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

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12 Highlights:

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- Samoan melt inclusions have higher H₂O/Ce—indicating less degassing—compared to
 Samoan pillow glasses.
- High ⁸⁷Sr/⁸⁶Sr melt inclusions have high H₂O/Ce, contrary to prior observations using pillow glasses.
 - Low H₂O/Ce in high ⁸⁷Sr/⁸⁶Sr glasses indicates extensive degassing has occurred, so cannot be used to infer mantle H₂O/Ce.
 - Melt inclusions show that enriched mantle (EM) lavas have H₂O/Ce similar to non-EM lavas.
 - Elevated CO₂ in EM melts leads to greater degassing and lower H₂O/Ce in erupted glasses compared to depleted mantle.
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- 37 K.T., Gaetani, G.A. and Price, A.A. (2024). Extensive H₂O degassing in deeply erupted
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40 Abstract

Submarine glasses erupted at intraplate volcanic hotspot settings sampling enriched mantle 41 (EM)—characterized by high ⁸⁷Sr/⁸⁶Sr—exhibit lower H₂O/Ce than glasses representing less 42 enriched mantle domains, leading to the interpretation that the EM mantle is H₂O-poor ("dry"). 43 We test whether low H₂O/Ce observed in pillow glasses of EM lavas resulted from degassing of 44 higher H₂O/Ce primary melts by measuring H₂O/Ce and ⁸⁷Sr/⁸⁶Sr in olivine-hosted melt 45 inclusions from two deeply-erupted (3950 and 2190 meters below sea level (mbsl)) Samoan 46 submarine lavas from Vailulu'u and Malumalu seamounts. Vailulu'u (H₂O/Ce=161-275) and 47 48 Malumalu (149–232) melt inclusions have an average H_2O/Ce (197±58 2SD, N=15) that is nearly twice as high as H₂O/Ce in pillow glasses from these two seamounts (average 49 $H_2O/Ce=106\pm51$, N=65). Notably, the average H_2O/Ce of Samoan melt inclusions (197±58) is 50 51 comparable to pillow glasses from non-EM hotspots. We show that lower H₂O/Ce in submarine Samoan glasses compared to melt inclusions results from greater closed-system degassing, and 52 concomitant loss of H₂O, because EM melts have higher initial concentrations of CO₂. We show 53 54 that the lower H₂O/Ce in global EM pillow glasses compared to non-EM pillow glasses can be modeled to be the result of more extensive degassing of H₂O in EM melts, which owes to higher 55 CO₂ in primary melts (20,000–90,000 ppm) of EM sources compared to non-EM melts (300– 56 50,000 ppm CO₂). Instead of originating from a dry mantle, we conclude that EM lavas derive 57 from a damp mantle, but EM melts lose more H₂O by degassing than non-EM melts. 58 Keywords: melt inclusion, Samoa, hotspot, degassing, enriched mantle, H₂O 59 60

62 **1. Introduction**

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

80 The ratios H₂O/La or H₂O/Ce measured in submarine glasses are commonly used to 81 evaluate H₂O enrichment or depletion in the mantle because H₂O, 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 H₂O/Ce (or H₂O/La) is lower at higher ⁸⁷Sr/⁸⁶Sr 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 ₂ O/La than more
87	geochemically depleted Samoan glasses; the high H ₂ O/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 ₂ O/La as the result of diffusive H ₂ O 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 ₂ O/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 ₂ O/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 ₂ O/Ce and high H ₂ O, a result of preferential partitioning of Ce into
99	clinopyroxene compared to H ₂ O.

Additional work highlights the low H₂O/Ce in enriched mantle domains (Kendrick et al.,
2017). In particular, classical EM1 and EM2 oceanic hotspots—Pitcairn and Societies,
respectively—exhibit negative correlations between ⁸⁷Sr/⁸⁶Sr and H₂O/Ce in submarine glasses
(Kendrick et al., 2014). Thus, low H₂O/Ce appears to be a defining feature of EM lavas, and
constraining the origin of this geochemical signature is critical for understanding the origin of the
EM mantle and/or the petrogenesis of EM lavas.

Existing models for the origin of low H₂O/La and H₂O/Ce in EM-flavored OIB pillow
glasses quenched in deep submarine environments are predicated on the assumption that the low

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

In this study, we test this assumption using combined H_2O/Ce and $^{87}Sr/^{86}Sr$ 115 measurements in individual olivine-hosted melt inclusions isolated from two well-characterized 116 submarine Samoan basalts that were characterized by Workman et al. (2006). We present 117 volatile (H₂O, CO₂, Cl, F, S), major, and trace element concentrations and ⁸⁷Sr/⁸⁶Sr on Samoan 118 119 melt inclusions from both samples—AVON3-78-1 and AVON3-71-2—which were obtained from Malumalu and Vailulu'u seamounts, respectively. Malumalu lavas reach ⁸⁷Sr/⁸⁶Sr of up to 120 0.708901, which is the most extreme EM2 composition that we explore in this study. In contrast, 121 Vailulu'u lavas have ⁸⁷Sr/⁸⁶Sr that range from 0.705352 to 0.706720, and thus represent a less 122 enriched composition at the Samoan hotspot. Previous ⁸⁷Sr/⁸⁶Sr analyses of Samoan melt 123 inclusions demonstrated extreme heterogeneity (0.70434 to 0.70926) that has been verified using 124 both *in situ* LA-ICP-MS approach (laser-ablation inductively coupled plasma mass spectrometry; 125 Jackson & Hart, 2006) and an approach involving wet chemistry followed by TIMS (thermal 126 127 ionization mass spectrometry; Reinhard et al., 2018). Critically for this study, the melt inclusions from the two lavas examined here span nearly the same range of ⁸⁷Sr/⁸⁶Sr (0.704858–0.709225) 128 as identified in prior melt inclusion studies (Jackson & Hart, 2006; Reinhard et al., 2018) and 129 have similar trace element characteristics as the Samoan glasses examined for H₂O/La and 130

⁸⁷Sr/⁸⁶Sr by Workman et al. (2006) (0.704521–0.708901). We interpret this to indicate that the
melt inclusions thus sample the same mantle sources as the pillow glasses studied by Workman
et al. (2006).

134 However, Samoan melt inclusions in this study exhibit two key differences with the Samoan submarine glasses reported in Workman et al. (2006): 1) the melt inclusions have higher 135 136 H₂O/Ce than Samoan submarine glasses and 2) the inclusions exhibit no relationship between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr, which contrasts with the negative correlation between ⁸⁷Sr/⁸⁶Sr and 137 H₂O/Ce observed in Samoan pillow glasses. We model the difference in H₂O/Ce between melt 138 139 inclusions and pillow glasses as being a result of closed-system degassing, a mechanism that 140 results in greatly diminished CO₂ and H₂O concentrations in the melt (in contrast to open-system degassing, which results in greatly diminished CO₂, but not H₂O, melt concentrations). In this 141 model, the melt inclusions experience less closed-system degassing compared to submarine 142 glasses because of deep entrapment of the melt inclusions in growing olivine crystals within 143 magma chambers. Melts that were not trapped continued to degas both CO₂ and H₂O up until 144 145 eruption and quenching on the seafloor, resulting in lower H₂O/Ce in the submarine glasses compared to the deeply entrapped melt inclusions. 146

We also present a model suggesting that, across global oceanic hotspots, primary melts
with higher ⁸⁷Sr/⁸⁶Sr (e.g., Samoan and Societies EM2 glasses, Pitcairn EM1 glasses) have
higher primary melt CO₂ than lower ⁸⁷Sr/⁸⁶Sr melts (e.g., Foundation, Hawai'i (Lō'ihi), and
Easter hotspots). Higher CO₂ in high ⁸⁷Sr/⁸⁶Sr (EM) melts results in greater degassing of both
CO₂ and H₂O (and a greater reduction in the H₂O/Ce ratio) compared to low ⁸⁷Sr/⁸⁶Sr melts,
which explains the negative global correlation between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr in OIB glasses.
This new result suggests that submarine glasses sourcing EM domains do not provide reliable

records for evaluating the H_2O and H_2O/Ce in the mantle source. In melt inclusions, degassing is arrested at great depth, making it possible to identify H_2O/Ce ratios that are closer to values in the primary melt.

2. Methods

Submarine pillow basalt samples in this study are from two Samoan seamounts (Figure 1) 158 159 that are young (<8 ka; Sims et al., 2008) and associated with visually fresh lavas: Malumalu (sample AVON3-78-1; 2260–2190 mbsl) and Vailulu'u (sample AVON3-71-2; 4420–3950 160 mbsl) are olivine-rich lavas with glassy chill margins on the pillow rims. Olivine-hosted melt 161 inclusions from Vailulu'u and Malumalu seamounts in this study were rehomogenized on a 162 heating stage (see supplement for methods), and these rehomogenized inclusions were then 163 characterized for ⁸⁷Sr/⁸⁶Sr (15 melt inclusions total), ¹⁴³Nd/¹⁴⁴Nd (only three melt inclusions), 164 stable hydrogen isotope ratios (δD), and major, trace and volatile element concentrations (Table 165 S1). This supplement also includes methodological details for the glass major element (electron 166 167 microprobe), volatile (ion probe), hydrogen isotope (ion probe), and trace element (LA-ICP-MS) analyses and the host olivine major element (electron microprobe) analyses. Strontium separation 168 chemistry and ⁸⁷Sr/⁸⁶Sr analyses by TIMS used in this study follow the same procedure as 169 170 described in Anderson et al. (2021). The supplement includes details of Nd separation chemistry for melt inclusions, and ¹⁴³Nd/¹⁴⁴Nd analyses by TIMS at the University of California, Santa 171 Barbara Isotope Geochemistry Facility. Only three melt inclusions (all from the Vailulu'u 172 Seamount sample) in this study had sufficient Nd for the isotopic analysis. 173 The results of *in situ* analyses (of δD , and major, trace and volatile element concentrations) 174

of geologic reference materials (ALV519-4-1, ALV1833-1, GL07 D52-5, and BCR-2) can be

found in Table S2, and ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd analyses of BCR-2 can be found in Tables S6
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% increments until the major element composition of the inclusion is in equilibrium with the host 180 181 olivine forsterite (Fo) content. In the calculation, two assumptions are made: (i) the olivine-melt Fe-Mg K_d = 0.30 (Roeder & Emslie, 1970; Ford et al., 1983; $K_d = (Fe^{2+}/Mg)_{olivine}/(Fe^{2+}/Mg)_{melt}$) 182 and (ii) Fe³⁺ comprises 10% of the total moles of iron in the melt (following Hauri, 1996). 183 Unless stated otherwise, all major, trace, and volatile element concentrations reported below 184 have been corrected for equilibrium olivine addition/subtraction so that the inclusion is in 185 equilibrium with the host olivine. 186

The supplement also details the method of accounting for all CO₂ within a melt inclusion, including both the CO₂ in the glass analyzed by ion probe, the CO₂ contained within the vapor bubble obtained by Raman spectroscopy, and the volumes of bubble and glass for each melt inclusion obtained by X-ray computed microtomography (see Table S3 for the method of reconstructing the total CO₂ content of each melt inclusion).

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3. Methods for data treatment

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

not consider these inclusions further in our data analysis and interpretation so as to focus on

198

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) <i>Diffusive proton loss</i> . Hydrogen isotopes can indicate whether H ₂ O 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 H_2O 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 H ₂ O 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±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 (~8.8 x $10^4 \mu\text{m}^3$ and 4.3 x $10^4 \mu\text{m}^3$). 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)	<i>Breaching</i> . Two melt inclusions have likely suffered breaching because CO_2 is <200
222		ppm and H ₂ O 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 CO ₂ 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		CO ₂ 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, CO ₂ 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		CO ₂ 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

4. Results 246

247

4.1 Hydrogen and strontium isotopes

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

Critically, ⁸⁷Sr/⁸⁶Sr measurements in melt inclusions provide a test for whether the Samoan 254 255 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 Samoan pillow lava glasses. The ⁸⁷Sr/⁸⁶Sr range for all of the Malumalu (sample AVON3-78-1) 258 melt inclusions reported here is large, from 0.706594 to 0.709225 (Figure 3, 4). The inclusions 259 largely fall within the range reported for Malumalu pillow glasses and whole rocks (0.706374– 260 261 0.708901; Workman et al., 2006). The ⁸⁷Sr/⁸⁶Sr range for all of the Vailulu'u (sample AVON3-71-2) melt inclusions reported here is smaller compared to AVON3-78-1 melt inclusions, from 262 0.704858 to 0.705718. The range of Vailulu'u melt inclusion ⁸⁷Sr/⁸⁶Sr overlaps with the range 263 reported for Vailulu'u pillow glasses (0.705352-0.706720; Workman et al., 2006) but, relative to 264

265	Vailulu'u pillow glasses and whole rocks, the Vailulu'u melt inclusions are shifted to less
266	radiogenic (lower) ⁸⁷ Sr/ ⁸⁶ Sr values. Taken together, the ⁸⁷ Sr/ ⁸⁶ Sr for the Malumalu and Vailulu'u
267	melt inclusions in this study bracket the ⁸⁷ Sr/ ⁸⁶ Sr obtained pillow glasses from each volcano: the
268	lowest 87 Sr/ 86 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 Sr/ ⁸⁶ 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 $(La/Sm)_N$ and
272	K_2O/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 Sr/ ⁸⁶ 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

After omitting melt inclusions that have been contaminated, breached, affected by hydrogen diffusion, and have unreliable CO₂ analyses by Raman, the magmatic volatile content of the Samoan melt inclusions can be explored. Figure 5 provides ratios (H₂O/Ce, CO₂/Nb, Cl/Nb, S/Gd, and F/Nd) of volatile (H₂O, CO₂, Cl, S, and F) to nonvolatile (Ce, Nb, Gd, and Nd) incompatible trace elements (ITEs) that have similar mineral-melt partition coefficients during mantle melting and magmatic differentiation processes. Below we examine the volatile concentrations and their ratios to nonvolatile ITEs.

287

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 of the melt inclusion. When comparing melt inclusion and vapor bubble CO₂, 3 to 94 mass 291 percent (average ~59 mass percent) of the total CO₂ (i.e., melt inclusion CO₂+vapor bubble CO₂) 292 293 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). Malumalu and Vailulu'u melt inclusions have relatively similar total CO₂ contents of 1506–5746 295 296 ppm and 658-4771 ppm, respectively. The associated host pillow glasses for the Malumalu and Vailulu'u samples have total CO₂ contents of 70 ppm and 179 ppm, respectively (Workman et 297 al., 2006), which is far lower than the melt inclusions from these two volcanoes. These 298 299 observations are consistent with greater CO₂-H₂O saturation pressures for the melt inclusions than the pillow glasses. 300

301 During melting and crystallization, the incompatibility (i.e., the bulk partition coefficient) of CO₂ is similar to Nb and Ba, thus the ratios of CO₂/Nb or CO₂/Ba have been used to estimate 302 upper mantle carbon content (Hirschmann, 2018; Michael & Graham, 2015; Saal et al., 2002; 303 Cartigny et al., 2008; Le Voyer et al., 2017). However, only undegassed, CO₂-undersaturated 304 melts will have CO₂/Nb or CO₂/Ba that are representative of the mantle source, but such melts 305 are rare (Hauri et al., 2018; Graham & Michael, 2021; Le Voyer et al., 2017; Michael & Graham, 306 2015; Saal et al., 2002). These CO₂-undersaturated melts tend to be geochemically depleted 307 (Hauri et al., 2018; Shimizu et al., 2023) and have higher CO₂/Nb than most submarine volcanic 308 309 glasses, which are CO₂-saturated and thus degassed (e.g., the Samoan pillow glasses and melt inclusions examined here). The Samoan melt inclusions in this study have a measured CO_2/Nb 310

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 ($CO_2/Nb > 283$; 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) CO2 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

range of 14–25 and Vailulu'u melt inclusions have a Cl/Nb range of 14–22 (excluding melt 332

inclusion sample AVON3-71-2#14, which has with Cl/Nb = 840) (Figure 5). The Samoan melt

inclusions have Cl/Nb that overlap with mid-ocean ridge basalts (MORB), where Cl/Nb_{MORB} is 5

to 17 (Lassiter et al., 2002; Le Roux et al., 2006), but the Samoan inclusions tend to be shifted to
higher Cl/Nb.

The pillow glasses for the Malumalu (AVON3-78-1) and Vailulu'u (AVON3-71-2) samples

hosting the Samoan melt inclusions have Cl/Nb of 13 and 27, respectively (Kendrick et al.,

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

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

not appear to have impacted ⁸⁷Sr/⁸⁶Sr (0.705471±0.000022) as it is at the lower end of the range
observed here (Figure 5).

4.2.3 S in Samoan melt inclusions versus Samoa pillow glasses.

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

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

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

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

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

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

³⁵⁹

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. H ₂ O in Samoan melt inclusions versus Samoa pillow glasses.
388	Malumalu melt inclusions have $1.56-1.95$ wt.% H ₂ O, and Vailulu'u melt inclusions have $1.13-$
388 389	Malumalu melt inclusions have 1.56–1.95 wt.% H ₂ O, and Vailulu'u melt inclusions have 1.13– 1.39 wt.% H ₂ O. The associated host glasses from these two submarine samples tend to have
389	1.39 wt.% H_2O . The associated host glasses from these two submarine samples tend to have
389 390	1.39 wt.% H_2O . The associated host glasses from these two submarine samples tend to have lower H_2O contents than the melt inclusions with 0.91 wt.% H_2O (AVON3-78-1) and 1.18 wt.%
389 390 391	1.39 wt.% H_2O . The associated host glasses from these two submarine samples tend to have lower H_2O contents than the melt inclusions with 0.91 wt.% H_2O (AVON3-78-1) and 1.18 wt.% H_2O (AVON3-71-2), respectively. The low H_2O in the AVON3-78-1 Malumalu glass sample
389 390 391 392	1.39 wt.% H ₂ O. The associated host glasses from these two submarine samples tend to have lower H ₂ O contents than the melt inclusions with 0.91 wt.% H ₂ O (AVON3-78-1) and 1.18 wt.% H ₂ O (AVON3-71-2), respectively. The low H ₂ O in the AVON3-78-1 Malumalu glass sample lies within the range of H ₂ O for pillow glass samples from Malumalu (0.89 to 1.43 wt.%), and
389 390 391 392 393	1.39 wt.% H ₂ O. The associated host glasses from these two submarine samples tend to have lower H ₂ O contents than the melt inclusions with 0.91 wt.% H ₂ O (AVON3-78-1) and 1.18 wt.% H ₂ O (AVON3-71-2), respectively. The low H ₂ O in the AVON3-78-1 Malumalu glass sample lies within the range of H ₂ O for pillow glass samples from Malumalu (0.89 to 1.43 wt.%), and the same applies for the AVON3-71-2 Vailulu'u glass sample as it also lies in the range of pillow
389 390 391 392 393 394	1.39 wt.% H ₂ O. The associated host glasses from these two submarine samples tend to have lower H ₂ O contents than the melt inclusions with 0.91 wt.% H ₂ O (AVON3-78-1) and 1.18 wt.% H ₂ O (AVON3-71-2), respectively. The low H ₂ O in the AVON3-78-1 Malumalu glass sample lies within the range of H ₂ O for pillow glass samples from Malumalu (0.89 to 1.43 wt.%), and the same applies for the AVON3-71-2 Vailulu'u glass sample as it also lies in the range of pillow glasses from this seamount (0.63 to 1.50 wt.%) (Figure 6). When the melt inclusions and pillow
389 390 391 392 393 394 395	1.39 wt.% H ₂ O. The associated host glasses from these two submarine samples tend to have lower H ₂ O contents than the melt inclusions with 0.91 wt.% H ₂ O (AVON3-78-1) and 1.18 wt.% H ₂ O (AVON3-71-2), respectively. The low H ₂ O in the AVON3-78-1 Malumalu glass sample lies within the range of H ₂ O for pillow glass samples from Malumalu (0.89 to 1.43 wt.%), and the same applies for the AVON3-71-2 Vailulu'u glass sample as it also lies in the range of pillow glasses from this seamount (0.63 to 1.50 wt.%) (Figure 6). When the melt inclusions and pillow glasses are corrected for olivine fractionation to be in equilibrium with mantle olivine (Fo ₉₀), a

399	measured H ₂ O 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 H ₂ O/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 H ₂ O/Ce (197 \pm 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	⁸⁷ Sr/ ⁸⁶ Sr (Figure 3), and have similar ITE ratios (Figure 4), suggesting they sample the same
410	mantle sources. This observation that melt inclusions have higher H ₂ O/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 CO ₂ -H ₂ O 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 87 Sr/ 86 Sr for 417 Samoan glasses, we find that the Samoan melt inclusions in this study exhibit *no correlation* 418 between H₂O/Ce and 87 Sr/ 86 Sr (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 87 Sr/ 86 Sr 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 87 Sr/ 86 Sr from 0.704858 to 0.709225,

422	and the melt inclusions with the strongest E	M2 mantle signatures (i.e	87 Sr/ 86 Sr > 0.7080, N=4)
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have elevated H₂O/Ce (193 \pm 19 2SD) that is indistinguishable from the H₂O/Ce (202 \pm 31) in melt

424 inclusions with weaker EM2 signatures (87 Sr/ 86 Sr < 0.7080, N=3).

While the Samoan pillow glasses and melt inclusions exhibit some overlap with each other in 425 H₂O/Ce at the lowest 87 Sr/ 86 Sr, they exhibit diverging trends in H₂O/Ce with increasing 87 Sr/ 86 Sr: 426 melt inclusions exhibit unchanging H₂O/Ce with increasing ⁸⁷Sr/⁸⁶Sr, and glass exhibit 427 decreasing H₂O/Ce with increasing 87 Sr/ 86 Sr. Thus, the difference in H₂O/Ce between melt 428 inclusions and glasses is largest at the highest ⁸⁷Sr/⁸⁶Sr (Figure 7). To illustrate this, we note that 429 all four pillow glasses with the strongest EM2 signatures (87 Sr/ 86 Sr > 0.7080) have H₂O/Ce < 90 430 (H₂O/Ce average of 75 ± 30 , 2SD) while the H₂O/Ce of the four melt inclusions with the highest 431 87 Sr/ 86 Sr (>0.7080) have H₂O/Ce that is more than twice as high as that in the pillow glasses 432 433 (H₂O/Ce average of 193±19, 2SD). Prior studies (e.g., Workman et al., 2006) often cite that pillow glasses erupted at depths >1000 mbsl retain volatile/ITE ratios of the mantle source. All 434 pillow glasses shown in Figure 7 have H₂O-CO₂ saturation pressures ≥ 0.1 kbar. Given that the 435 melt inclusions and glasses in Figure 7 exhibit deep saturation pressures and appear to sample 436 the same mantle source (Figure 4), we might expect the deeply-erupted pillow glasses should 437 have the same H₂O/Ce as melt inclusions. These observations raise a key question that we will 438 address in the discussion: why do melt inclusions and pillow glasses erupted at depths >1000 439 mbsl from the same volcanoes and with the same ⁸⁷Sr/⁸⁶Sr (i.e., sampling the same mantle 440 sources) have H₂O/Ce that differ, on average, by nearly a factor of two? 441

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	CO ₂ 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 H ₂ O/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 Samoan melt inclusions through closed-system degassing; the new insight gained here is that, 450 when compared with genetically-related melt inclusions, it is clear that even deeply erupted 451 452 glasses (with CO₂-H₂O saturation pressures ≥ 0.1 kbar) have lost significant H₂O and have lower H₂O/Ce compared to their primary melt (Figure 3). This is evident in models we have run using a 453 set of open- and closed-system degassing paths while also varying the fraction of CO₂+H₂O fluid 454 in equilibrium with the initial melt (Figure 6). In the models, we define the variable M as the 455 percentage of fluid in equilibrium with the melt, where M = 0% means that no initial fluid is in 456 equilibrium with the melt (i.e., all volatiles are dissolved in the melt, no fluid is present), and 457 where M = 100% means that all volatiles are in the fluid (i.e., no melt is present). The higher the 458 M value, the deeper degassing starts. We generate degassing paths assuming a starting H_2O and 459 460 CO_2 composition equivalent to the melt inclusion with the highest H₂O content from Malumalu seamount (sample AVON3-78-1#3) to model Malumalu data, and the equivalent high-H₂O melt 461 inclusion from Vailulu'u (sample AVON3-71-2#10) to model Vailulu'u data. We use MagmaSat 462 463 (Ghiorso & Gualda, 2015) to calculate the fluid composition (i.e., XCO₂ and XH₂O) in equilibrium with the two melt inclusions (see Table S9 for model melt inclusion compositions). 464 Additionally, we use rhyolite-MELTS v.1.2 (which incorporates the same fluid solubility model 465 as MagmaSat) to simulate degassing because this model is well-suited for high CO₂ contents in 466

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

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

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

490 **6. Discussion**

H₂O has incompatibility during mantle melting similar Ce (Michael, 1995), thus H₂O/Ce 491 492 of the melt inclusions and glasses should reflect the mantle source unless the samples have degassed. Clear negative correlations between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr in pillow glasses have been 493 used to infer the H₂O/LREE (light rare earth element) ratios of the mantle source, assuming the 494 495 H₂O has not been degassed. The primary observation in this study that we seek to explain is that Samoan pillow glasses and olivine-hosted melt inclusions span the same range of ⁸⁷Sr/⁸⁶Sr and 496 trace element ratios—and thus sample the same mantle sources, yet the melt inclusions have 497 498 H₂O/Ce ratios that are approximately twice as high as the pillow glasses. The second key observation is that the melt inclusion H₂O/Ce ratios are relatively constant over a wide range of 499 ⁸⁷Sr/⁸⁶Sr, in contrast to the pillow glasses whose H₂O/Ce ratios anticorrelate with ⁸⁷Sr/⁸⁶Sr. This 500 501 raises two key questions: Why do Samoan EM2 pillow glasses exhibit H₂O/Ce that are approximately half the values in Samoan EM2 melt inclusions at the same seamounts, and what 502 does this mean for the H₂O content of the EM2 mantle? 503 504 6.1. Higher H₂O/Ce in melt inclusions relative to pillow glasses: Diffusive H₂O gain through 505 host olivine and/or assimilation of seawater-derived materials? 506 In order to compare the volatile contents of the Samoan melt inclusions and pillow 507 glasses in this study, it is important to assess whether the higher H₂O/Ce in the inclusions reflects 508 processes operating in the magma during ascent, such as diffusive proton gain (i.e., addition of 509 H) or assimilation of seawater-derived materials. Prior work has shown that, compared to large 510 melt inclusions, small inclusions are more susceptible to diffusive loss or addition of protons, 511

and this results in modified δD (Hauri, 2002; Portnyagin et al., 2008; Gaetani et al., 2012; 512 Bucholz et al., 2013; Hartley et al., 2015). Given enough time, the δD of all inclusions will 513 eventually equilibrate with the external melt. Diffusive proton loss from the inclusion can be 514 identified by an increase in δD , which is associated with decreasing melt inclusion volume. 515 Conversely, diffusive gain of protons by the inclusion is identified by a decrease in δD , where 516 the magnitude of the δD reduction is greater in the smaller volume melt inclusions. The new δD 517 analyses on melt inclusions show a lack of variation in δD (-35.8±17.0‰, 2SD, N=19) with melt 518 inclusion size for melt inclusions with volumes $>10^5 \,\mu\text{m}^3$, which indicates no water loss or gain 519 in the larger inclusions (Figure 2). However, the two smallest melt inclusions (AVON3-78-1#13 520 and AVON3-78-1#32), both with melt inclusion volume $<10^5 \,\mu\text{m}^3$, have significantly higher δD 521 (+128‰ and +6‰, respectively) than the other melt inclusions from this lava, which indicates 522 that the small volume melt inclusions have experienced diffusive H₂O loss, not H₂O addition 523 (Figure 2). These two small volume inclusions are excluded from the discussion below. 524 Assimilation of seawater-derived materials can increase H₂O in magmas (except if the 525 magma is saturated in H_2O), and this process can be traced by monitoring Cl/Nb, a ratio that is 526 elevated in seawater-derived materials. One hypothesis for the higher H₂O/Ce in melt inclusions 527 is that they have experienced more assimilation of seawater-derived materials compared to 528 Samoan pillow glasses, and this hypothesis can be tested by measurement of ⁸⁷Sr/⁸⁶Sr. A plot of 529 Cl/Nb versus ⁸⁷Sr/⁸⁶Sr shows that Samoan pillow glasses and melt inclusions have an 530 overlapping range of Cl/Nb at any given ⁸⁷Sr/⁸⁶Sr, so the offset to higher H₂O/Ce in the melt 531 inclusions is not explained by greater assimilation experienced by melt inclusions (Figure 5). We 532 do acknowledge that one melt inclusion with exceptionally high Cl/Nb (840)—a ratio consistent 533

534 with assimilation of seawater-derived materials (Table S1)—also has elevated H₂O/Ce (366),

535	suggesting a role for assimilation in increasing the H ₂ O/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 H ₂ O and preferential assimilation of seawater-derived materials
538	by the melt inclusions relative to the pillow glasses do not explain the higher H_2O/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 H_2O and the H_2O/Ce of pillow glasses. In
541	contrast, limited H ₂ O degassing has occurred in the melt inclusions in this study, leaving the melt
542	inclusion H ₂ O/Ce relatively unchanged, thereby explaining why melt inclusions have higher
543	H ₂ O/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 H ₂ O/LREE ratios of the
545	mantle source.
546	6.2 Higher H ₂ O/Ce in melt inclusions relative to pillow glasses: H ₂ O loss in Samoan glasses
546 547	6.2 Higher H ₂ O/Ce in melt inclusions relative to pillow glasses: H ₂ O loss in Samoan glasses caused by degassing
547	caused by degassing
547 548	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions
547 548 549	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses
547 548 549 550	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from
547 548 549 550 551	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from great depth all the way to eruption and quenching on the seafloor, melt inclusions trap melts at
547 548 549 550 551 552	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from great depth all the way to eruption and quenching on the seafloor, melt inclusions trap melts at magma chamber depths and act as pressure vessels, which inhibits degassing at shallower levels
547 548 549 550 551 552 553	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from great depth all the way to eruption and quenching on the seafloor, melt inclusions trap melts at magma chamber depths and act as pressure vessels, which inhibits degassing at shallower levels during magma ascent. To evaluate this hypothesis, we build on the indistinguishable ⁸⁷ Sr/ ⁸⁶ Sr
547 548 549 550 551 552 553 554	caused by degassing We argue that the difference in H ₂ O/Ce between Samoan EM2-flavored melt inclusions and pillow glasses from the same seamounts relates to greater degassing of the pillow glasses relative to the melt inclusions. Unlike the pillow glasses, which can experience degassing from great depth all the way to eruption and quenching on the seafloor, melt inclusions trap melts at magma chamber depths and act as pressure vessels, which inhibits degassing at shallower levels during magma ascent. To evaluate this hypothesis, we build on the indistinguishable ⁸⁷ Sr/ ⁸⁶ Sr and nonvolatile incompatible trace element ratios between pillow glasses and melt inclusions and

crystallization of magmas with MgO as high as identified in the data reported here (Figure S1) and 87 Sr/ 86 Sr data obtained on the melt inclusions indicate that they derive from the same parental melts as the pillow glasses and thus should have started with the same H₂O/Ce). The H₂O/Ce of the pillow glasses, but not the melt inclusions, was then lowered by H₂O degassing during ascent.

563 The hypothesis of H₂O 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 AVON3-78-1 starts with a melt inclusion composition like AVON3-78-1#3 which has an elevated CO₂ 565 566 concentration of 2810 ppm, the highest H₂O concentration from this lava (1.95 wt.%), and a high 567 entrapment pressure of 2.63 kbar (i.e., the CO₂-H₂O saturation pressure calculated for the melt inclusion using MagmaSat). Closed-system degassing of this melt composition from 2.63 kbar to 568 569 0.2 kbar—the approximate CO₂-H₂O saturation pressure for the pillow glass from this lava, sample AVON3-78-1—at M=1.6 lowers the water content by a factor of ~2.1 to 0.90 wt.%, and 570 the CO₂ content by a factor of ~40 to 69 ppm. The red "x" in Figure 6a defines the CO₂ and H₂O 571 572 composition of the model melt following degassing, and the degassed model melt is very similar in composition to the pillow glass sample AVON3-78-1 and helps explain the low H₂O (0.91 573 wt.%) and CO₂ (70 ppm) of AVON3-78-1. This is important because this particular pillow glass 574 sample anchors the highest 87 Sr/ 86 Sr (0.7089) and lowest H₂O/Ce (59) portion of the 87 Sr/ 86 Sr 575 versus H₂O/Ce array produced by Workman et al. (2006) who interpreted that the low H₂O/Ce in 576 this EM2 glass reflects melting of a water-poor ("dry") EM2 mantle. In contrast, we show that 577 dramatic H₂O-loss during closed-system degassing of an ascending EM2 melt with an initially 578 high H_2O/Ce ratio ($H_2O/Ce = 200$) is responsible for the low H_2O/Ce (59) in the AVON3-78-1 579 580 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 H ₂ O/Ce ratio in melt inclusions over a
584	wide range of 87 Sr/ 86 Sr—melt inclusions with strong EM2 mantle signatures (i.e., 87 Sr/ 86 Sr >
585	0.7080) have elevated H ₂ O/Ce (193 \pm 19 2SD, N=4) that is indistinguishable from H ₂ O/Ce
586	(202±31, N=3) in melt inclusions with weaker EM2 signatures (87 Sr/ 86 Sr < 0.7080). This also
587	contrasts with Workman et al.'s (2006) observation that $H_2O/LREE$ is lower in the Samoan EM2
588	pillow glasses with higher ⁸⁷ Sr/ ⁸⁶ Sr. Unlike Workman et al. (2006), who argued that the low
589	H ₂ O/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	87 Sr/ 86 Sr and low 87 Sr/ 86 Sr melts have the same initial H ₂ O/Ce—as supported by observations
593	from melt inclusions in Figure 5a—then the negative correlation between 87 Sr/ 86 Sr in H ₂ O/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 H_2O (to achieve lower H_2O/Ce) than Samoan
596	pillow glasses with weaker EM2 signatures (which have higher H ₂ O/Ce). Therefore, we next
597	focus on identifying the mechanism that results in greater H ₂ O degassing in more extreme EM
598	melts relative to non-EM melts.

599

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

602 The global OIB dataset on submarine pillow glasses exhibits an inverse relationship 603 between 87 Sr/ 86 Sr 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 Sr/ ⁸⁶ Sr
605	tend to have higher H_2O/Ce than glasses with high ${}^{87}Sr/{}^{86}Sr$ (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 Sr/ 86 Sr are shifted to higher, relatively constant H ₂ O/Ce
608	(197 \pm 58 2SD, N=15) compared to the H ₂ O/Ce (108 \pm 58, 2SD, N=41) in a global database of OIB
609	glasses (including Samoa) that have similarly high ⁸⁷ Sr/ ⁸⁶ Sr (i.e., >0.7037) (Figure 7). In fact, the
610	high H ₂ O/Ce of Samoan inclusions (197 \pm 58 2SD, N=15) is similar to the H ₂ O/Ce (209 \pm 92, 2SD,
611	N=32) of pillow glasses characterized by low 87 Sr/ 86 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	H_2O/Ce between low ${}^{87}Sr/{}^{86}Sr$ (<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 H ₂ O/Ce, but the latter suffer more degassing of H ₂ O than the former during magma ascent.
617	If the inverse correlation between H_2O/Ce and ${}^{87}Sr/{}^{86}Sr$ 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 ₂ O 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 ₂ O by closed-system degassing during ascent than primary melts with the same
626	H ₂ O but lower CO ₂ concentrations. As a result, EM lavas that were initially more CO ₂ -rich erupt

on the seafloor with lower H_2O/Ce than their geochemically-depleted non-EM counterparts that started with lower primary melt CO₂, even though both EM and non-EM primary melts started with the same H_2O concentrations and H_2O/Ce . At the extreme end, non-EM (i.e., geochemically depleted) melts erupted at, for example, MORB settings, can have such low primary melt CO₂ that they never saturate and neither CO₂ nor H_2O are lost by degassing (Saal et al., 2002; Michael & Graham, 2015; Hauri et al., 2018).

By contrast, we argue that CO₂-rich primary melts, typical of geochemically-enriched 633 OIB settings, saturate CO₂ at great depths and lose significant CO₂ and H₂O by closed-system 634 635 degassing. In order to show this, we first estimate primary melt CO₂ for a suite of global OIB glasses using a set of relationships shown in Figures 8 and 9. Because OIB glasses are degassed 636 in CO₂ to variable degrees, we estimate primary melt (undegassed) CO₂ for OIB glasses in the 637 638 following way. First, using a new correlation between undegassed CO₂/Nb and (La/Sm)_N in MORB and OIB (see equation in Figure 9a and discussion in Supplementary Information section 639 S1.8), together with the measured (La/Sm)_N available in the suite of OIB glasses examined here, 640 we can calculate the primary melt CO₂/Nb in the OIB glasses (Figure 8c). (It is worth noting that 641 the correlation between CO₂/Nb and (La/Sm)_N in Figure 9a is similar to a relationship previously 642 suggested for MORB by Cartigny et al. (2008) (Figure 9b).) We then calculate the primary melt 643 Nb concentrations for each of the OIB glasses by correcting for olivine addition or subtraction so 644 the melts are in equilibrium with mantle (Fo₉₀) olivine (Figure 8d). By multiplying calculated 645 646 primary melt CO₂/Nb (Figure 8c) by the calculated primary melt Nb concentrations (Figure 8d), we obtain primary melt CO₂ concentrations for the OIB glasses (Figure 8e). These calculations 647 suggest that the most extreme EM OIB glasses (which have the lowest H₂O/Ce)—all from the 648 Samoa, Societies, and Pitcairn hotspots—tend to have the highest primary melt CO₂ (Figure 8e), 649

with CO₂ concentrations commonly as high as 5 to 6 wt.% in Samoa and Societies lavas (and
higher than 80,000 ppm CO₂ in two Samoan lavas). These high OIB primary melt CO₂
concentrations calculated with our new model are in broad agreement with CO₂ concentrations
calculated using the petrologic model of Sun and Dasgupta (2020) (see supplementary Figure S9
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 clustering near ~60,000 ppm CO₂ (Figure 8e). With few exceptions, the non-EM OIB (which 657 658 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 is consistent with prior suggestions that geochemically enriched mantle domains with higher 660 ⁸⁷Sr/⁸⁶Sr generate primary melts with higher CO₂ than geochemically depleted mantle domains 661 (Burnard et al., 2014; Cartigny et al., 2008). Like Burnard et al. (2014), we argue that melts with 662 higher initial CO₂—characteristic of EM melts (Figure 8e)—undergo greater degrees of 663 degassing than melts with lower initial CO₂. We then show that, everything else being the same, 664 higher initial CO₂ melts experience greater degassing of H₂O (and thus have lower erupted 665 H_2O/Ce) than melts with lower initial CO_2 (Figure 8). 666

In order to demonstrate this quantitatively, we use the calculated primary melt CO_2 of the OIB glasses in Figure 8e, as well as estimated primary melt H_2O (see below), as inputs to a closed-system degassing model. We then show that the CO_2 -rich (60,000 ppm) model primary melt degasses by closed-system degassing to have H_2O concentration and H_2O/Ce similar to values measured in Samoan EM pillow glasses. To test our hypothesis that high primary melt CO_2 concentrations results in more degassing of H_2O , and thus, lower H_2O/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 CO ₂ concentrations: the two melt endmembers are given the same starting
676	H ₂ O (2 wt.%), H ₂ O/Ce (200), and major and trace element chemistry (see compositions in Table
677	S9). The first model melt is assigned a higher CO ₂ concentration of 60,000 ppm, meant to
678	approximate the elevated CO ₂ concentration of EM glasses in Figure 8e (see previous
679	paragraph), and comes from our new model for calculating CO ₂ in OIB primary melts (Figure
680	8c, 9a) for which calculated Samoan primary melt CO ₂ concentrations tend to cluster near 60,000
681	ppm CO ₂ . The second model melt is assigned an initial CO ₂ concentration of 5,000 ppm, and is
682	meant to approximate the CO ₂ concentration of the non-EM glasses from Foundation, Easter,
683	and $L\bar{o}$ 'ihi in Figure 8e. In order to illustrate the impact of H_2O loss during degassing as a
684	function of initial primary melt CO ₂ concentration, we model the closed-system degassing paths
685	of the two melts using rhyolite-MELTS. Degassing of the high CO ₂ (60,000 ppm) melt starts at
686	26 kbar (i.e., where CO ₂ first saturates; see dark green line in Figure 10), which is higher than the
687	4 kbar pressure where the lower CO ₂ melt saturates (see light green line in Figure 10). After both
688	the high- and low-CO ₂ melts degas to the same low eruptive pressure (Figure 10)—0.5 kbar,
689	meant to represent pressure for eruption on the seafloor at \sim 5000 mbsl—the high CO ₂ melt has a
690	significantly lower H ₂ O concentration and lower H ₂ O/Ce (\sim 0.94 wt.% and 94, respectively)
691	compared to the low CO ₂ melt (~1.56 wt.% wt.% and 156, respectively), even though both melts
692	started with the same H_2O (2 wt.%) and H_2O/Ce (200). In summary, a melt with initial CO_2 of
693	60,000 ppm degases nearly 53% of its H_2O (and 99.4% of its CO_2) during ascent to 0.5 kbar, but
694	the melt with 5000 ppm initial CO ₂ degases just 22% of its H_2O (and 96.8% of its CO ₂) during

ascent to 0.5 kbar. Thus, everything else being the same, high CO_2 melts degas more H₂O and have lower H₂O/Ce than low CO₂ melts.

The simple degassing model in Figure 10 helps explain the observation that EM pillow 697 698 glasses erupted on the seafloor have lower H₂O/Ce compared to non-EM pillow glasses: EM primary melts, which are associated with higher initial CO₂ (Figure 8e), saturate in volatiles 699 700 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, similar to non-EM melts, because CO₂ and H₂O degassing was arrested following melt inclusion 702 703 entrapment in olivine at high pressures (0.870 to 5.13 kbar). Although the Samoan melt inclusions lost significant amounts of CO₂ prior to being entrapped by olivine, these melt 704 inclusions still preserve higher H₂O/Ce than the erupted pillow glasses due to having degassed 705 706 less CO₂ and, thus, less H₂O. However, we acknowledge that, prior to entrapment, even the melt inclusions may have already lost some H₂O due to concomitant loss of both H₂O and CO₂ during 707 708 closed-system degassing. Nonetheless, melt inclusions preserve higher H_2O and H_2O/Ce than 709 pillow glasses, and thus preserve values closer to the primary melts.

6.4 Comparison with prior models for the origin of low H₂O/Ce in EM lavas, and implications for a "damp" EM mantle.

Previous studies have suggested that the negative correlation between H₂O/Ce and ⁸⁷Sr/⁸⁶Sr is the result of dehydration (H₂O depletion) in the EM source, which has low H₂O/Ce that gives rise to EM primary melts with low H₂O/Ce. In these models, the EM mantle source has low H₂O/Ce because subducted materials contributing to the EM mantle lose H₂O during subduction (Dixon et al., 2002) or via diffusion during residence in the mantle (Workman et al., 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	H_2O/Ce in high ${}^{87}Sr/{}^{86}Sr$ glasses from Samoa, then the Samoan melt inclusions with high
720	87 Sr/ 86 Sr should also exhibit lower H ₂ O/Ce, but this is not the case.
721	Thus, an important implication is that submarine glasses cannot be reliably used to
722	estimate the H ₂ O/Ce content of OIB primary melts, particularly glasses for EM OIB that appear
723	to experience greater degassing (owing to higher initial CO ₂) than non-EM OIB. Our data show
724	that, unlike Samoan submarine glasses, Samoan melt inclusions have similar H ₂ O/Ce (197 \pm 58,
725	2SD, N=15) that does not vary with 87 Sr/ 86 Sr. In fact, the H ₂ O/Ce ratio (193±19, 2SD, N=4) for
726	extreme Samoan EM2 (87 Sr/ 86 Sr > 0.708) melt inclusions overlaps with H ₂ O/Ce suggested for
727	depleted mantle domains that are sampled by non-EM OIB (87 Sr/ 86 Sr<0.7037; H ₂ O/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 CO_2 and H_2O
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 CO ₂ in
736	the former relative to the latter-future melt inclusion studies will be important for determining
737	the initial H ₂ O/Ce in EM1 (Pitcairn) and other EM2 (Societies) lavas, where existing low
738	H ₂ O/Ce values measured in high ⁸⁷ Sr/ ⁸⁶ Sr Pitcairn and Societies submarine glasses (Kendrick et
739	al. 2014) may also be due to the same degassing mechanism that lowers H_2O/Ce in Samoan OIB.
740	If so, H ₂ O/Ce in the mantle is not likely to be as variable as previously supposed, and much of

the mantle sampled by MORB and OIB have very similar H₂O/Ce that is, on average, close to a
value of 200, and not as low as values found in pillow glasses of EM lavas (down to 59 in
Samoan pillow glasses, 86 in Societies glasses, and 95 in Pitcairn glasses). Thus, like the Pb/Ce
ratio, which is similar in OIB and MORB globally (Hofmann et al., 1986), the H₂O/Ce ratio may
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 subduction zone (White & Hofmann, 1982; Farley et al., 1992; Jackson et al., 2007), Samoan 748 749 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 role in governing the H₂O budgets of mantle domains. This could be because the amount of 751 752 recycled continental crust in the mantle sources of OIB is small, and thus has a diminished impact on the overall H₂O and H₂O/Ce of the mantle source. For example, Samoan lava 753 AVON3-78-1 examined in this study, which has a strong EM2 signature (⁸⁷Sr/⁸⁶Sr of 0.7089), is 754 755 estimated to have only ~1% continental crust (Reinhard et al., 2018) that is added to a depleted plume component that constitutes the rest (99%) of the mantle source. In this model, the H₂O and 756 Ce budgets of the EM2 mantle source is primarily controlled by the depleted plume component, 757 even if the recycled continental crust component has low H₂O/Ce. In this way, both depleted 758 mantle and EM OIB can have similar H₂O/Ce. 759

760

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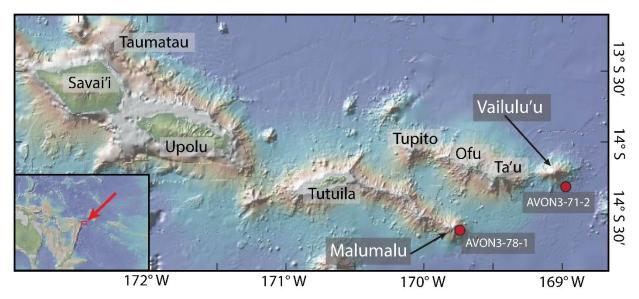
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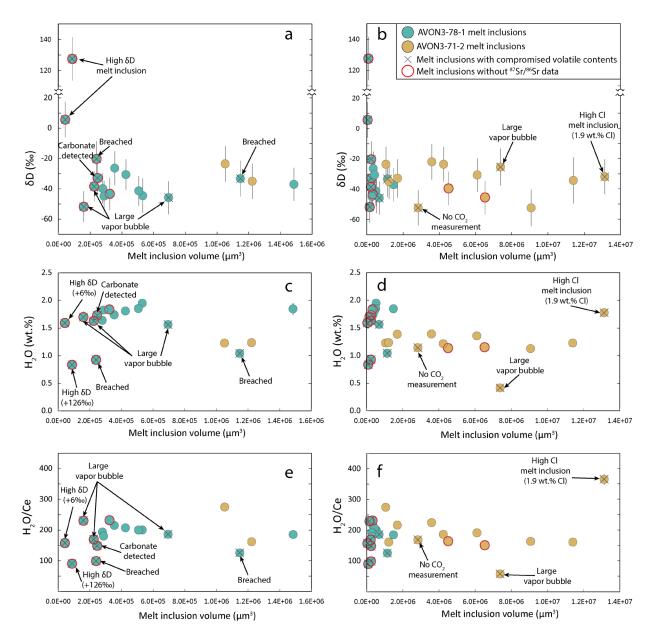
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1088 FIGURES



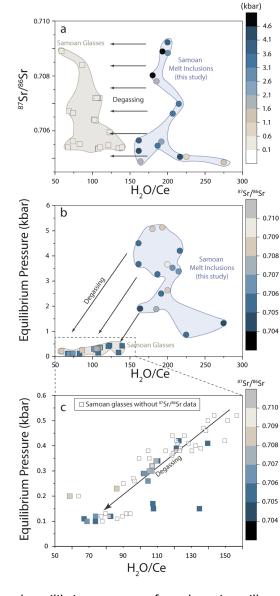
- 1089 Figure 1. Map of the Samoan Islands. Red dots indicate the location of AVON3 cruise dredge sites 71 and
- 1090 78, from the flanks of Vailulu'u and Malumalu, respectively. Map created using GeoMapApp1091 (www.geomapapp.org).



1093 Figure 2. (a–b) δD (‰), (c–d) H₂O (wt.%), and (e–f) H₂O/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 standard ALV1833-1 (i.e., ±16‰, 2SD; see Table S2). Melt inclusion H₂O compositions are corrected for 1097 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 H₂O, and reproducibility of H₂O 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 CO₂ data—and are marked 1104 with an "x" symbol. With the exception of the high Cl melt inclusion (which is individually identified in

Equilibrium Pressure

figures throughout the paper), the compromised melt inclusions are not shown in subsequent volatileelement figures.



1108 Figure 3. ⁸⁷Sr/⁸⁶Sr, H₂O/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 Vailulu'u sample AVON3-71-2. (a) ⁸⁷Sr/⁸⁶Sr versus H₂O/Ce for Samoan melt inclusions and glasses with 1110 1111 the color bar representing equilibrium pressure (kbar). The pillow glass data show separation in H₂O/Ce 1112 from the melt inclusion data, even though both datasets span a similar range in ⁸⁷Sr/⁸⁶Sr. Circles represent melt inclusions and squares represent Samoan pillow glasses from Workman et al. (2006). 1113 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 MagmaSat model (lacovino et al., 2021; Wieser et al., 2022) assuming oxygen fugacity (QFM) and 1116 temperature (1200°C). Samoan pillow glass data are from Workman et al. (2006), except major elements 1117 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 H₂O/Ce for Samoan melt inclusions and pillow glasses with the
- 1120 color bar representing ⁸⁷Sr/⁸⁶Sr. (c) Expanded view of panel b that shows equilibrium pressure versus
- 1121 H₂O/Ce for Samoan pillow glasses only. Smaller square data points with black outlines are pillow glasses
- 1122 lacking ⁸⁷Sr/⁸⁶Sr data. Only samples with CO₂-H₂O saturation pressures ≥ 0.1 kbar are shown (just one
- 1123 Samoan glass with ⁸⁷Sr/⁸⁶Sr data has a saturation pressure <0.1 kbar, sample AVON3-68-03 Rpt, so its
- 1124 removal does not significantly impact the dataset).
- 1125

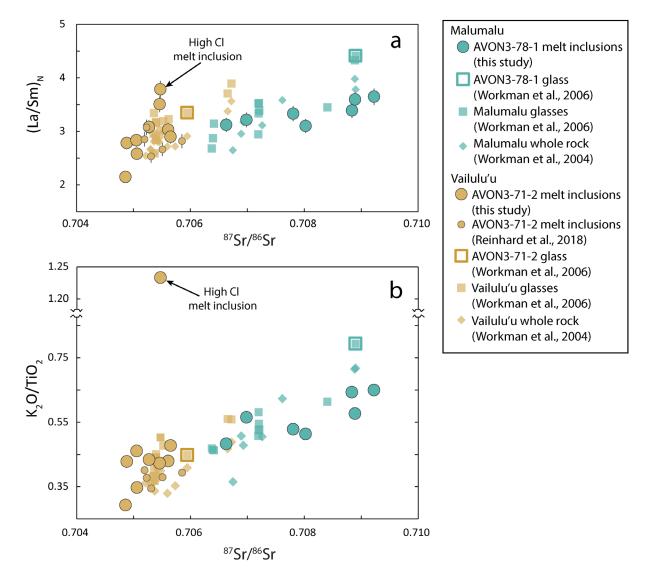




Figure 4. Incompatible trace element ratios versus ⁸⁷Sr/⁸⁶Sr are shown for Samoan pillow glasses from
 Malumalu and Vailulu'u seamounts and new melt inclusion data from Malumalu sample AVON3-78-1
 and Vailulu'u sample AVON3-71-2. The melt inclusions have incompatible trace element ratios and
 ⁸⁷Sr/⁸⁶Sr compositions that fall within the range identified in Samoan pillow glasses, indicating that the
 Samoan melt inclusions sample melts represented by the pillow glass dataset. (a) (La/Sm)_N versus
 ⁸⁷Sr/⁸⁶Sr, where N signifies normalization to primitive mantle (McDonough & Sun, 1995). (b) K₂O/TiO₂

- 1133 versus ⁸⁷Sr/⁸⁶Sr. 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 ((La
- error)²+(Sm error)²)^{0.5}, where the 2RSD of the secondary standard BCR-2 is used for La error (1.9%) and
- 1136 Sm error (3.8%) (see Table S2). Error bars on K_2O/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.

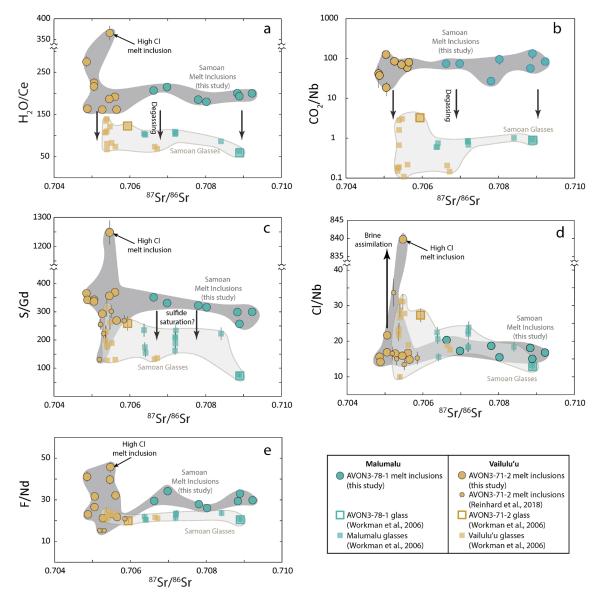
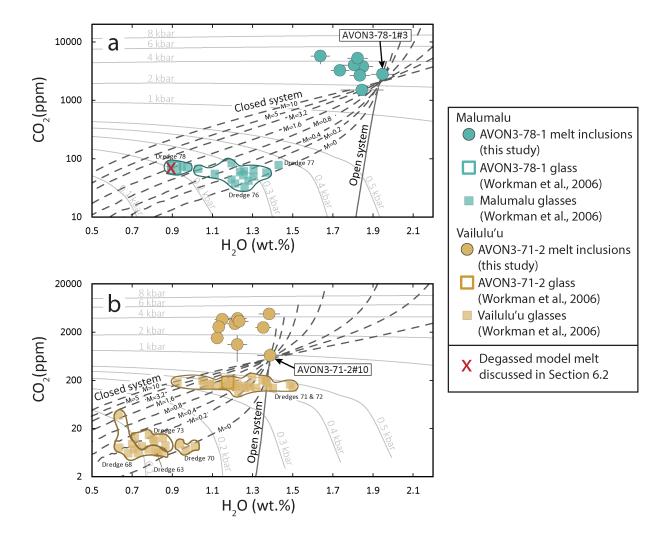


Figure 5. Element ratios (volatile/incompatible trace element) are plotted against ⁸⁷Sr/⁸⁶Sr for Samoan pillow glasses from Malumalu and Vailulu'u seamounts and the new melt inclusion data from Malumalu sample AVON3-78-1 and Vailulu'u sample AVON3-71-2. See Supplementary Text section S1.6 for a discussion on the calculation of the errors associated with the element ratios presented here; the error bars for the ⁸⁷Sr/⁸⁶Sr 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).

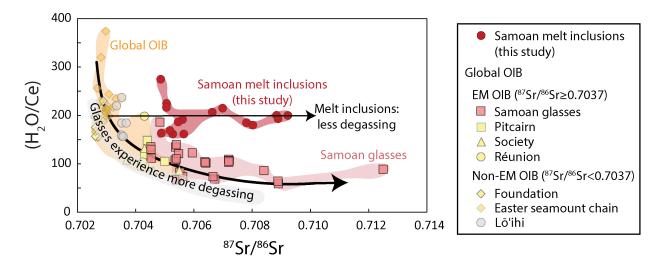
- 1149
- 1150



1151

1152 **Figure 6.** CO_2 versus H_2O 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
- $1163 \qquad \text{compositions used in the degassing calculation are in Table S9. Melt inclusion CO_2 and H_2O$
- 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.



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 glasses—have higher H₂O/Ce than Samoan pillow glasses, and thus fall off of the global submarine OIB 1169 pillow glass trend that shows decreasing H₂O/Ce with increasing ⁸⁷Sr/⁸⁶Sr. Only OIB glasses with ⁸⁷Sr/⁸⁶Sr 1170 1171 (to establish the level of source enrichment) and MgO > 4.5 wt.% (to minimize the impact of fractional crystallization) are shown. Sources of data (see Table S11): Pitcairn (Kendrick et al., 2014; Woodhead & 1172 Devey, 1993), Society (Devey et al., 1990; Kendrick et al., 2014), Réunion (Kendrick et al., 2017; Fretzdorf 1173 1174 & Haase, 2002), Foundation (Kendrick et al., 2017), Easter seamount chain (Dixon et al., 2002), Lo'ihi 1175 (Dixon & Clague, 2001; Staudigel et al., 1984). Samples from Pitcairn, Society, Réunion, and Foundation can be found in a data compilation by Kendrick et al. (2017). Samples marked as having experienced 1176 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 other OIB melt inclusions characterized for both ⁸⁷Sr/⁸⁶Sr and H₂O/Ce. Only samples with CO₂-H₂O 1182 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).

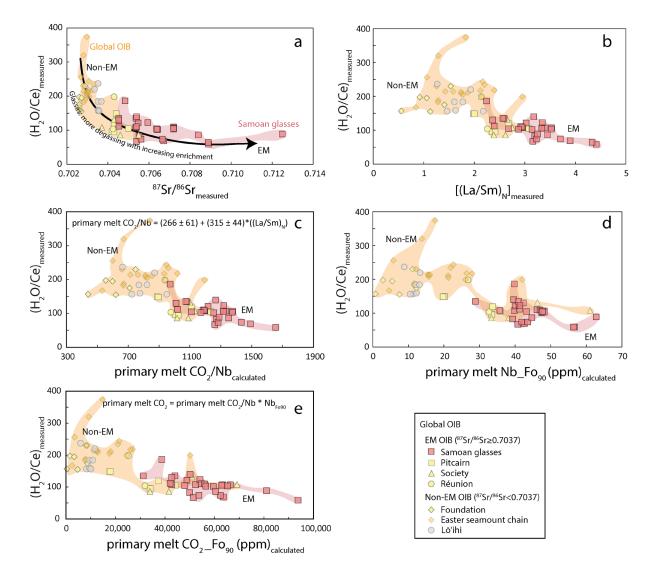
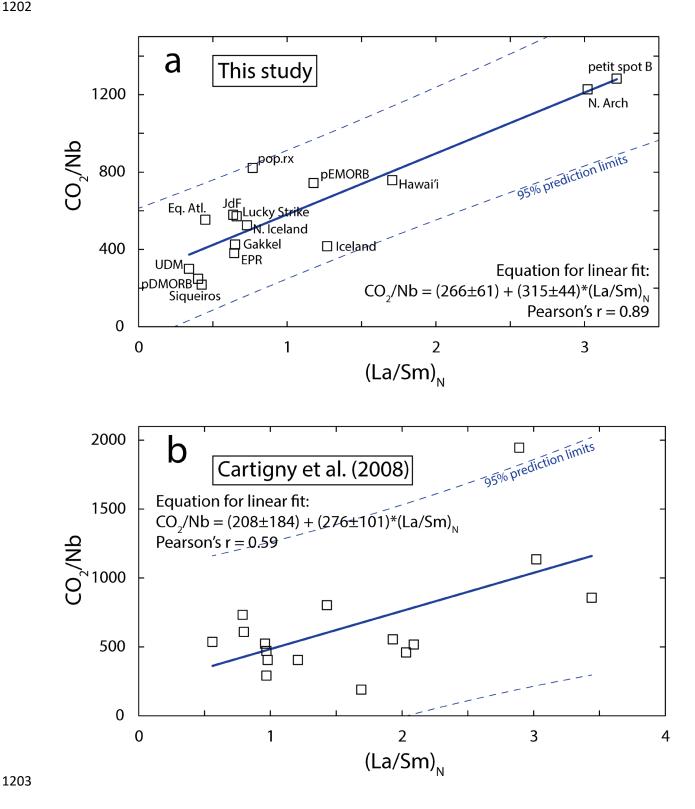


Figure 8. Samoan pillow glasses compared to a global dataset of submarine OIB glasses, which show a 1186 trend of decreasing H₂O/Ce with increasing ⁸⁷Sr/⁸⁶Sr. The exact same OIB dataset is shown in all panels: 1187 1188 only OIB with ⁸⁷Sr/⁸⁶Sr data (to establish the level of source enrichment) and MgO > 4.5 wt.% (to minimize the impact of fractional crystallization) are shown. (a) H_2O/Ce versus ⁸⁷Sr/⁸⁶Sr. (b) H_2O/Ce 1189 versus $(La/Sm)_N$. (c) H₂O/Ce versus primary melt CO₂/Nb, where CO₂/Nb is calculated from the measured 1190 1191 $(La/Sm)_N$ ratios using a linear fit between CO₂/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 $F_{0,0}$ olivine. (e) H_2O/Ce versus calculated primary melt CO_2 , where the CO_2 is 1196 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 Fo₉₀ (ppm) values for 1199 the global OIB data set presented here are given in Table S11. Only samples with CO₂-H₂O saturation

pressures ≥0.1 kbar are shown (just one Samoan glass with ⁸⁷Sr/⁸⁶Sr data has a saturation pressure <0.1 1200

1201 kbar, sample AVON3-68-03 Rpt, so its removal does not significantly impact the dataset).



- 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 $(La/Sm)_N$. Data compilation is the same as what is presented in Figure 1 of Hirschmann
- 1206 (2018). The values for CO_2/Nb and $(La/Sm)_N$ in panel (a) are given in Table S10. The blue dashed lines
- represent the 95% prediction interval. The 95% confidence interval of the linear fit is given with the
- equation of the linear fit. The linear relationship calculated in panel a is used to estimate the CO₂/Nb
 values for glasses and melt inclusions in Figure 8. (b) Linear fit (blue line) to the Mid-Atlantic Ridge
- CO_2/Nb versus (La/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
- 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).

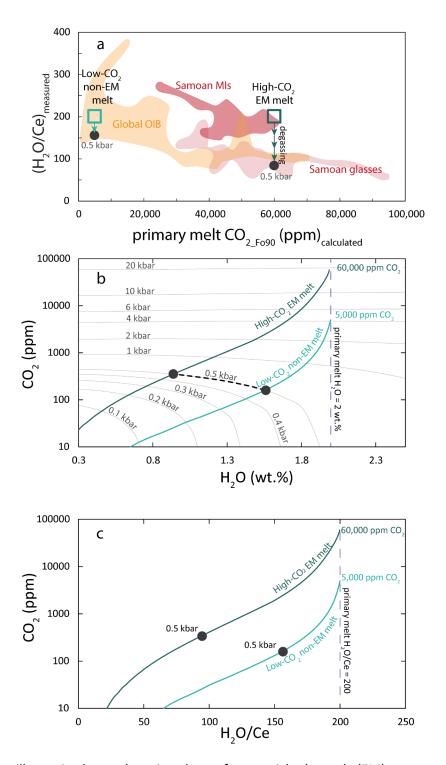


Figure 10. Figure illustrating how submarine glasses from enriched mantle (EM) sources acquire low
 H₂O/Ce relative to glasses from non-EM sources. We test two melt compositions that are identical in

1223 every way (major and trace element compositions are identical and H_2O is 2 wt.%) except for CO_2 , where

1224 one melt starts with 60,000 ppm CO_2 (meant to represent an EM melt) and the other melt starts with

1225 5000 ppm CO_2 (meant to represent the non-EM melt). (a) H_2O/Ce versus primary melt CO_2 , reproduced

in cartoon form from Figure 8e. The black circle indicates the H₂O/Ce value for melts at 0.5 kbar after

degassing. (b) In a plot of CO_2 versus H_2O , 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 H_2O , those with higher initial CO_2 degas more H_2O and have lower H_2O 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 H_2O/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 H_2O/Ce instead of H_2O . Calculation of H_2O/Ce along the degassing paths assumes 1) an initial 1235 H_2O/Ce value of 200 (similar to the average H_2O/Ce value of Samoan melt inclusions examined here) and 1236 2) a constant melt Ce concentration (100 ppm) that is calculated using the initial H_2O/Ce ratio (i.e., 200) 1237 and the initial H_2O (2 wt.%). Similar to the relationship between CO_2 and H_2O for high and low CO_2 melts, 1238 at a given isobar the melt with high initial CO_2 has significantly lower H_2O/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 CO_2 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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