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1 MULTIPLE PARAMETERS ENABLE DECONVOLUTION OF WATER-ROCK
2 REACTION PATHS IN LOW-TEMPERATURE VENT FLUIDS OF THE
3 KAMA‘EHUAKANALOA (LŌ’IHI) SEAMOUNT

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21 Key words: hydrothermal vents; active intraplate volcano; low-temperature vent fluids; fluid geochemistry;
22 water-rock reactions; geochemical modeling; ocean Fe budget

23

Highlights

24 New data for vent-fluid compositions at Kama‘ehuakanaloa including CO₂ and CH₄ concentrations

25 Persistent vent-fluid composition for three decades

26 Geochemical modeling of water-rock-gas reactions that produce the 20-50 °C vent fluids

27 Low-temperature basalt alteration results in high Fe/low H₂S vent fluids

28 Key role of active intraplate volcanoes on ocean Fe-cycle

29

30

Abstract

31 The contribution of venting fluids at mid-ocean ridges to global ocean biogeochemical cycles is well
32 recognized. Less is known about the role of magmatically-active intra-plate volcanoes. In this study, new
33 compositional fluid data were acquired from 20-50 °C vent fluids at Kama‘ehuakanaloa (previously known
34 as Lō‘ihi) seamount (Hawai’ian archipelago) and used to model the wide diversity of reaction conditions
35 capable of producing the Fe-, Si- and CO₂-rich vent fluids observed. Our conceptual model includes a first
36 step where seawater reacts with increasing proportions of basalt and gas as the temperature increases, and
37 a second step where the resulting hydrothermal fluid mixes with unaltered seawater while continuing to
38 react with basalt until the fluid mixture reaches 20 °C. A series of reaction paths were chosen to vary: the
39 maximum temperature during Step 1 (50 to 400 °C) and the proportions of basalt and gas reacting; the
40 degree, *F*, of low-temperature basalt alteration during Step 2, which corresponds to the extent to which the
41 hot fluid generated during Step 1 continues to react with more basalt as it ascends to the seafloor. Our model
42 shows that the 20-50 °C vent fluids are greatly dependent on the degree of low-temperature basalt alteration
43 during fluid upwelling. Indeed, the compositions of Kama‘ehuakanaloa vent fluids cannot be reconciled
44 with a general model of subsurface mechanical mixing of high-temperature end-member vent fluid and
45 seawater alone. Instead, they require both subsurface equilibrium mixing between a ≥ 350 °C hydrothermal

46 fluid end-member and seawater and further basalt alteration that must occur as the fluid mixture rises to the
47 seafloor. Although it involves only ~4% of the amount of basalt having reacted during Step 1, this low-
48 temperature basalt alteration during Step 2 leads to the characteristic enrichments in Fe observed in the
49 Kama‘ehuakanaloa vent fluids and a concomitant depletion in H₂S. We hypothesize that low-temperature
50 basalt alteration during an extended path of fluid upwelling through the subseafloor might arise as a direct
51 consequence of the height and steep-sloped topography of Kama‘ehuakanaloa seamount. If correct, this
52 suggests a more general case - that input from magmatically-active intraplate volcanoes, which have been
53 relatively overlooked throughout the history of submarine vent investigations to date, could differ
54 significantly from global mid-ocean ridge fluxes and contribute more substantially than previously
55 recognized to the global ocean Fe cycle.

56 1. Introduction

57 Hydrothermal circulation in the oceanic lithosphere plays a major role in global-scale ocean biogeochemical
58 budgets (Edmond et al., 1979; German and Seyfried, 2014) and in supporting microbial life at and beneath
59 the seafloor (e.g., Jannasch and Mottl, 1985; McCollom and Shock, 1997; Dick, 2019). Although
60 hydrothermal activity at mid-ocean ridges has received much attention since its discovery in the late 1970's,
61 that associated with active intraplate seamounts has been relatively overlooked (Beaulieu et al., 2015). Yet,
62 new evidence reveals that such systems may sustain major biogeochemical fluxes to the ocean that need to
63 be considered in global inventories (Bennett et al., 2011; Jenkins et al., 2020).

64 At the Kama'ehuakanaloa seamount (previously known as Lō'ihī), the southernmost and youngest
65 submarine volcano of the Hawai'ian hot-spot trace, it is well established that dissolved Fe released from
66 low-temperature vent fluids produces redox disequilibria that support vast microbial communities
67 dominated by iron-oxidizing bacteria (Emerson and Moyer, 2002; Emerson, 2009; Sylvan et al., 2017).
68 During the GEOTRACES era, it has become apparent that dissolved Fe from mid ocean ridge hydrothermal
69 venting can be traced long distances throughout every ocean basin (German et al., 2016). In the case of the
70 South Pacific, it has been calculated that upwelling of this Fe into high nutrient low chlorophyll surface
71 waters may account for ~30% of the drawdown of atmospheric CO₂ into the Southern Ocean (Resing et al.,
72 2015). Only more recently has it been revealed, however, that dissolved Fe released from the
73 Kama'ehuakanaloa seamount may also persist sufficiently far as it disperses through the ocean to stimulate
74 primary productivity in similar fashion in the high latitude North Pacific (Jenkins et al., 2020).

75 The Kama'ehuakanaloa seamount is located 35 kms from the island of Hawai'i on the southern
76 flank of Mauna Loa volcano and rises ~ 4 km above the abyssal plain to a depth of 950 m below sea level.
77 Prior to the most recent eruptive activity in 1996, hydrothermal venting had been reported from the upper
78 portion of the south rift zone; and on the east flank of the volcano as well as at its summit (Gamo et al.,
79 1987; Sakai et al., 1987; Karl et al., 1988). After the eruption, venting was also established within a series
80 of summit pit craters (Wheat et al., 2000; Glazer and Rouxel, 2009; Rouxel et al., 2018). Except for the

81 one-year survey period following the 1996 eruptive activity where temperatures up to 200 °C were reported
82 (Wheat et al., 2000), the vent fluids temperatures measured at Kama‘ehuakanaloa through a series of
83 expeditions between 1987 and 2018 were mostly between 20 and 50 °C. At these temperatures, the vent
84 fluids exhibit pH values from 5.5 to 6.2 and are enriched in Si, Fe, CO₂, NH₄⁺, PO₄²⁻ and Mn and depleted
85 in H₂ and H₂S relative to mid-ocean ridge hydrothermal systems (Karl et al., 1988; Sedwick et al., 1992;
86 Wheat et al., 2000; Glazer and Rouxel, 2009; Rouxel et al., 2018). The associated hydrothermal deposits
87 consist of yellow-brown, well-crystallized goethite and smectite ranging in composition from Fe-
88 montmorillonite to nontronite (Malahoff et al., 1982; De Carlo et al., 1983). This is quite distinct from
89 basalt-hosted mid-ocean ridge hydrothermal systems where high temperature (~350 °C) black smoker fluids
90 enriched in H₂S and variable amounts of chalcophile transition metals (e.g., Cu, Zn, Pb) result in the
91 formation of polymetallic massive sulfide mounds (German and Von Damm, 2006).

92 Sedwick et al. (1992) proposed that pre-eruption Kama‘ehuakanaloa vent fluids resulted from a
93 two-component subsurface mixing of seawater with a >350 °C hydrothermal fluid endmember produced
94 from water-rock-gas interactions. In that interpretation, the high Fe concentrations of the vent fluids resulted
95 from the leaching of basalt walls by the resulting CO₂-rich vent-fluid mixture during upwelling to the
96 seafloor. But the process, as discussed by Sedwick et al. (1992), could also explain the origin of the Sr
97 isotope signature and Si and alkali metal enrichments of the vent fluids that would otherwise serve as
98 evidence for a hot (>350 °C) hydrothermal fluid endmember. Thus, the origin of Kama‘ehuakanaloa vent
99 fluids and, especially, the relative contribution of low- and high-temperature water-rock interactions has
100 never been fully resolved. Here we provide a quantitative evaluation of the water-rock-gas interactions at
101 Kama‘ehuakanaloa to improve our understanding of the contribution that venting fluids associated with
102 active intraplate seamounts could make to global-scale ocean biogeochemical budgets.

103 Specifically, we use newly collected geochemical data to calculate a series of reaction paths for
104 water-rock-gas interactions associated with hydrothermal circulation and explore the diversity of reaction
105 conditions capable of producing the low-temperature vent-fluid compositions observed at

106 Kama‘ehuakanaloa. Data were acquired during the 2018 SUBSEA expedition aboard the *E/V Nautilus* to
107 the Kama‘ehuakanaloa seamount (Lim et al., 2019), to build upon earlier time-series and augment them
108 with new data for dissolved CO₂ and CH₄ concentrations. Our study demonstrates how the chemical
109 composition of low-temperature vent fluids can be used as a guide to water-rock reactions occurring at low-
110 temperature in the shallow subsurface, and how those fluid compositions can be influenced by preceding
111 water-rock reactions at higher temperatures. Our model results reveal a combination of parameters that can
112 produce metal depletion or enrichment in low-temperature vent fluids which, in turn, can set export fluxes
113 to the global ocean.

114 2. Material and Methods

115 2.1. Sampling and measurement

116 From August 21 to September 12, 2018, an exploratory mission to the Kama‘ehuakanaloa seamount was
117 conducted aboard the *E/V Nautilus* as part of the SUBSEA research program. The Remotely Operated
118 Vehicle *Hercules*, equipped with Isobaric Gas-Tight (IGT) sampling devices (Seewald et al., 2002), was
119 used to collect duplicate fluid samples at 6 vents for a total of 12 samples. The pH (25 °C) value, the
120 alkalinity and the CH₄ and H₂ concentrations, which are time-sensitive analyses, were measured onboard
121 daily. A Gas Chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and a Flame
122 Ionization Detector (FID) was used to measure H₂ and CH₄, respectively, with detection limits of 3 μM and
123 0.05 μM. H₂S concentrations were below the detection limits of the analytical method of Cline (1969)
124 available onboard ship, i.e., <1 μM. At the Woods Hole Oceanographic Institution laboratory, major cations
125 and anions were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) and ion
126 chromatography. Concentrations reported for major cations are from ICP-MS except for Ca for which
127 interference with ⁴⁰Ar⁺ prevents accurate measurements. GC-TCD was used to measure total dissolved
128 inorganic carbon (DIC) as CO₂ after acidification of samples with a 25 wt.% phosphoric acid solution.

129 2.2. Modeling

130 Geochemical modeling was performed with the EQ3/6 geochemical software (Wolery, 2010) using
131 thermodynamic data for minerals and dissolved inorganic aqueous species from Helgeson et al. (1978),
132 Shock and Helgeson (1988), Shock et al. (1989, 1992, 1997) and Sverjensky et al. (1997). The Gibbs free
133 energies for clay minerals were estimated using the method of Wolery and Jove-Colon (2004). The other
134 thermodynamic parameters (S, V, Cp) are from Helgeson et al. (1978). All modeling was performed in the
135 system Na₂O-Cl-MgO-CaO-K₂O-SiO₂-SO₂-CO₂-Al₂O₃-FeO-CuO-ZnO-TiO₂. MnO was excluded from the
136 modeling because the limited number of Mn-bearing minerals in our database prevents a realistic
137 description of Mn behavior. The model used for the calculation of activity coefficients is based on the B-
138 dot equation for electrically charged species (Helgeson, 1969). For neutral solute species, the activity
139 coefficient is taken equal to that of aqueous CO₂ in pure sodium chloride solutions of the same ionic strength
140 (Garrels and Thompson, 1962; Helgeson, 1969). Using this approach, the activity coefficient of neutral
141 solute species increases with increasing ionic strength, which is consistent with the “salting out” effect.

142 Although the Kama‘ehuakanaloa summit is 950 m below sea level, the seafloor heat source could
143 be much deeper as the volcano rises from >5000 m depth at its base. We considered a single constant
144 pressure of 500 bars for all our calculations, which corresponds to a depth of ~5000 m below sea level. This
145 assumption is reasonable because the pressure has relatively little effect on thermodynamic equilibria
146 involving condensed phases and dissolved aqueous species compared to the effects of temperature. Our
147 model assumptions hit their limits if phase separation were to occur due to a combination of high
148 temperature (>400 °C) and low pressure (<300 bars) (Bischoff and Rosenbauer, 1985), as might happen
149 during eruptive events (Wheat et al., 2000).

150 Our conceptual model of water-rock reactions during hydrothermal circulation involves two reaction
151 steps as illustrated in Figure 1. In Step 1, we quantify the results as seawater reacts in open systems with
152 Kama‘ehuakanaloa basalt while the temperature rises progressively and volcanic gases are added (CO₂,
153 SO₂ and H₂O). In Step 2, the resulting high-temperature fluid is mixed with seawater in a second open
154 system, while continuing to react with the basaltic interior of the volcano as it rises toward the summit,

155 until the fluid mixture reaches the temperature of 20 °C. This scenario was chosen to account for the water-
156 rock-gas reactions proposed by Sedwick et al. (1992) that produce the Kama‘ehuakanaloha vent fluids. In
157 order to investigate a large range of possible reaction conditions varying in terms of temperature, rock/water
158 ratios and gas inputs, we used the programming language Python to automate the multiple runs and data
159 processing of model results following the approach of Ely (2020) and Milesi et al. (2021).

160 During Step 1, the temperature increases from 2 °C to a temperature maximum (T_{max}) ranging from
161 50 to 400 °C, at intervals of 50 °C (Figure 1a). The composition of seawater is taken from Bruland and
162 Lohan (2006). Basalt composition at Kama‘ehuakanaloha includes tholeiitic, transitional and alkalic basalt
163 as well as basanite (Moore et al., 1982; Dixon and Clague, 2001). On the upper portion of the south rift
164 zone where the vent fields visited during the 2018 SUBSEA expedition are located, the basalt is moderately
165 alkalic in composition, weakly phyrlic, containing 1-2 vol.% of olivine, plagioclase and augite, and becomes
166 more tholeiitic going south (Karl et al., 1988). In our model, we used the basalt composition reported by
167 Karl et al. (1988) at the Kama‘ehuakanaloha summit which falls within the compositional range described
168 by Dixon and Clague (2001). The rock/water ratio (R/W) of Step 1, *i.e.*, the mass of basalt in kilograms
169 reacting with 1 kg of water, increases as the temperature maximum increases (Figure 1b), following the
170 equation:

$$171 \quad R/W_{Step1} = \frac{T_{max}}{350} . \quad (1)$$

172 There is essentially an infinite number of temperature-rock/water ratio paths, only a few of which are
173 considered through Equation (1). After several iterations, we settled on this particular path as it is consistent
174 with previous practices and observational data (Bowers and Taylor, 1985). Especially, Equation (1) leads
175 to a rock/water ratio of 1 at 350 °C, consistent with literature estimates (Von Damm et al., 1985).

176 The Lo‘ihi vent fluids are known to be impacted by magmatic degassing (Karl et al., 1988; Sedwick et
177 al., 1992; Wheat et al., 2000); however, the timing of CO₂ and SO₂ inputs during hydrothermal circulation
178 is unconstrained. Inputs of magmatic gas were considered to be a linear function of the primary

179 concentrations of volatiles in basalt and the rock/water ratio. Because CO₂, SO₂ and H₂O are volatile species
180 that tend to degas during eruption, their primary concentrations were reconstructed using ratios of volatile
181 to non-volatile elements that may behave similarly during melting and crystallization (Michael, 1988; Saal
182 et al., 2002; Aubaud, 2004; Cartigny et al., 2008; Rosenthal et al., 2015). The CO₂, SO₂, and H₂O
183 concentrations were reconstructed using Ba, Ce, and Dy concentrations, respectively (Saal et al., 2002;
184 Rosenthal et al., 2015). Values of 133, 168 and 225 were adopted for the CO₂/Ba, H₂O/Ce and S/Dy ratios,
185 respectively. The Ba, Ce and Dy concentrations for Kama‘ehuakanaloa basalt are from Dixon and Clague
186 (2001) (Table S 1).

187 During Step 2 of the model, seawater at 2 °C is added to the hydrothermal fluid endmember until the
188 fluid mixture reaches 20 °C (Figure 1a). Temperature is controlled only by mixing of the fluids, so that the
189 addition of each increment of seawater lowers the temperature of the fluid mixture. As the temperature is
190 lowered, proportionally greater amounts of seawater are required to lower the temperature further. Because
191 the reaction progress of Step 2 is proportional to the amount of added seawater, most of the water-rock
192 interaction occurs at low temperature, <50 °C. The rock/water ratio of Step 2 is defined by:

$$193 \quad R/W_{Step2} = F * R/W_{Step1} \quad (2)$$

194 where F (referred hereafter as the ‘degree of low-temperature basalt alteration’) is the fraction of basalt
195 altered relative to Step 1 and was varied from 0 to 20% (Figure 1b). The small proportion of basalt reacting
196 during Step 2 (F) compared to that reacting during the initial high-temperature reactions at depth (Step 1)
197 is meant to account for rapid flow rates and temperature decreases from the temperature maximum reached
198 during Step 1 as the fluids continue to upwell and mix. The proportion of gas reacting during Step 2 is
199 calculated similarly as in Step 1.

200 Step 2 was modeled considering either equilibrium chemistry (referred to hereafter as ‘equilibrium
201 mixing’) or non-equilibrium chemistry for which only aqueous speciation reactions proceed but redox
202 reactions and mineral precipitation are suppressed (referred hereafter as ‘mechanical mixing’). The latter

203 case aims to account for possible disequilibrium between rapidly ascending high-temperature fluids, the
204 rock, and the added seawater. During mechanical mixing, no low-temperature basalt alteration is considered
205 as it would otherwise lead to unrealistically high solute concentrations. In our equilibrium calculation,
206 methane is suppressed because the reduction of seawater-derived CO₂ during hydrothermal circulation
207 within the oceanic crust is known to be kinetically inhibited (McDermott et al., 2015). Quartz and dolomite
208 are also suppressed because kinetic limitations are expected to prevent their formation at low temperature,
209 especially during Step 2 (Rimstidt and Barnes, 1980; Von Damm et al., 1991; Arvidson, 1999). After
210 several iterations and for consistency with observational data, nontronite was also removed from our
211 mineral database, leaving saponite, montmorillonite and beidellite among the minerals of the smectite-
212 group that can form.

213 For all fluid samples, *in situ* pH values were calculated with EQ3 by speciating the fluid composition
214 at 25 °C and 1 bar with charge balance on chloride, then speciating the resulting fluid composition at the
215 temperature of sampling (Reed and Spycher, 1984). Published data of vent-fluid composition are taken
216 from prior studies by Karl et al. (1988), Sedwick et al. (1992, 1994), Hilton et al. (1998), Glazer and Rouxel
217 (2009) and Rouxel et al. (2018). Sedwick et al. (1992) reported ranges of concentrations: only the maximum
218 and minimum values from that work are considered in this study. Sedwick et al. (1994) and Hilton et al.
219 (1998) reported only concentrations for dissolved silica and dissolved inorganic carbon, so no *in situ* pH
220 was calculated from these data.

221 3. Results

222 3.1. Measured vent-fluid compositions

223 The location and chemical composition of the Kama‘ehuakanaloa vent fluids sampled during the 2018
224 SUBSEA expedition are shown in Table 1. The composition of the vent fluid sampled at Marker 34 is
225 compared to seawater values and to the end-member compositions of vent fluids from hydrothermal
226 systems in a variety of geologic environments on the seafloor in Table 2. Basalt-hosted hydrothermal
227 systems on mid-ocean ridges are represented by the 21°N East Pacific Rise (EPR) vent field, characterized

228 by 350°C fluids exiting black smoker chimneys (Von Damm et al., 1985). Hydrothermal systems in back-
229 arc basins associated with felsic volcanic rocks are represented by the Mariner vent field located along the
230 Eastern Lau Spreading Center. There, input of acidic volatiles (CO₂, SO₂, HCl and HF) in the circulating
231 hydrothermal fluids produces >350 °C vent fluids with a low pH value (2.7) and high metal concentrations
232 (Mottl et al., 2011). Ridge flank systems are represented by Baby Bare, an isolated seamount on the eastern
233 flank of the Juan de Fuca Ridge where low-temperature (<100 °C) hydrothermal reactions in the basement
234 produce 25 °C hydrothermal springs (Wheat and Mottl, 2000).

235 The temperature range of 15° to 41°C measured during the 2018 SUBSEA expedition is comparable
236 to that of Baby Bare springs (25 °C) and much lower than the temperatures that characterize vent fluids at
237 21°N EPR and Mariner. The pH (25 °C) values ranging from 5.4 to 6.2 at Kama‘ehuakanaloha are lower than
238 at Baby Bare but higher than the values of 3.4 and 2.7 in 21°N EPR and Mariner vent fluids, respectively.
239 One of the most striking features of the Kama‘ehuakanaloha vent fluids is the high values of alkalinity up to
240 14.3 meq/kg whereas alkalinity values in the 21°N EPR, Mariner, and Baby Bare vent fluids are either
241 negative or close to 0. In comparison to the other vent fluids, the Cl, sulfate, Na, K and Mg concentrations
242 at Kama‘ehuakanaloha are relatively close to seawater values. In the Spillway and Lohiau areas, the
243 Kama‘ehuakanaloha vent fluids are slightly depleted in Mg and sulfate but to a much lower extent that what
244 is observed in the 21°N EPR, Mariner, and Baby Bare vent fluids. With concentrations up to 16.3 mmol/kg,
245 Ca can be enriched at Kama‘ehuakanaloha relative to seawater, but the enrichment is less than at Mariner
246 and Baby Bare. The Si concentration up to 2.8 mmol/kg at Kama‘ehuakanaloha is 5 to 10 times higher than
247 seawater and Baby Bare values but it is lower than that of the >350 °C vent fluids. Similarly, Fe and Mn
248 are enriched compared to seawater and Baby Bare springs, with concentrations up to 0.98 and 0.07
249 mmol/kg, respectively. These values are 1 to 2 orders of magnitude lower than at 21°N EPR and Mariner.
250 CH₄ at Kama‘ehuakanaloha is enriched compared to seawater but to a lesser extent than in black smoker
251 systems, whereas H₂ and H₂S are not detected. Finally, the CO₂ concentration ranging from 14 to 126

252 mmol/kg at Kama‘ehuakanaloa is one order of magnitude higher than in seawater and comparable to values
253 of the Marnier vent field (Mottl et al., 2011).

254 New data for Kama‘ehuakanaloa vent-fluid compositions from the 2018 SUBSEA expedition are
255 compared to previously published data for vent fluids sampled at the summit of the volcano (Karl et al.,
256 1988; Sedwick et al., 1992, 1994; Hilton et al., 1998; Glazer and Rouxel, 2009; Rouxel et al., 2018) (Figure
257 2). This comparison indicates that overall, the composition and temperature of the vent fluids were
258 relatively constant through time from 1988 to 2018 except for the short-lived event in 1996. Small variations
259 exist for pH, Si, DIC and Fe concentrations but no trend with time is identified. The tectonic-volcanic event
260 of July-August 1996 created a pit crater (Pele's Pit) and several sites of vigorous hydrothermal venting,
261 with temperature up to 200 °C measured in September 1997 (Davis and Clague, 1998; Wheat et al., 2000);
262 however, subsequent exploratory dives over three cruises between 2006 and 2008 (Glazer and Rouxel,
263 2009; Rouxel et al., 2018) and the 2018 SUBSEA exploration reported temperatures (15-41 °C, Table 1)
264 and fluid compositions similar to pre-eruptive values (Karl et al., 1988; Sedwick et al., 1992, 1994).

265 As a hydrothermal fluid end-member mixes with seawater beneath the seafloor, the chemical
266 signatures inherited from the water-rock-gas reactions can be progressively lost. The degree of loss depends
267 on the involvement of chemical species in the water-rock-gas reactions and their concentrations in seawater.
268 Therefore, we prioritized the use of Si, pH, DIC, Ca and Fe to constrain the geochemical models because
269 these are the species that differ most from seawater values. Although CH₄ is also enriched relative to
270 seawater, unambiguous information is less likely to be obtained from modelling this species distribution
271 because its concentration can be the result of numerous processes including biogenic formation (e.g.,
272 Bradley and Summons, 2010), pyrolysis of organic matter (Welhan, 1988), kinetic limitations inhibiting
273 abiotic formation and oxidation (McDermott et al., 2015, 2020) and leaching of fluid inclusions and gas
274 vesicles (Klein et al., 2019; Grozeva et al., 2020).

275 *Table 1. Locations and chemical compositions of fluid samples collected during the 2018 SUBSEA*
 276 *expedition*

Sample (NA100-)	002	001	039	040	019	054	053	061	060	080	079	059
Marker ^a	34	34	38	38	31 ^a	2	2	57	57	57 ^a	57 ^a	Bottom seawater
Site ^c (lat; long; depth (m))	Spillway Area (18.906; -155.257; 1270±3)				Lohiau area (18.909; -155.257; 1179±2)			Pohaku (18.901; -155.258; 1184±2)				
Temperature max. (°C) ^a	41	41	39	37	31	22	21	15	18	21	21	-
pH (25 °C)	5.8	6.0	6.0	6.1	6.0	6.2	6.2	5.4	5.7	5.7	5.7	7.4
Alkalinity ^b (meq/kg)	14.3	14.3	13.5	9.2	8.4	8.8	8.9	6.5	11.6	13.6	12.9	2.3
Na (mmol/kg)	459	463	464	460	462	490	464	465	463	466	464	-
Cl ^b (mmol/kg)	-	545	545	542	544	541	543	540	538	537	538	539
Mg (mmol/kg)	51.5	51.5	52.0	52.2	50.0	52.5	52.8	54.0	55.0	54.7	54.5	-
Ca ^b (mmol/kg)	15.1	15.8	15.3	14.3	14.9	16.0	16.3	10.9	11.3	11.4	10.6	10.3
K (mmol/kg)	12.2	-	12.1	11.3	12.4	16.6	11.4	10.7	11.1	11.7	11.7	-
Sulfate (mmol/kg) ^c	27.0	26.7	26.9	27.3	25.8	27.0	27.0	27.9	27.3	26.6	26.8	28.2
Si (mmol/kg)	2.8	2.7	2.7	1.5	1.9	1.7	1.5	0.6	1.4	1.8	1.9	-
Fe (μmol/kg)	413	517	579	289	384	369	285	308	758	980	978	0
Mn (μmol/kg)	40	40	38	24	25	73	45	10	18	21	22	-
Al (μmol/kg)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
Sr (μmol/kg)	104	103	103	95	98	-	102	87	88	87	87	-
Ba (μmol/kg)	0.7	0.7	0.9	0.7	0.9	-	0.7	0.7	1.0	0.6	1.0	-
B (μmol/kg)	398	402	424	410	398	553	388	424	452	491	484	-
Li (μmol/kg)	53	53	52	42	44	76	40	32	38	45	45	-
Rb (μmol/kg)	5.0	4.9	4.7	3.3	4.6	5.8	3.5	2.0	2.8	3.4	3.4	-
Cs (μmol/kg)	0.24	0.24	0.26	0.23	0.26	0.48	0.24	0.24	0.24	0.24	0.25	-
Cu (μmol/kg)	0.9	1.1	1.4	5.3	1.6	6.4	0.5	1.6	1.3	0.9	1.8	-
Zn (μmol/kg)	27.6	27.9	7.7	6.0	32.5	134.4	12.4	22.9	4.3	4.0	14.2	-
H ₂ (μmol/kg) ^d	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	-
CO ₂ (mmol/kg) ^d	31.2	31.2	30.0	18.3	17.4	14.2	14.0	43.8	94.1	124.3	125.8	-
CH ₄ (μmol/kg) ^e	1.5	1.3	1.2	0.8	1.4	0.6	0.6	1.6	2.8	4.3	3.8	-
H ₂ S (μmol/kg) ^f	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	-

277 ^aMarker and site from Rouxel et al. (2018)

278 ^aTemperature maximum recorded during the IGT sampling

279 Analysis with ICP-MS, unless otherwise noted: ^bGran titration, ^cion chromatography, ^dGC-TCD, ^eGC-FID, ^fspectrophotometry Cline (1969)

280 ^gDuplicate sample leaked

281 n.d. = not detected

282 Estimated uncertainties (2σ) are as follow: pH (25°C) values ±0.1 unit; Na, Mg, Cl, Ca, K, sulfate concentrations ±3%; SiO₂, Fe, Mn, Sr, Ba, Li,
 283 Rb, Cs, Cu, Zn concentrations ±5%; CH₄ and CO₂ concentrations ±10% and ±5%, respectively.

284

285 *Table 2. Vent-fluid compositions from Kama‘ehuakanaloa compared with submarine vent fields from*
 286 *various other geologic settings*

Vent field	Seawater	Kama‘ehuakanaloa ^a	21°N, EPR ^b	Mariner	Baby Bare (Spring water)
Geologic setting	-	Intraplate volcano	Mid ocean ridge	Back arc	Ridge flank
Max. T (°C)	2	41	350	363	25
pH (25 °C)	7.8	5.9	3.4	2.7	8.3
Alk. (meq/kg)	2.3	14.3	-0.4	-2.25	0.43
Cl (mmol/kg)	546	546	489	605	554
SO ₄ (mmol/kg)	28	26.9	0.5	-	17.8
Na (mmol/kg)	468	460.8	432	439	473
K (mmol/kg)	10.2	12.4	23	36.9	6.9
Ca (mmol/kg)	10.3	15.5	16	43.8	55.2
Mg (mmol/kg)	53	51.5	0	1.9	0.98
Si (mmol/kg)	0.1	2.8	18	15.1	0.4
Fe (μmol/kg)	<0.001	465	1,664	12991	<0.1
Mn (μmol/kg)	<0.001	40	960	5723	7.8
CH ₄ (μmol/kg)	-	1.4	70	-	-
H ₂ (mmol/kg)	-	b.d.1	1.7	-	-
CO ₂ (mmol/kg)	-	31.2	5.7	39.8	0.4

H ₂ S (mmol/kg)	-	b.d.l	7.3	9.3	-
287	^a Average values of the 2018 SUBSEA fluids sampled at Marker 34.				
288	^b Measured composition of vent fluids are corrected for entrainment of seawater during sampling based on the quantitative removal of Mg from the fluid during water-rock reactions.				
289	Data are from Bruland et al. (2006) for seawater, Humphris and Klein (2017) for 21°N EPR and Mariner vent fields (original data from Von Damm et al. (1985) and Mottl et al. (2011), respectively), Wheat and Mottl (2000) for Baby Bare.				
291	Abbreviation: Max. T = maximum temperature; Alk. = Alkalinity; - = not determined; b.d.l = below detection limit.				
292					
293					

294 3.2. Modeled fluid compositions

295 3.2.1. pH, Ca and DIC

296 Our calculations predict a wide diversity of fluid compositions over the range of Step 1 and Step 2 reaction
 297 conditions as shown in Figure 3. During Step 1, the increase of temperature and rock/water ratio results in
 298 a decrease of pH (Figure 3a). After a sharp increase, the Ca concentration decreases as well because of the
 299 precipitation of smectite, epidote and tremolite which fixes Ca (Figure 3b, Figure S 1 to Figure S 3 in
 300 supplementary information). The DIC concentration increases in parallel due to the inputs of CO₂ (Figure
 301 3c), linearly correlated to the rock/water ratio (see section 2.2). As a result, the hydrothermal fluid is at
 302 equilibrium with calcite all along Step 1, except for temperatures above 350 °C (Figure 3d).

303 At the beginning of the mixing between the hydrothermal fluid and seawater during Step 2, the pH
 304 value decreases drastically (Figure 3a). H⁺ is produced by the precipitation of minerals in response to the
 305 supply of cations by seawater. As the mixing progresses and the temperature of the fluid mixture decreases,
 306 the pH values increase. Overall, the pH values of the 20 °C fluids at the end of Step 2 decrease with the
 307 increase of Step 1 temperature maximum. In addition, there is an increase of pH with the degree of low-
 308 temperature basalt alteration during Step 2 as H⁺ is consumed by basalt dissolution. This is especially
 309 pronounced in 20 °C fluids produced by reaction paths with temperature maxima >300 °C. Consequently,
 310 the diversity of pH values in the 20 °C fluids decreases with the increase of low-temperature basalt
 311 alteration. For F values >7%, all reaction paths converge toward the same pH values at the end of Step 2,
 312 regardless of the temperature maximum reached during Step 1.

313 As mixing with seawater progresses during Step 2, the Ca concentrations in fluids produced by
 314 reaction paths with Step 1 temperature maxima >250 °C increase whereas the DIC concentrations decrease

315 (Figure 3b and c). This trend is reversed for reaction paths with lower temperature maxima. Overall, the Ca
316 and DIC concentrations in the 20 °C fluids decrease and increase, respectively, as the temperature maximum
317 in Step 1 increases. In addition, these concentrations increase with the degree of low-temperature basalt
318 alteration because the dissolution of basalt supplies both Ca and CO₂. Although less apparent than in the
319 case of pH, there is also a loss of diversity for the Ca and DIC concentrations of the 20 °C fluids as low-
320 temperature basalt alteration increases. For F values >7%, all reaction paths tend to produce similar Ca and
321 DIC concentrations, independently of Step 1 reaction conditions.

322 The combined behavior of pH, Ca and DIC concentrations leads the fluid mixture to depart from
323 equilibrium with calcite at the beginning of Step 2 before returning to saturation with calcite at high degrees
324 of mixing at the end of Step 2 (Figure 3d). Equilibrium with calcite is especially common in 20 °C fluids
325 inherited either from reaction paths with low Step 1 temperature maxima or high degrees of low-
326 temperature basalt alteration. By buffering the pH value of 20 °C fluids produced by reaction paths with F
327 values >7%, equilibrium with calcite causes a loss of chemical diversity. Therefore, the dependence of the
328 20 °C fluid compositions on Step 1 and Step 2 reaction conditions relies on the capacity of the system to
329 counterbalance the pH increase that leads to calcite saturation at the end Step 2. Two competing effects
330 influence the evolution of pH: (1) high CO₂ supply and high-temperature mineral precipitation during Step
331 1 tend to lower the pH values of the resulting 20 °C fluids, whereas (2) H⁺ consumption by low-temperature
332 basalt alteration tends to increase the pH values.

333 3.2.2. Sulfate, Mg, K, Si, Na and Cl

334 During Step 1, the increase of temperature and rock/water ratio result in the decrease of sulfate and Mg
335 concentrations as sulfur is fixed into pyrite and Mg into saponite (Figure 4a and b, Figure S 4 and Figure S
336 1 in supplementary information). After a sharp decrease, the K concentrations increase, controlled by the
337 precipitation of muscovite at high temperature (Figure 4c, Figure S 5 in supplementary information). The
338 Si concentrations increase reaching values close to equilibrium with quartz (Figure 4d, Figure S 6 in
339 supplementary information).

340 During Step 2, mixing with seawater supplies sulfate and Mg to the fluid mixture (Figure 4a and
341 b). The sulfate and Mg concentrations converge toward seawater values as mixing progresses such that the
342 chemical signature inherited from the water-rock reactions during Step 1 and Step 2 is lost. The K
343 concentrations progress as well toward the seawater value during Step 2, except for degrees of low-
344 temperature basalt alteration > 7% (Figure 4c). In these cases, the fluid mixtures reach equilibrium with K-
345 feldspar at the end of Step 2, the precipitation of which fixes K (Figure S 7 in supplementary information).
346 For Si, the 20 °C fluids retain the chemical signatures of the Step 1 and Step 2 reaction conditions (Figure
347 4d). The Si concentrations of the fluid mixtures at the end of Step 2 increase with Step 1 temperature
348 maxima. For degrees of low-temperature basalt alteration > 7%, the diversity of Si concentrations in the 20
349 °C fluids decreases, as observed for pH values, Ca and DIC concentrations.

350 The Cl and Na concentrations are marginally impacted by the reaction paths (Figure S 8 in
351 supplementary information). Cl is not directly involved in the water-rock reactions and the consumption of
352 H₂O in the formation of hydrated minerals is low enough that the Cl concentration is not impacted
353 significantly. Because of the high Na concentration in seawater, the relative impact of water-rock reactions
354 such as albitization is low and erased by the mixing with seawater during Step 2.

355 3.2.3. Fe and H₂S

356 As the temperature and rock/water ratio increase during Step 1, the water-rock reactions produce H₂ from
357 the oxidation of ferrous iron in the basalt. Therefore, sulfate is reduced to H₂S, which increases in
358 concentration such that the fluid reaches equilibrium with pyrite (Figure 5a, Figure S 4 in supplementary
359 information). The concentration of Fe increases as well (Figure 5b), controlled by the precipitation of pyrite
360 and Fe-chlorite (Figure S 4 and Figure S 9 in supplementary information).

361 The redox conditions in the 20 °C fluids at the end of Step 2 are determined by a balance among
362 the reduced species inherited from Step 1, the ferrous iron supplied by the low-temperature basalt alteration
363 during Step 2, and the inputs of oxidizing species during mixing with seawater. The 20 °C fluids produced

364 by reaction paths with Step 1 temperature maxima $> 300\text{ }^{\circ}\text{C}$ and degrees of low-temperature basalt alteration
365 $< 1\%$ have high concentrations of H_2S ($> 10^{-4}\text{ M}$) (see square-root shaped curve in Figure 5a). Under these
366 reaction conditions, the oxidized species supplied by seawater during mixing are the limiting reactants in
367 the redox reactions taking place during Step 2 because of the large quantity of reduced species inherited
368 from Step 1 including H_2S . In parallel, the Fe concentrations in the $20\text{ }^{\circ}\text{C}$ fluids are low ($\sim 10^{-12}\text{ M}$, Figure
369 5b) because the high H_2S concentrations maintain equilibrium with pyrite, the precipitation of which fixes
370 Fe.

371 Several reaction paths produce $20\text{ }^{\circ}\text{C}$ fluids with extremely low H_2S concentrations ($\ll 10^{-12}\text{ M}$)
372 (Figure 5a). If the Step 1 temperature maximum is $\leq 300\text{ }^{\circ}\text{C}$, a lower quantity of H_2S is inherited from Step
373 1 such that H_2S becomes one of the limiting reactants in the overall redox reactions during Step 2 (see
374 curves dropping vertically during Step 2 in Figure 5a). The reaction paths involving a degree of low-
375 temperature basalt alteration of 1% similarly result in extremely low H_2S concentrations in the $20\text{ }^{\circ}\text{C}$ fluids.
376 This is rather counterintuitive as one could expect more reduced conditions to form due to the supply of
377 ferrous iron from the dissolution of basalt. However, the supply of Fe from low-temperature basalt alteration
378 during mixing results in precipitation of additional pyrite, which fixes a larger amount of H_2S . As a result,
379 the oxidized species supplied by seawater cease to be the limiting reactants in the redox reactions of Step
380 2. H_2S is effectively completely oxidized at the end of mixing and O_2 accumulates in the fluid mixture
381 (Figure S 10 in supplementary information). The Fe concentrations remain low ($\ll 10^{-12}\text{ M}$, see curves
382 dropping vertically during Step 2 in Figure 5b) because the $20\text{ }^{\circ}\text{C}$ fluids reach equilibrium with goethite
383 while the O_2 concentration is high (Figure S 11 in supplementary information).

384 Increasing the degree of low-temperature basalt alteration to 4% re-establishes relatively reduced
385 conditions in the $20\text{ }^{\circ}\text{C}$ fluids yielding H_2S and Fe concentrations of ca. 10^{-9} M and $10^{-5}\text{-}10^{-3}\text{ M}$, respectively
386 (Figure 5a and b). The extra supply of Fe from low-temperature basalt alteration consumes the seawater-
387 derived oxidized species during mixing, such that O_2 no longer accumulates in the fluid mixture (Figure S
388 10 in supplementary information) and, instead, Fe does. As a result, the $20\text{ }^{\circ}\text{C}$ fluids reach equilibrium with

389 both pyrite and goethite at the end of mixing (Figure S 4 and Figure S 11 in supplementary information).
390 For degrees of low-temperature basalt alteration >4%, the Fe concentration in the 20 °C fluids has no degree
391 of freedom because of O₂ depletion, equilibrium with calcite which buffers the pH, and equilibrium with
392 goethite which fixes the Fe. As a result, all reaction paths converge toward a single Fe concentration in the
393 20 °C vent fluids (Figure 5b), as observed for pH, Ca, DIC and Si.

394 4. Discussion

395 4.1. Reaction conditions at Kama'ehuakanaloa

396 Comparison of the measured temperature and composition of Kama'ehuakanaloa vent fluids through time
397 (Figure 2) suggests that the overall water-rock interactions that characterize the hydrothermal circulation
398 have remained roughly constant for 30 years and were not substantially modified by the 1996 eruptive event
399 over a period longer than a decade. The 20-50 °C venting regime observed during a series of expeditions
400 since 1987 might, thus, correspond to a chronic state that is only temporarily modified by transient volcano-
401 tectonic events. However, our comparison gives only a broad picture of fluid evolution through time
402 because (1) the morphology of the seafloor hosting venting was completely reshaped by the formation of
403 Pele's Pit during the 1996 eruptive event, (2) not all expeditions sampled the same vent sites, systematically
404 and (3) the datasets for individual samples are not always complete. This large-scale comparison, therefore,
405 does not preclude evolution of vent fluid chemistry and temperature at smaller spatial and temporal scales.
406 Nor do these data allow us to address what happens during the course of a volcanic eruption which, although
407 transient, might release important chemical fluxes that could dominate the time-integrated hydrothermal
408 output from a submarine volcano.

409 Sedwick et al. (1992) used Cl⁻ depletion, alkali metal enrichment, Sr isotopes and correlations between
410 Si and fluid temperature in 5-31°C samples exiting the seafloor at Kama'ehuakanaloa to infer the occurrence
411 of high-temperature water-rock interactions at depth, as had been done previously for mid-ocean ridge
412 'black smokers' based on the early discoveries at the Galapagos Rift (Edmond et al., 1979). The general
413 model of Si behavior during hydrothermal circulation is that hydrothermal fluids equilibrate with quartz at

414 high temperature ($>300\text{ }^{\circ}\text{C}$) and then rise so rapidly through the ocean crust that they neither gain nor lose
415 Si, despite the high degree of quartz supersaturation that results from the corresponding pressure drop (Von
416 Damm et al., 1991). However, as mentioned by Sedwick et al. (1992), the low-temperature basalt alteration
417 required to explain the Fe enrichment in Kama‘ehuakanaloa vent fluids could also produce chemical
418 signatures like those expected from the presence of a $>300\text{ }^{\circ}\text{C}$ fluid endmember.

419 In Figure 6, the measured compositions of our Kama‘ehuakanaloa vent-fluid samples are compared to
420 modeled compositions at the end of Step 2, where the fluid mixtures reach temperatures between $50\text{ }^{\circ}\text{C}$ and
421 $20\text{ }^{\circ}\text{C}$, i.e., the range of temperature measured during the 2018 SUSBEA expedition. Only the results of
422 reaction paths involving mechanical mixing during Step 2 or a narrow degree of low-temperature basalt
423 alteration, F , between 2% and 8% are shown here. Further figures showing the full range of reaction
424 conditions considered in our work, across a broader range of F values, are provided in supplementary
425 information: Figure S 12 to Figure S 20. Our model shows that while the measured Si concentrations are
426 indeed consistent with mechanical mixing between seawater and a $\geq 350\text{ }^{\circ}\text{C}$ hydrothermal fluid endmember,
427 the pH and alkalinity values and the concentrations of Ca, K and Fe are not. Rather, the use of multiple
428 tracers allows us to narrow down the range of possible reaction conditions for the Kama‘ehuakanaloa vent
429 fluids and makes it possible to distinguish between the influence of (Step 1) the maximum temperature and
430 the rock/water ratio reached at depth and (Step 2) the degree of low-temperature basalt alteration during
431 fluid upwelling and mixing.

432 Regardless of Step 1 temperature maxima, mechanical mixing is not able to explain the observed
433 distribution of vent-fluid compositions (e.g., Figure 6, left column). Instead, the modeled Si concentrations
434 and pH values (Figure 6a-d) only migrate towards our measured values as one increases the degree of low-
435 temperature basalt alteration, F , during Step 2. For these two parameters, our 2018 data are matched most
436 closely by models in which reaction paths involve either: (Figure 6b) Step 1 temperature maxima of 300-
437 $350\text{ }^{\circ}\text{C}$ and a degree of low-temperature basalt alteration of $F=2\%$ during Step 2 or (Figure 6c) Step 1
438 temperature maxima of $\geq 350\text{ }^{\circ}\text{C}$ and a degree of low-temperature basalt alteration of 4% during Step 2.

439 Increasing the degree of low-temperature basalt alteration any further only leads to a decrease of the
440 chemical diversity and departure of the modeled fluid compositions from the measured fluid concentrations
441 (Figure 6d and Figure S 12 in supplementary information).

442 However, if alkalinity is considered (Figure 6e-h), an even narrower range of possible reaction
443 conditions is revealed. The high alkalinity values of at Kama'ehuakanalao compared to other submarine
444 vent fields (Table 2) are best explained by reaction paths involving Step 1 temperature maxima of ≥ 350 °C
445 and a low-temperature basalt alteration of 4% during Step 2 whereas a F value of 2% is less consistent
446 (Figure 6f and g, Figure S 13 in supplementary information). For the case of vent-fluid Ca and K
447 compositions, our approach is less diagnostic: a broad range of reaction paths can account for the measured
448 Ca and K concentrations in the 20-50 °C vent fluids because the modeled concentrations are less sensitive
449 to the reaction conditions than the pH values, Si concentrations or alkalinity (Figure 6i to 6p, Figure S 15
450 and Figure S 16 in supplementary information). For instance, reaction paths involving Step 1 temperature
451 maxima >300 °C and mechanical mixing during Step 2 or equilibrium mixing with a degree of low-
452 temperature basalt alteration of 2% show some consistency with the measured Ca and K concentrations
453 (Figure 6i, j, m and n) even though those reaction conditions are precluded by the Si and alkalinity data. In
454 contrast, reaction paths with Step 1 temperature maxima of ≥ 350 °C and a degree of low-temperature basalt
455 alteration of 4% are required to offer consistency with all of our measured pH, Si, alkalinity and Ca
456 concentrations (Figure 6k and o). For higher degrees of low-temperature basalt alteration, F, the diversity
457 of Ca and K concentrations in the 20-50 °C vent fluids decrease, as seen for Si and alkalinity, and the
458 modeled concentrations deviate from our measured vent-fluid values (Figure 6l and p).

459 Unlike the case for Ca and K, consideration of Fe concentration data *does* help narrow the range of
460 possible reaction conditions at Kama'ehuakanalao (Figure 6q to 6t, Figure S 17 in supplementary
461 information). Our measured Fe concentrations are only consistent with a highly constrained set of tested
462 reaction conditions: a Step 1 temperature maximum of ≥ 350 °C and a degree of low-temperature basalt
463 alteration of F=4% during Step 2 (Figure 6s). Reaction paths involving these same reaction conditions also

464 predict low H₂ and H₂S concentrations (<10⁻⁹M), which are consistent with those species being below our
465 detection limits during the 2018 field program (Table 1, Figure S 10 in supplementary information). Under
466 these same reaction conditions, the modeled sulfate, Mg and Na concentrations in 20-50 °C vent fluids at
467 the end of Step 2 are also consistent with measured vent-fluid values (Figure S 18, Figure S 19 and Figure
468 S 20 in supplementary information). Note that the measurements of Mg and sulfate concentrations in
469 Kama‘ehuakanaloa vent fluids slightly lower than seawater values suggest that any Mg and sulfate
470 depletion produced by the formation of Mg-smectite and anhydrite during fluid upwelling is not completely
471 overprinted by mixing with seawater in the shallow subsurface (Figure S 1 and Figure S 21).

472 In addition to the chemical compositions of the vent-fluid samples collected from our expedition, our
473 model is also consistent with mineral observations in high and low-temperature basalt alteration at the
474 seafloor and with mineral observations from Kama‘ehuakanaloa that have been reported in previous studies.
475 As seawater percolates downward beneath the seafloor and is heated above ~150 °C, Mg tends to be fixed
476 into smectite and chlorite (Alt, 1995). At higher temperatures, the precipitation of epidote, amphibole,
477 prehnite and secondary plagioclase controls Ca and Na concentrations (Alt et al., 2010). Consistent with
478 this, our modeled Step 1 hydrothermal fluids reach equilibrium with Ca-Na-saponite, daphnite (Fe-chlorite),
479 epidote, tremolite, prehnite and albite (Figure S 1, Figure S 9, Figure S 2, Figure S 3, Figure S 22, Figure
480 S 23 in supplementary information).

481 In general, the oxidizing alteration of oceanic basalts at low-temperature in the upper portion of the
482 volcanic section is characterized by the formation of Fe-oxyhydroxides – mostly goethite, replacing olivine
483 – and celadonite and smectite replacing plagioclase and fixing alkalis (Alt, 1995). In extreme cases of
484 oxidizing alteration, K-feldspar replaces plagioclase in the shallowest section of the seafloor (Alt, 1995;
485 Santiago Ramos et al., 2020). Drilling within altered basalts of the Nintoku Seamount, which lies in the
486 Emperor Seamount Chain, revealed a secondary mineralogy made of smectite, Fe-oxyhydroxide, iddingsite
487 and Ca-carbonates, produced by the circulation of large quantities of cold oxidizing seawater (Révillon et
488 al., 2007). Similarly, at Kama‘ehuakanaloa, altered basalts are characterized by extensive hydrothermal

489 deposits of Fe-oxyhydroxides, including goethite, and smectite ranging in composition from Fe-
490 montmorillonite to nontronite (Malahoff et al., 1982; De Carlo et al., 1983; Emerson and Moyer, 2002;
491 Toner et al., 2012; Rouxel et al., 2018). Recently, Ca-carbonates were also reported as ubiquitous secondary
492 minerals at Kama‘ehuakanaloha, filling vesicles of altered basalt at vent sites (Garcia, 2019). Consistent with
493 these observations, reaction paths involving Step 1 temperature maxima of ≥ 350 °C and a degree of low-
494 temperature basalt alteration of $F=4\%$ predict 20-50 °C vent fluids at equilibrium with Na-Ca-Mg
495 saponite/montmorillonite, K-feldspar, goethite, and calcite (Figure S 1, Figure S 7, Figure S 11 in
496 supplementary information and Figure 3d). In contrast to field observations, K-fixation in our model is
497 controlled by the precipitation of muscovite (K-Al-endmember of micas) because celadonite (ferric-mica)
498 is absent from our database. Although nontronite is reported to occur in hydrothermal deposits at
499 Kama‘ehuakanaloha, better consistency between modelled and observed vent-fluid composition can only be
500 achieved when suppressing nontronite precipitation during Step 2. This suggests that either the upwelling
501 fluid in the shallow subsurface does not precipitate nontronite at equilibrium or that the precipitation of
502 nontronite only occurs beyond the end of Step 2, as 20-50°C vent fluids exit the seafloor. Alternatively, the
503 thermodynamic properties of nontronite available in our database may not accurately represent those of
504 nontronite precipitated at Kama‘ehuakanaloha.

505 To summarize, our modeling indicates that a temperature maximum of ≥ 350 °C and a rock/water ratio
506 of ≥ 1 during Step 1 together with a degree of low-temperature basalt alteration, F , of $\sim 4\%$ during fluid
507 upwelling and mixing (Step 2) represent the reaction conditions most consistent with production of the
508 vent-fluid compositions observed at Kama‘ehuakanaloha during our expedition. These reaction conditions
509 represent a unifying solution that explains most of the chemical features of the Kama‘ehuakanaloha vent
510 fluids reported here as well as mineral observations that have been reported elsewhere. The general model
511 of simpler mechanical mixing between high temperature fluids and seawater that has previously been used
512 to describe Si behavior during high-temperature hydrothermal circulation at mid-ocean ridges is not
513 applicable at Kama‘ehuakanaloha because low-temperature basalt alteration during fluid upwelling and

514 mixing mobilizes Si, among other species, but can also remove it from solution through the precipitation
515 of alkalic feldspar and smectite.

516 Other mechanisms beyond our preferred model output might also exist, of course, beyond the range of
517 parameter-space that we have considered. Notably, only a limited set of temperature-rock/water ratio paths
518 during Step 1 were considered. Cool hydrothermal circulation involving very low rock/water ratios ($<5 \cdot 10^4$
519 ⁴) at temperature <10 °C (Coogan and Gillis, 2018) was not investigated, but such systems fall below the
520 range of temperatures reported for most vent-fluids exiting the summit of Kama‘ehuakanaloha (Figure 2).
521 Similarly, the effect of conductive heat loss was not investigated in our models. While our mixing model is
522 consistent with both the measured temperature and the measured concentrations of chemical species that
523 behave close to mechanical mixing during Step 2 (Mg, sulfate), this would not be the case if conductive
524 heat loss played a significant role in the temperature decrease of the fluid mixture. The relationship between
525 temperature and the degree of mixing during Step 2 is exponential such that the temperature gradient that
526 drives conductive heat loss decreases exponentially with the degree of mixing. Therefore, it seems
527 reasonable to assign most of the temperature decrease during Step 2 to mixing with seawater.

528 Like all models, the effectiveness of our model in relating it to the hydrothermal circulation at
529 Kama‘ehuakanaloha is only as good as our assumptions. However, the wide range of reaction conditions
530 considered, and the consistency of the solution presented above in accounting for the array of tracers
531 investigated reassures us of its applicability to Kama‘ehuakanaloha in its current state.

532 4.3. Kama‘ehuakanaloha as a model for low-temperature vent fluids at intraplate volcanoes?

533 In addition to the maximum temperatures and the rock/water ratios reached at depth at Kama‘ehuakanaloha
534 (Step 1), the low-temperature basalt alteration during fluid upwelling and mixing (Step 2) exerts strong
535 controls on the modeled composition of the 20-50 °C vent fluids. On the one hand, the increase of basalt
536 alteration during Step 2 decreases the diversity of vent-fluid compositions as a function of Step 1 reaction

537 conditions; on the other hand, it leads to a dramatic change in the dominant reduced species in the 20-50 °C
538 vent fluids: an enrichment in Fe and a concurrent depletion in H₂S and H₂.

539 The occurrence and extent of low-temperature basalt alteration during fluid upwelling may depend on
540 the geometric arrangement of the steep-sloped Kama‘ehuakanaloha seamount and the associated
541 hydrogeologic plumbing of its hydrothermal convection cell. In parallel work pursued by the SUBSEA
542 team, oxygen and hydrogen isotopic compositions of Kama‘ehuakanaloha vent fluids were used to argue
543 that the seawater recharging the hydrothermal system comes from Pacific Deep Waters at >3000 m, much
544 deeper than the summit crater vents at ~1150-1300m. That study suggests that such a convection cell is
545 made possible specifically because of the steepness of Kama‘ehuakanaloha’s flanks which allow deep ocean
546 waters to be drawn in through porous ocean crust across much shorter lateral distances from the site of
547 discharge than would be possible across the more gently-sloping flanks of mid-ocean ridge hydrothermal
548 systems. Simultaneously, this geometric arrangement could accommodate a much longer circulation path
549 from the reaction zone, where maximum temperatures are reached at depth, to the summit where topography
550 forces hydrothermal fluids to vent (Titarenko and McCaig, 2016). The magma chamber at
551 Kama‘ehuakanaloha could be as deep as 7 km below the summit of the volcano (Duennenbier et al., 1997),
552 significantly deeper than at mid ocean ridges. In mid-ocean ridge systems, the hydrogeological plumbing
553 of the hydrothermal convection cell is accommodated by ridge-parallel bounding faults which allow for
554 rapid fluid flow. This contrasts with the Kama‘ehuakanaloha seamount where the stacking of basalt flows
555 can lead to much greater tortuosity in the up-flow path, leading to a much greater surface area of basaltic
556 material being exposed to fluid interactions and, as a consequence, greater basalt reactivity. This
557 combination of greater depth and tortuosity could also lead to significantly longer fluid residence times
558 and/or flow-paths in the subsurface at Kama‘ehuakanaloha when compared to mid-ocean ridge systems.
559 These, in turn, might be expected to give rise to the more extensive low-temperature basalt alteration that
560 we argue for, here, as Step 2 of our conceptual model. If correct, we can hypothesize that active intraplate

561 seamounts should predominantly produce low-temperature Fe-rich vent fluids, as observed at
562 Kama‘ehuakanaloa.

563 Intraplate hydrothermal activity across the vast interior of Earth’s Ocean basins has been
564 disproportionately overlooked, to date, when compared to the attention paid to venting at mid-ocean ridges.
565 Only four sites of venting on intraplate seamounts have been reported to the InterRidge vents data base
566 across the entire Pacific (Beaulieu et al., 2013). Interestingly, two of them share characteristics with
567 Kama‘ehuakanaloa in terms of their reported vent fluid and hydrothermal plume characteristics. In the late
568 1980s, low-temperature hydrothermal venting was reported at the summit of the Teahitia seamount, the
569 most westerly active seamount of the Society Islands hotspot in the Central Pacific Ocean (Cheminee et al.,
570 1989; Binard et al., 1992). Vent fluids were observed exiting from small Fe oxyhydroxide chimneys with
571 fluid temperatures of ~30 °C, pH values ranging from 5.3 to 5.6, high concentrations of Si (0.8–0.9
572 mmol/kg), Fe (170–190 µmol/kg) and Mn (6–13 µmol/kg) but no detectable dissolved H₂S (Michard et al.,
573 1993). More recently, German et al. (2020) measured high concentrations of total dissolvable Fe (≤186
574 nmol/L) and Mn (≤33 nmol/L) in the hydrothermal plume overlying the Teahitia seamount, comparable to
575 hydrothermal plume values measured at Kama‘ehuakanaloa (Sakai et al., 1987; Bennett et al., 2011).

576 At the Vailulu’u seamount, an active submarine volcano located 45 km east of the easternmost island
577 in the Samoan archipelago, Staudigel et al. (2006) reported low-temperature vents (<81 °C) exiting from
578 centimeter-to-meter-sized Fe-oxide chimneys together with evidence of high concentrations of dissolved
579 CO₂. As at Kama‘ehuakanaloa, the Teahitia and Vailulu’u seamounts stand >1500m above the surrounding
580 seafloor. The similarity between the Kama‘ehuakanaloa, Teahitia and Vailulu’u seamounts suggests that
581 chronic hydrothermal activity associated with submarine intraplate hotspot volcanoes may predominantly
582 lead to low-temperature vent fluids enriched in Fe, Mn, Si, CO₂ compared to seawater and depleted in H₂
583 and H₂S compared to mid-ocean ridge ‘black smokers’.

584 It has long been known that hydrothermal activity can inject detectable amounts of He enriched in ³He
585 into the oceans from submarine venting, from both mid-ocean ridges and intraplate volcanoes (Lupton et

586 al., 1977; Lupton, 1998). Recent work from the US GEOTRACES program has shown that important fluxes
587 of Fe can also be injected along with that venting which can be upwelled to the surface ocean (Resing et
588 al., 2015). However, while the principal source for Fe at mid-ocean ridges is considered to be from low-
589 temperature venting with Fe concentrations in the 10-100 μM range (German et al., 2015), the Fe
590 concentrations of vent fluids at intraplate systems like Kama‘ehuakanaloa are 1-2 orders of magnitude
591 higher and are injected into the ocean at much shallower depths beneath the photic zone (Jenkins et al.,
592 2020). Therefore, Fe fluxes associated with intraplate volcanoes may be disproportionately important in
593 terms of global biogeochemical cycles, beyond the deep, dark seafloor.

594 5. Conclusions

595 New data on submarine vent-fluid compositions acquired at the Kama‘ehuakanaloa seamount during the
596 SUBSEA exploration aboard the *E/V Nautilus* in 2018, coupled with a 30-year record of Kama‘ehuakanaloa
597 fluid composition data, were used to develop geochemical models of water-rock-gas reactions that produce
598 low-temperature vent fluids at intraplate submarine volcanoes. Our model indicates that the compositions
599 of 20-50 $^{\circ}\text{C}$ vent fluids at Kama‘ehuakanaloa, which are enriched in Fe, Si and CO_2 and depleted in H_2S ,
600 are not consistent with a simple model of mechanical mixing between seawater and high-temperature vent-
601 fluid. Instead, they appear to reflect an additional stage of subsurface equilibrium mixing between a ≥ 350
602 $^{\circ}\text{C}$ hydrothermal fluid end-member and seawater (Step 1), followed by low-temperature chemical alteration
603 of basalt (Step 2) as the resultant hot fluid mixture rises toward the overlying seafloor. Despite the low
604 proportion of additional basalt involved at Step 2 of this process (i.e., only $\sim 4\%$ of the amount of basalt
605 involved in the initial high-temperature reactions at depth), this late reaction step has dramatic impacts on
606 the compositions of the 20-50 $^{\circ}\text{C}$ vent fluids that are emitted into the ocean, decreasing their Si and H^+
607 concentrations compared to mechanical mixing and determining which of Fe^{2+} or $\text{H}_2\text{S}+\text{H}_2$ is the dominant
608 reduced species released from the seafloor. We hypothesize that it is the low-temperature basalt alteration
609 during Step 2 fluid upwelling that gives the Kama‘ehuakanaloa vent fluids their distinctive composition
610 and that this process, in turn, may arise directly from Kama‘ehuakanaloa’s seamount topography.

611 Specifically, the very steepness of the seamount's flanks could accommodate recharge at great depths where
612 the high-temperature reaction zone could be located, resulting in a much longer circulation pathway from
613 there to the (potentially thousands of meters shallower) summit where the vent-fluids are emitted. Thus,
614 while the recharge path at Kama'ehuakanaloa may be shorter than for submarine vents at Mid-Ocean
615 Ridges, the up-flow path prior to exit at the seafloor may be significantly longer. Such a circulation
616 geometry could provide an opportunity for extensive low-temperature chemical alteration of basalt via a
617 mechanism that should not be expected at mid-ocean ridges where recharge and discharge are predicted to
618 occur along axis from one another. By contrast, the work we present here could be representative of
619 processes at several other active intraplate seamounts which, as recently shown for Kama'ehuakanaloa,
620 could contribute substantially to the global Fe-ocean cycle. Such systems could produce low-temperature
621 venting with Fe concentrations 1-2 orders of magnitude higher than at mid-ocean ridges which they would
622 discharge at much shallower depths, injecting this essential micro-nutrient into the oceans closer to the
623 sunlit upper ocean where it can regulate CO₂ draw down by stimulating primary productivity.

624 6. Research data

625 The output files of the EQ3/6 reaction path calculation can be found in a Mendeley data repository at the
626 following address: <https://data.mendeley.com/datasets/n6rbd534h3/1>

627 7. Appendix A. Supplementary Material

628 A supplementary file associated with this paper contains one additional table and 23 figures:

- 629 - the chemical composition of the basalt used in the modeling
- 630 - the saturation indexes for saponite, epidote, tremolite, pyrite, muscovite, quartz, K-feldspar,
631 daphnite, goethite, anhydrite, prehnite, albite as functions of temperature during modeled reaction
632 pathways
- 633 - Na, Cl, O₂ and H₂ concentrations as functions of temperature during modeled reaction pathways

634 - the Si, alkalinity, DIC, Ca, K, Fe, sulfate, Mg and Na concentrations as functions of pH values for
635 modeled and measured 20-50 °C vent fluids

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- 841 Kama'ehuakanaloa

Table 1. Locations and chemical compositions of fluid samples collected during the 2018 SUBSEA expedition

Sample (NA100-)	002	001	039	040	019	054	053	061	060	080	079	059
Marker ^a	34	34	38	38	31 ^a	2	2	57	57	57 ^a	57 ^a	Bottom seawater
Site ^a (lat; long; depth (m))	Spillway Area (18.906; -155.257; 1270±3)				Lohiau area (18.909; -155.257; 1179±2)			Pohaku (18.901; -155.258; 1184±2)				
Temperature max. (°C) ^a	41	41	39	37	31	22	21	15	18	21	21	-
pH (25 °C)	5.8	6.0	6.0	6.1	6.0	6.2	6.2	5.4	5.7	5.7	5.7	7.4
Alkalinity ^b (meq/kg)	14.3	14.3	13.5	9.2	8.4	8.8	8.9	6.5	11.6	13.6	12.9	2.3
Na (mmol/kg)	459	463	464	460	462	490	464	465	463	466	464	-
Cl ⁻ (mmol/kg)	-	545	545	542	544	541	543	540	538	537	538	539
Mg (mmol/kg)	51.5	51.5	52.0	52.2	50.0	52.5	52.8	54.0	55.0	54.7	54.5	-
Ca ^b (mmol/kg)	15.1	15.8	15.3	14.3	14.9	16.0	16.3	10.9	11.3	11.4	10.6	10.3
K (mmol/kg)	12.2	-	12.1	11.3	12.4	16.6	11.4	10.7	11.1	11.7	11.7	-
Sulfate (mmol/kg) ^c	27.0	26.7	26.9	27.3	25.8	27.0	27.0	27.9	27.3	26.6	26.8	28.2
Si (mmol/kg)	2.8	2.7	2.7	1.5	1.9	1.7	1.5	0.6	1.4	1.8	1.9	-
Fe (μmol/kg)	413	517	579	289	384	369	285	308	758	980	978	0
Mn (μmol/kg)	40	40	38	24	25	73	45	10	18	21	22	-
Al (μmol/kg)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
Sr (μmol/kg)	104	103	103	95	98	-	102	87	88	87	87	-
Ba (μmol/kg)	0.7	0.7	0.9	0.7	0.9	-	0.7	0.7	1.0	0.6	1.0	-
B (μmol/kg)	398	402	424	410	398	553	388	424	452	491	484	-
Li (μmol/kg)	53	53	52	42	44	76	40	32	38	45	45	-
Rb (μmol/kg)	5.0	4.9	4.7	3.3	4.6	5.8	3.5	2.0	2.8	3.4	3.4	-
Cs (μmol/kg)	0.24	0.24	0.26	0.23	0.26	0.48	0.24	0.24	0.24	0.24	0.25	-
Cu (μmol/kg)	0.9	1.1	1.4	5.3	1.6	6.4	0.5	1.6	1.3	0.9	1.8	-
Zn (μmol/kg)	27.6	27.9	7.7	6.0	32.5	134.4	12.4	22.9	4.3	4.0	14.2	-
H ₂ (μmol/kg) ^d	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	-
CO ₂ (mmol/kg) ^d	31.2	31.2	30.0	18.3	17.4	14.2	14.0	43.8	94.1	124.3	125.8	-
CH ₄ (μmol/kg) ^e	1.5	1.3	1.2	0.8	1.4	0.6	0.6	1.6	2.8	4.3	3.8	-
H ₂ S (μmol/kg) ^f	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	-

^aMarker and site from Rouxel et al. (2018)

^aTemperature maximum recorded during the IGT sampling

Analysis with ICP-MS, unless otherwise noted: ^bGran titration, ^cion chromatography, ^dGC-TCD, ^eGC-FID, ^fspectrophotometry Cline (1969)

^gDuplicate sample leaked

n.d. = not detected

Estimated uncertainties (2σ) are as follow: pH (25°C) values ± 0.1 unit; Na, Mg, Cl, Ca, K, sulfate concentrations $\pm 3\%$; SiO₂, Fe, Mn, Sr, Ba, Li, Rb, Cs, Cu, Zn concentrations $\pm 5\%$; CH₄ and CO₂ concentrations $\pm 10\%$ and $\pm 5\%$, respectively.

Table 1. Vent-fluid compositions from Lō'ihi compared with submarine vent fields from various other geologic settings

Vent field	Seawater	Lō'ihi ^a	21°N, EPR ^b	Mariner	Baby Bare (Spring water)
Geologic setting	-	Intraplate volcano	Mid ocean ridge	Back arc	Ridge flank
Max. T (°C)	2	41	350	363	25
pH (25 °C)	7.8	5.9	3.4	2.7	8.3
Alk. (meq/kg)	2.3	14.3	-0.4	-2.25	0.43
Cl (mmol/kg)	546	546	489	605	554
SO ₄ (mmol/kg)	28	26.9	0.5	-	17.8
Na (mmol/kg)	468	460.8	432	439	473
K (mmol/kg)	10.2	12.4	23	36.9	6.9
Ca (mmol/kg)	10.3	15.5	16	43.8	55.2
Mg (mmol/kg)	53	51.5	0	1.9	0.98
Si (mmol/kg)	0.1	2.8	18	15.1	0.4
Fe (μmol/kg)	<0.001	465	1,664	12991	<0.1
Mn (μmol/kg)	<0.001	40	960	5723	7.8
CH ₄ (μmol/kg)	-	1.4	70	-	-
H ₂ (mmol/kg)	-	b.d.l	1.7	-	-
CO ₂ (mmol/kg)	-	31.2	5.7	39.8	0.4
H ₂ S (mmol/kg)	-	b.d.l	7.3	9.3	-

^a Average values of the 2018 SUBSEA fluids sampled at Marker 34.

^b Measured composition of vent fluids are corrected for entrainment of seawater during sampling based on the quantitative removal of Mg from the fluid during water-rock reactions.

Data are from Bruland et al. (2006) for seawater, Humphris and Klein (2017) for 21°N EPR and Mariner vent fields (original data from Von Damm et al. (1985) and Mottl et al. (2011), respectively), Wheat and Mottl (2000) for Baby Bare.

Abbreviation: Max. T = maximum temperature; Alk. = Alkalinity; - = not determined; b.d.l = below detection limit.

Figure 1. (a) Conceptual model of hydrothermal circulation producing low-temperature vent fluids at Kama'ehuakanaloa. In Step 1, seawater reacts progressively with basalt and volcanic gases (CO_2 , SO_2 and H_2O) in an open system along an increase of temperature from 2°C to a temperature maximum that ranges between 50°C and 400°C , and a corresponding increase of rock/water ratio from 0.1 to 1.1. In Step 2, the hydrothermal fluid produced during Step 1 mixes with 2°C seawater in an open system in which it also continues to react with basalt until the fluid mixture reaches 20°C . The proportion of basalt and gas reacting during Step 2 is modelled as a fraction, $F=0\%$ to $F=20\%$, of the amount of basalt reacting during Step 1. Both mechanical and equilibrium mixing were considered during Step 2. (b) Rock/water weight ratios during Step 1 (black line) and Step 2 (colored lines) are shown as functions of the maximum model temperatures reached during Step 1.

Figure 2. Evolution of Kama'ehuakanaloa vent fluid compositions and temperatures through time. The blue, orange, white and red boxes represent the periods of pre-eruption, 1988-1993 (Karl et al., 1988; Sedwick et al., 1992, 1994; Hilton et al., 1998), syn-eruption, 1996-1997 (Hilton et al., 1998; Wheat et al., 2000), post-eruption, 2006-2008 (Glazer and Rouxel, 2009; Rouxel et al., 2018) and our SUBSEA data (2018; this study). The numbering above each box indicates the number of measurements for each species within each dataset. Note that no data are available for Na, Cl and DIC concentrations from Glazer and Rouxel (2009) and Rouxel et al. (2018) and that the estimations of DIC concentrations from Karl et al. (1988) and Sedwick et al. (1992) were excluded. The samples considered are from Pele's vents for the pre-eruption period and from Pele's Pit (Spillway, Lohiau and Hiolo areas) and the Pohaku area for the post-eruption period. Alk. stands for alkalinity and T ($^\circ\text{C}$) for temperature.

Figure 3. pH values, Ca concentrations, DIC concentrations and calcite saturation indexes as functions of temperature during modeled reaction pathways at Kama'ehuakanaloa. Seawater composition is shown with an open star and the solid black line represents Step 1 fluid compositions. The color gradation from purple to red represents families of paths for Step 2 fluid compositions originating with

Step 1 fluid compositions calculated for temperatures that range from 50 to 400 °C, at 50°C increments. In each set, the thin dotted line represents mechanical mixing during Step 2. The thickness of the remaining lines increases with the degree of low-temperature basalt alteration, F, during Step 2. For readability, the reaction paths for which F=20% are represented by dashed lines. In subplot (d), the dashed-dotted horizontal black line represents mineral equilibrium.

Figure 4. Sulfate, Mg, K, and Si concentrations as functions of temperature during modeled reaction pathways at Kama'ehuakanaloo. Seawater composition is shown with an open star and the solid black line represents Step 1 fluid compositions. The color gradation from purple to red represents families of paths for Step 2 fluid compositions originating with Step 1 fluid compositions calculated for temperatures that range from 50 to 400 °C, at 50°C increments. In each set, the thin dotted line represents mechanical mixing during Step 2. The thickness of the remaining lines increases with the degree of low-temperature basalt alteration, F, during Step 2. For readability, the reaction paths for which F=20% are represented by dashed lines.

Figure 5. H₂S and Fe concentrations as functions of temperature during modeled reaction pathways at Kama'ehuakanaloo. The solid black line represents Step 1 fluid compositions. The color gradation from purple to red represents families of paths for Step 2 fluid compositions originating with Step 1 fluid compositions calculated for temperatures that range from 50 to 400 °C, at 50°C increments. In each set, the thin dotted line represents mechanical mixing during Step 2. The thickness of the remaining lines increases with the degree of low-temperature basalt alteration, F, during Step 2. For readability, the reaction paths for which F=20% are represented by dashed lines.

Figure 6. Si, alkalinity, Ca, K and Fe concentrations as functions of pH values for 20-50 °C vent fluids at Kama'ehuakanaloo. The colored areas within the frame of each plot represent probability density functions of modeled compositions for vent fluids at the end of Step 2, when fluid mixtures reach

temperature between 50 and 20 °C. Temperature maxima from 50 to 400 °C during Step 1 are shown with color gradation from purple to red. Open symbols are for pre-eruptive vent-fluid compositions from Karl et al. (1988) and Sedwick et al. (1992) [squares and triangles, respectively]. The black contour lines within the frame of each panel indicate the probability density functions for post-eruptive vent-fluid compositions (Glazer and Rouxel, 2009; Rouxel et al., 2018). Closed circles show the SUBSEA data. The open star represents background seawater composition. Also shown along the top and right-hand side of each panel are projections of the same probability density functions onto the corresponding axes for each plot (a-h) for the SUBSEA data (dark grey) and modeled fluid compositions (colored according to Step 1 reaction temperature). Reaction conditions during Step 2 arise from mechanical mixing (left column: a, e, i, m, q) or equilibrium mixing with a degree of low-temperature basalt alteration, F , of 2%, 4% and 8% (2nd, 3rd and 4th column). Note the scale change from the 2nd column ($F=2\%$) to the 3rd ($F=4\%$) column for the panels showing Fe concentrations. The red box outlines the reaction conditions that are most consistent with our measured vent-fluid compositions.

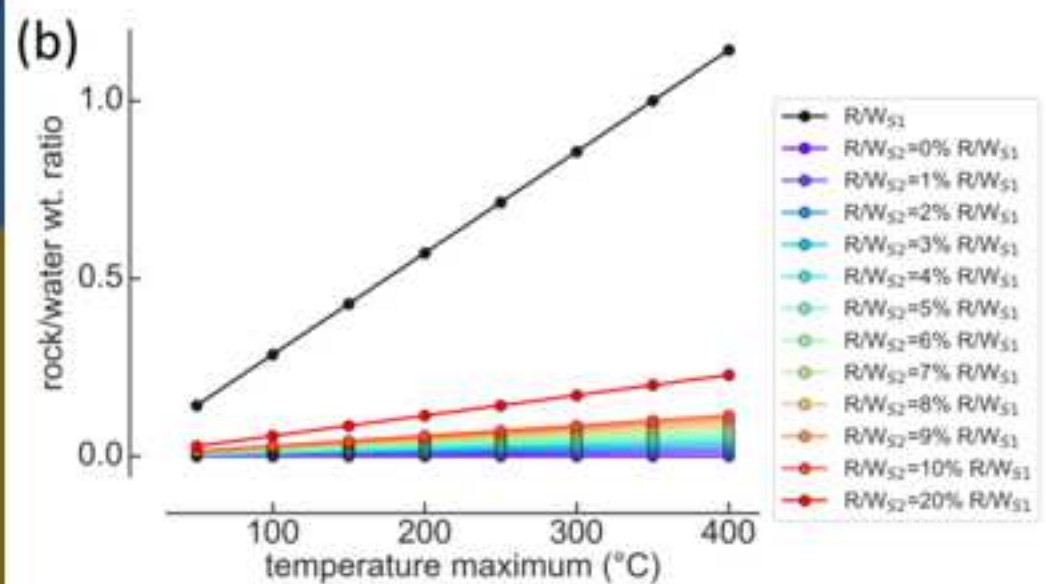
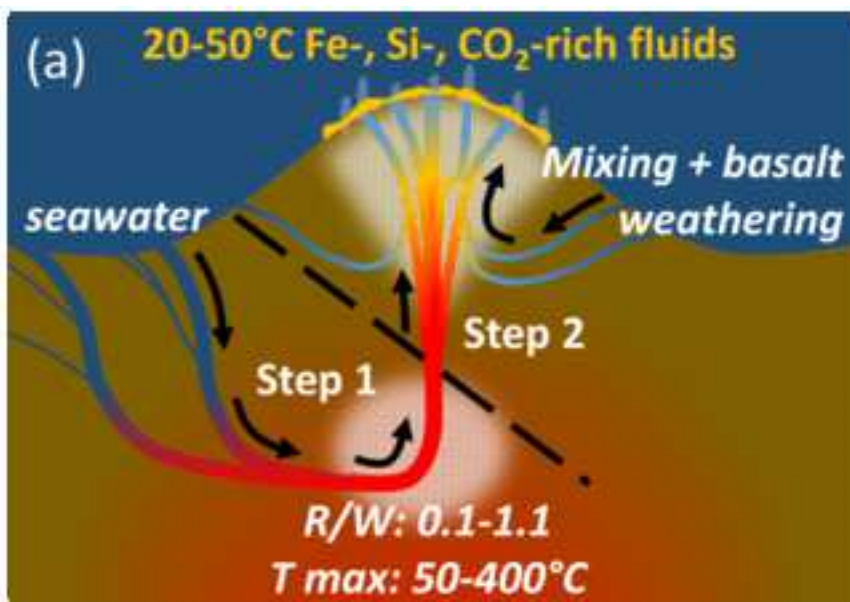
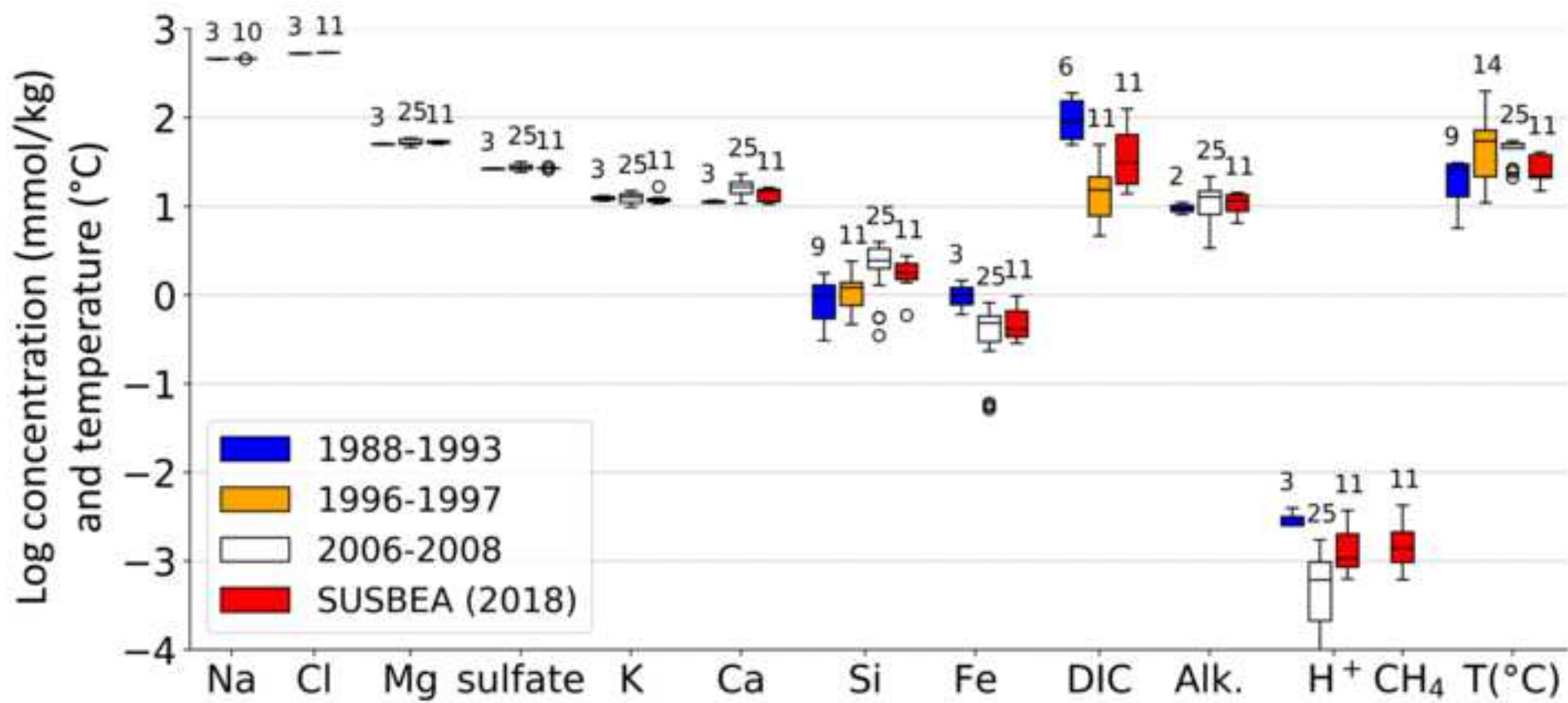


Figure 2

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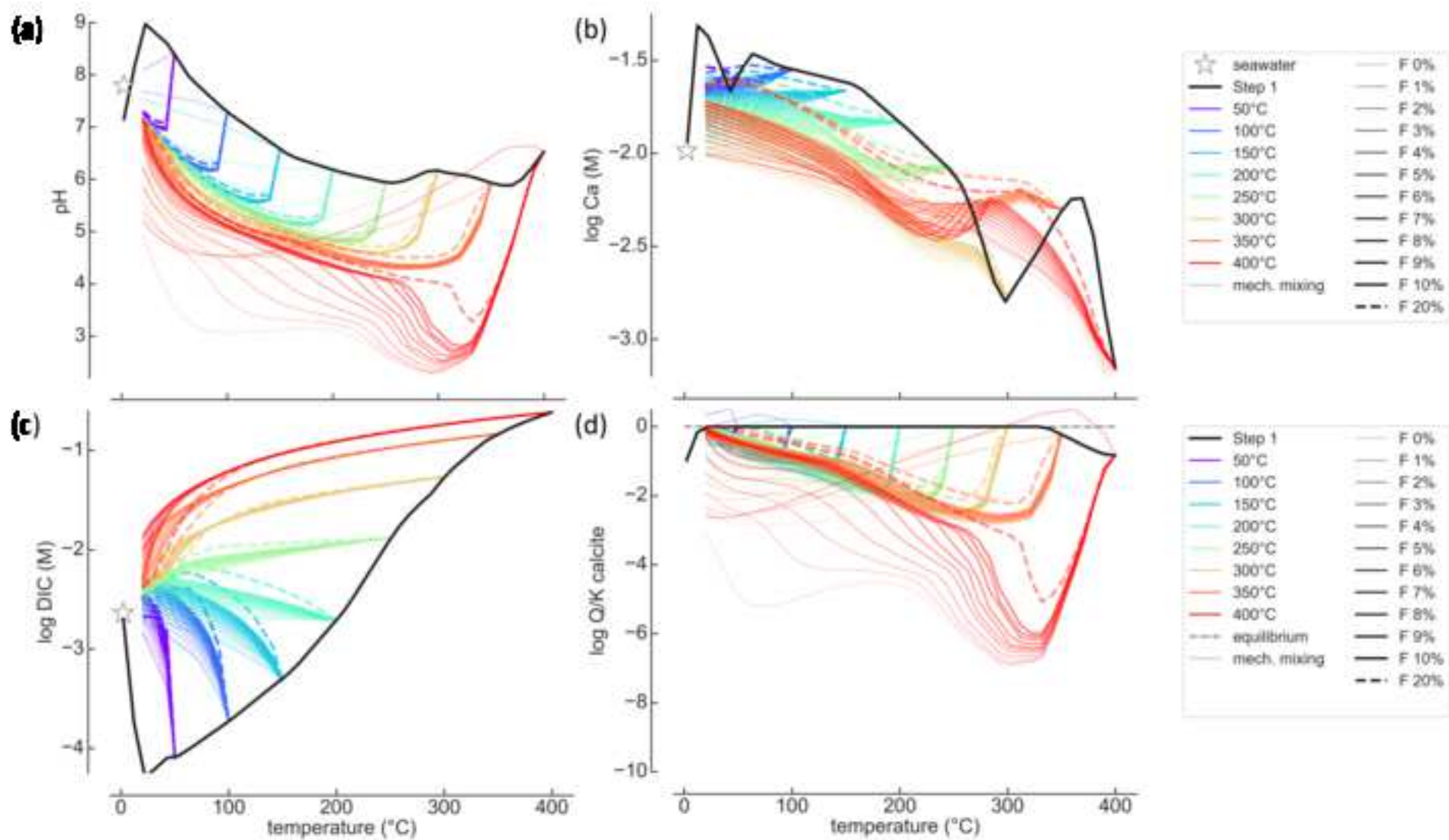


Figure 4

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