OIB glasses, which show a
 1187 trend of decreasing H_2O/Ce with increasing $^{87}Sr/^{86}Sr$. The exact same OIB dataset is shown in all panels:
 1188 only OIB with $^{87}Sr/^{86}Sr$ data (to establish the level of source enrichment) and $MgO > 4.5$ wt.% (to
 1189 minimize the impact of fractional crystallization) are shown. (a) H_2O/Ce versus $^{87}Sr/^{86}Sr$. (b) H_2O/Ce
 1190 versus $(La/Sm)_N$. (c) H_2O/Ce versus primary melt CO_2/Nb , where CO_2/Nb is calculated from the measured
 1191 $(La/Sm)_N$ ratios using a linear fit between CO_2/Nb and $(La/Sm)_N$ (see equation shown in panel c) that is
 1192 produced from a global data compilation of least degassed glasses and melt inclusions from OIB and
 1193 MORB in Figure 9. (d) H_2O/Ce versus calculated primary melt Nb for each sample, where primary melt
 1194 Nb is calculated by olivine addition (or subtraction) from melt—following methods in text—until the
 1195 melt is in equilibrium with Fo_{90} olivine. (e) H_2O/Ce versus calculated primary melt CO_2 , where the CO_2
 1196 is calculated for each lava by multiplying the calculated CO_2/Nb (panel c) with the calculated primary melt
 1197 Nb (panel d) (see equation in panel e). The same sources of data and data treatment as that described in
 1198 the Figure 7 caption are used here. The calculated primary melt CO_2/Nb and $CO_2_{Fo_{90}}$ (ppm) values for
 1199 the global OIB data set presented here are given in Table S11. Only samples with CO_2 - H_2O saturation

1200 pressures ≥ 0.1 kbar are shown (just one Samoan glass with $^{87}\text{Sr}/^{86}\text{Sr}$ data has a saturation pressure < 0.1
 1201 kbar, sample AVON3-68-03 Rpt, so its removal does not significantly impact the dataset).

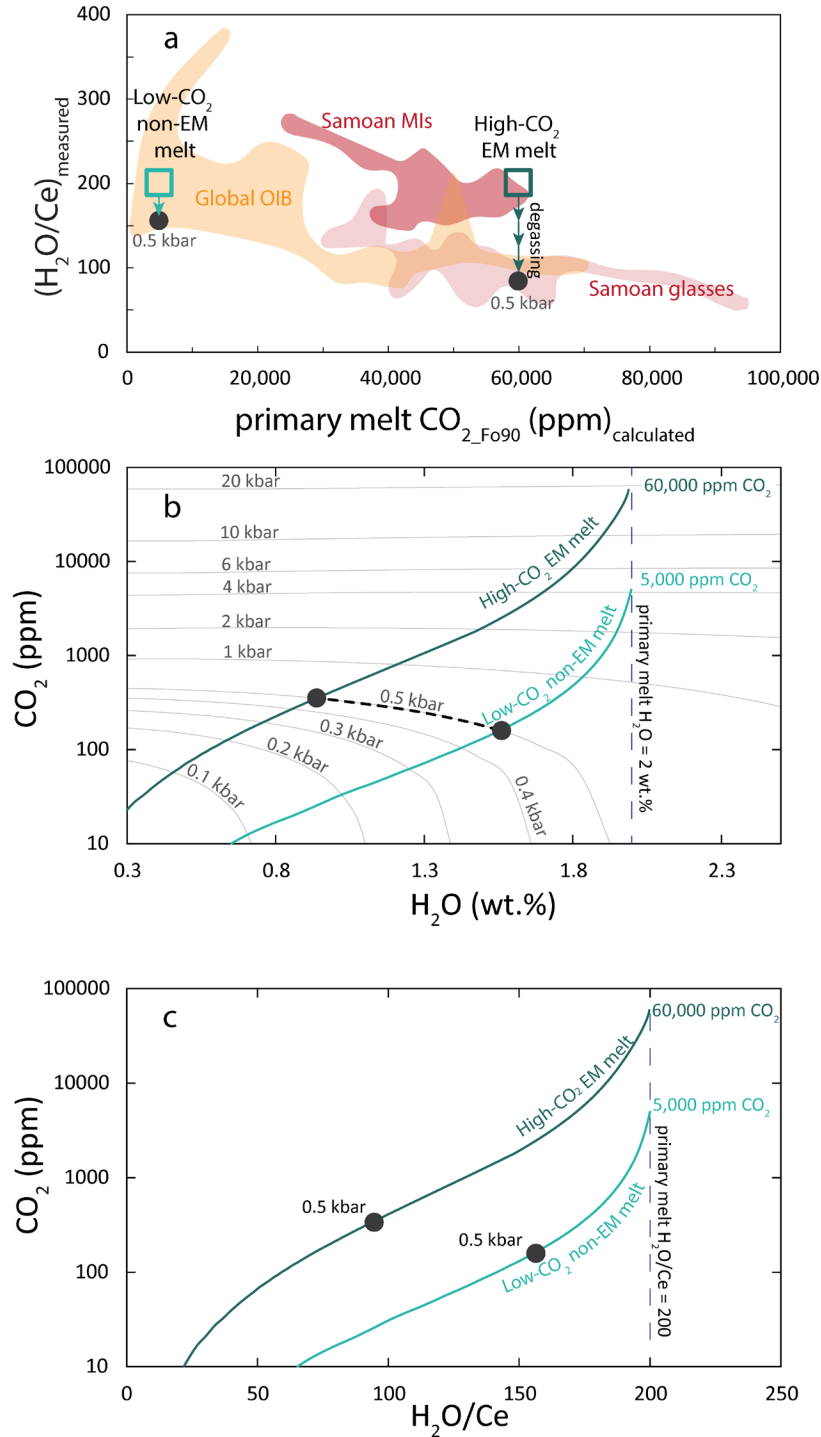
1202



1203

1204 **Figure 9.** (a) Linear fit (blue line) of global MORB and OIB glasses and melt inclusions with respect to
1205 CO_2/Nb and $(\text{La}/\text{Sm})_N$. Data compilation is the same as what is presented in Figure 1 of Hirschmann
1206 (2018). The values for CO_2/Nb and $(\text{La}/\text{Sm})_N$ in panel (a) are given in Table S10. The blue dashed lines
1207 represent the 95% prediction interval. The 95% confidence interval of the linear fit is given with the
1208 equation of the linear fit. The linear relationship calculated in panel a is used to estimate the CO_2/Nb
1209 values for glasses and melt inclusions in Figure 8. (b) Linear fit (blue line) to the Mid-Atlantic Ridge
1210 CO_2/Nb versus $(\text{La}/\text{Sm})_N$ data from Cartigny et al. (2008). The blue dashed lines are the 95% prediction
1211 bands for the linear fit using Cartigny et al. (2008) data. Sources of data for panel a: L. Strike (Lucky
1212 Strike): Wanless et al. (2015); JdF, EPR (Juan de Fuca, East Pacific Rise): Wanless and Shaw (2012);
1213 Gakkel: Wanless et al. (2014); Siqueiros: Saal et al. (2002); pEMORB and pDMORB (Pacific enriched and
1214 depleted MORB): Shimizu et al. (2016); UDM (ultra-depleted MORB): Michael and Graham (2015);
1215 pop.rx (North Atlantic popping rocks): Cartigny et al. (2008); Eq. Atl. (Equatorial Atlantic): Le Voyer et al.
1216 (2017); Iceland: Hartley et al. (2014), Neave et al. (2014); N. Iceland (Borgarhraun): Hauri et al. (2018); N.
1217 Arch (North Arch, Hawai'i): Dixon et al. (1997), Frey et al. (2000); Hawai'i (Kīlauea): Anderson and Poland
1218 (2017); Petit Spot B (Western Pacific seamounts): Machida et al. (2015).

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1220

1221 **Figure 10.** Figure illustrating how submarine glasses from enriched mantle (EM) sources acquire low
 1222 H₂O/Ce relative to glasses from non-EM sources. We test two melt compositions that are identical in
 1223 every way (major and trace element compositions are identical and H₂O is 2 wt.%) except for CO₂, where
 1224 one melt starts with 60,000 ppm CO₂ (meant to represent an EM melt) and the other melt starts with
 1225 5000 ppm CO₂ (meant to represent the non-EM melt). (a) H₂O/Ce versus primary melt CO₂, reproduced
 1226 in cartoon form from Figure 8e. The black circle indicates the H₂O/Ce value for melts at 0.5 kbar after

1227 degassing. (b) In a plot of CO₂ versus H₂O, modeled closed system degassing paths show the impact of
1228 varying initial CO₂ on a melt that has the same initial H₂O content of 2 wt.%. While both melts start with
1229 the same initial H₂O, those with higher initial CO₂ degas more H₂O and have lower H₂O at a given isobar
1230 compared to a melt that has lower initial CO₂, demonstrating how higher initial CO₂ results in lower H₂O
1231 (and lower H₂O/Ce) in the erupted lavas. Degassing trends assume oxygen fugacity (QFM) and
1232 temperature (1200°C) and are calculated in rhyolite-MELTS v1.2 using AVON3-78-1#3 major element
1233 melt inclusion composition. Bottom panel shows the same degassing paths as the upper panels but
1234 shows H₂O/Ce instead of H₂O. Calculation of H₂O/Ce along the degassing paths assumes 1) an initial
1235 H₂O/Ce value of 200 (similar to the average H₂O/Ce value of Samoan melt inclusions examined here) and
1236 2) a constant melt Ce concentration (100 ppm) that is calculated using the initial H₂O/Ce ratio (i.e., 200)
1237 and the initial H₂O (2 wt.%). Similar to the relationship between CO₂ and H₂O for high and low CO₂ melts,
1238 at a given isobar the melt with high initial CO₂ has significantly lower H₂O/Ce compared to the melt with
1239 lower initial CO₂. Isobars are calculated using MagmaSat for the average Malumalu melt inclusion
1240 composition at 1200°C. We consider only the case of M=0 to highlight the role of initial CO₂ and
1241 saturation pressure on the H₂O content of a glass, and non-zero M values would result in even more
1242 rapid H₂O loss.

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