Fluid mixing and spatial geochemical variability in the Lost City hydrothermal field chimneys

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Abstract

Carbonate-brucite chimneys are a characteristic of low- to moderate-temperature, ultramafic-hosted alkaline hydrothermal systems, such as the Lost City hydrothermal field located on the Atlantis Massif at 30°N near the Mid-Atlantic Ridge. These chimneys form as a result of mixing between warm, serpentinization-derived vent fluids and cold seawater. Previous work has documented the evolution in mineralogy and geochemistry associated with the aging of the chimneys as hydrothermal activity wanes. However, little is known about spatial heterogeneities within and among actively venting chimneys. New mineralogical and geochemical data (87Sr/86Sr and stable C, O, and clumped isotope) indicate that brucite and calcite precipitate at elevated temperatures in vent fluid-dominated domains in the interior of chimneys. Exterior zones dominated by seawater are brucite-poor and aragonite is the main carbonate mineral. Carbonates form mostly out of oxygen and clumped isotope equilibrium due to rapid precipitation upon vent fluid-seawater mixing. In contrast, the carbonates precipitate close to carbon isotope equilibrium, with dissolved inorganic carbon in seawater as the dominant carbon source, and have δ 13C values within the range of marine carbonates. Our data suggest that calcite is a primary mineral in the active hydrothermal chimneys and does not exclusively form as a replacement of aragonite during later alteration with seawater. Elevated formation temperatures and lower 87Sr/86Sr relative to aragonite in the same sample suggest that calcite may be the first carbonate mineral to precipitate.

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3	field chimneys
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17	Key Points:
18	• The mineralogy and geochemistry of Lost City chimneys are controlled by the extent
19	of mixing between hydrothermal fluids and seawater
20	• Brucite and calcite precipitate in vent fluid dominated zones while aragonite forms in
21	the exterior of the structures in seawater-rich zones
22	• Carbonates precipitate in isotopic disequilibrium and record the O and C stable
23	isotope composition of seawater dissolved inorganic carbon.
24	
25	Abstract

- 26 Carbonate-brucite chimneys are a characteristic of low- to moderate-temperature, ultramafic-
- 27 hosted alkaline hydrothermal systems, such as the Lost City hydrothermal field located on the

28 Atlantis Massif at 30°N near the Mid-Atlantic Ridge. These chimneys form as a result of 29 mixing between warm, serpentinization-derived vent fluids and cold seawater. Previous work has documented the evolution in mineralogy and geochemistry associated with the aging of 30 the chimneys as hydrothermal activity wanes. However, little is known about spatial 31 32 heterogeneities within and among actively venting chimneys. New mineralogical and geochemical data (⁸⁷Sr/⁸⁶Sr and stable C, O, and clumped isotope) indicate that brucite and 33 34 calcite precipitate at elevated temperatures in vent fluid-dominated domains in the interior of 35 chimneys. Exterior zones dominated by seawater are brucite-poor and aragonite is the main carbonate mineral. Carbonates form mostly out of oxygen and clumped isotope equilibrium 36 37 due to rapid precipitation upon vent fluid-seawater mixing. In contrast, the carbonates precipitate close to carbon isotope equilibrium, with dissolved inorganic carbon in seawater 38 as the dominant carbon source, and have δ^{13} C values within the range of marine carbonates. 39 Our data suggest that calcite is a primary mineral in the active hydrothermal chimneys and 40 does not exclusively form as a replacement of aragonite during later alteration with seawater. 41 Elevated formation temperatures and lower ⁸⁷Sr/⁸⁶Sr relative to aragonite in the same sample 42 43 suggest that calcite may be the first carbonate mineral to precipitate.

44

45 **Plain Language Summary**

At the Lost City hydrothermal field, warm, alkaline fluids are discharging in uplifted mantle 46 47 rocks. When vent fluids mix with seawater at the seafloor, carbonate and brucite minerals 48 form spectacular towers up to 60 m high. Systems like Lost City are important because the 49 reaction between water and rocks provide carbon and energy sources for microbial life. However, we still do not fully understand what controls the mineralogy and geochemistry of 50 the Lost City hydrothermal chimneys. In this paper, we suggest that the extent of mixing 51 52 between the hydrothermal fluids and seawater influence the mineralogy and geochemistry of 53 the chimneys. Calcite, which is previously known to form only during alteration of aragonite 54 by seawater, can also form during seawater-hydrothermal fluid mixing. Both calcite and 55 brucite form in the interior of the chimneys where vent fluid is more dominant. Aragonite, on 56 the other hand, forms in the exterior of the structures from seawater-rich fluids. Lastly, 57 because minerals precipitate rapidly during fluid mixing, the stable isotope geochemistry of 58 the carbonates mostly record the composition and temperature of seawater and not the mixed 59 fluid. Thus, care should be exercised in interpreting geochemical data from similar systems.

60 1 Introduction

Since the discovery of the Lost City hydrothermal field (LCHF; Kelley et al., 2001), 61 62 carbonate-brucite deposits associated with serpentinite-hosted hydrothermal systems are 63 increasingly being recognized in different tectonic settings and are possibly widespread 64 components of serpentinizing environments on the seafloor. Carbonate-brucite deposits occur at or near slow- and ultraslow-spreading mid-oceanic ridges (Kelley et al., 2001; Lartaud et 65 al., 2011; Lecoeuvre et al., 2020), in subduction forearc regions (Ohara et al., 2012; Okumura 66 et al., 2016), in magma-poor continental margins (Klein et al., 2015; Schwarzenbach, Früh-67 68 Green, et al., 2013), and they are also associated with continental ophiolitic settings (Launay & Fontes, 1985; Monnin et al., 2014; Pisapia et al., 2017). Unlike high-temperature black-69 70 smoker hydrothermal systems (>350°C) that are characterized by acidic (pH 2-6), metal- and 71 sulfide-rich vent fluids (Von Damm, 1990; German & Seyfried, 2013), fluids derived from the serpentinization of ultramafic rocks are relatively cool (~30-120°C), alkaline (pH 9-11), 72 73 metal- and CO₂-poor, and often rich in dissolved volatiles such as H₂, CH₄, and other short 74 chain hydrocarbons (Cipolli et al., 2004; Eickenbusch et al., 2019; Kelley et al., 2005; Lang 75 et al., 2010; Monnin et al., 2014; Schwarzenbach, Lang, et al., 2013; Seyfried et al., 2015). Instead of sulfide structures typical of black-smoker systems, delicate carbonate-brucite 76 77 chimneys are formed in zones where serpentinization-derived hydrothermal fluids mix with 78 oxygenated, Mg- and CO₂-rich seawater (Früh-Green et al., 2003; Kelley et al., 2001; 79 Ludwig et al., 2006; Okumura et al., 2016; Pisapia et al., 2017):

$$Mg^{2+} + 20H^- \to Mg(OH)_2 \tag{1}$$

]

seawate vent fluid

d brucite

r

$$Ca^{2+} + OH^{-} + HCO_{3}^{-} \to CaCO_{3} + H_{2}O.$$
 [2]

vent fluid seawater Ca-carbonate

- 80 Serpentinization reactions, which can provide both carbon and energy sources for
- chemoautotrophy (Amend et al., 2011; Dick & Shock, 2021; McCollom, 2007; McCollom &
- 82 Seewald, 2007), are likely to have been widespread in the early Earth (Sleep, 2010) and could
- 83 potentially be occurring in other planetary bodies such as Enceladus and Europa (Glein et al.,

2015; McKay et al., 2008; Waite et al., 2017). Therefore, systems like the LCHF can improve
our understanding of the geochemical evolution of life on Earth and elsewhere.

86 The LCHF is the first documented and remains one of the best studied examples of 87 such low temperature, marine hydrothermal systems to date. It is located approximately 15 km west of the Mid-Atlantic Ridge at 30°N at the inside corner of the intersection with the 88 Atlantis Transform Fault (Figure 1). The field is at the top of a terrace on the southern wall of 89 90 the Atlantis Massif at about 700-800 m below sea level. At least 30 carbonate-brucite structures (Figure 2), up to 60 m high, span across the approximately 400 m wide vent field 91 and include actively venting and inactive spires, pinnacles, parasitic flanges, and veins 92 (Kelley et al., 2001). Ludwig et al. (2006; 2011) extensively studied the mineralogical, 93 94 geochemical, and textural transformation during ageing of the chimneys from nascent to inactive and extinct structures. They documented that young, active chimneys precipitate 95 predominantly as aragonite and brucite, characterized by low ⁸⁷Sr/⁸⁶Sr and low trace element 96 contents. Progressive reaction with seawater results in the conversion of aragonite to calcite, 97 dissolution of brucite, as well as increases in ⁸⁷Sr/⁸⁶Sr and trace element concentrations 98 (Ludwig et al., 2006). In our companion paper (Aquino et al., 2023), we show that calcite is 99 also a primary mineral in active chimneys and does not only form from aragonite alteration. 100 101 Calcite is associated with brucite and occurs in the interior of actively venting spires as well 102 as the downward-facing side of flanges. In contrast, aragonite generally comprises the 103 exterior of the chimneys (Figure 3).



Figure 1. Location of the Lost City hydrothermal field (LCHF) and the vent sites 105 106 investigated in this study. (a) Overview of the LCHF situated on the southern wall of the 107 Atlantis Massif at 30°N west of the Mid-Atlantic Ridge. (b) 3-Dimensional map of the LCHF (after Kelley et al., 2005) including the vents studied here. The massive 60-m structure 108 Poseidon is a composite of multiple active vents in the center of the field. Active vents are 109 also found along the northeast trending escarpment called eastern wall. Carbonate veins were 110 collected close to the eastern wall and west of Marker 8. Also shown are vent fluid flow paths 111 112 showing the relationship between vent sites after Aquino et al. (2022): thick solid line, 1st

- 113 order vent Beehive; thin solid line, 2nd order vents Marker C and Marker 2; thin dashed
- 114lines,3rdordervents.



Figure 2. Dive photos of vent sites investigated. (a) Marker 3 located at the top of the Poseidon structure. (b) Location of active venting at what used to be the Beehive structure. White box indicates the general location of the Beehive structure and inset shows the structure in 2005 (Kelley et al., 2005). (c) Marker C flange. (d) Marker 2 or IMAX flange. (e) Marker 8 flange. (f) Carbonate veins or fissure-filling deposits located west of Marker 8. (g) Carbonate spires along the eastern wall. (h) Calypso spire, also located along the eastern wall.

- 123 structure. (j) Marker 6 spire. Images courtesy of S. Lang, UofSC / NSF / ROV Jason / 2018
- 124 © WHOI



Figure 3. Mineral abundances of samples collected at each site. (a) Subsamples representative of the bulk sample. (b) Chimney interior. (c) 126 chimney exterior. (d) Inactive chimneys. Notes: Number of samples analyzed for each site is shown in parentheses. Blue = aragonite; orange = 127 brucite; yellow = calcite. Dark and light shades represent minimum and maximum mineral abundances, respectively. Data from Aquino et al. 128 (2023). Samples classified as "inactive" from the active structures Beehive and Marker 3 are older parts of the chimney that are yellowish and 129 higher degree of bright chimney 130 show а induration and form the substrate for new white growth.

131 The objective of this study is to understand the controls on the spatial variations 132 observed in the mineralogy of the active chimneys, more specifically, to determine when and 133 where calcite or aragonite precipitates. Our geochemical data show that heterogenous 134 precipitation conditions (e.g., pH, temperature, Mg/Ca ratios) at Lost City are largely 135 controlled by the variability in mixing proportions of vent fluid and seawater, which affects the mineralogy and geochemistry of the resulting hydrothermal chimneys. Stable carbon and 136 137 oxygen isotope data suggest that during the very rapid precipitation of carbonate upon fluid 138 mixing, the dissolved inorganic carbon (DIC) behaves as a closed system preventing 139 equilibration between DIC, which is mostly sourced from seawater, and H₂O or OH⁻. As a 140 result, the carbonates record oxygen and clumped isotope compositions that do not reflect the 141 temperature of the formation fluid.

142 **2 Sampling sites**

143 The locations of the sampled vent structures are shown in Figure 1 and listed in Table S1. Here we only briefly summarize the morphology of the structures which has been 144 145 discussed in previous studies (Früh-Green et al., 2003; Kelley et al., 2001, 2005; Ludwig et 146 al., 2006). We use location names described in earlier studies and names of field markers 147 deployed during previous sampling campaigns. Carbonate-brucite chimneys occur in a wide variety of morphologies. The central and most prominent part of the field is the 60-m high 148 149 Poseidon structure, which is a composite of actively venting towers and spires including 150 Marker 3 and Camel humps, and parasitic vent structures forming cone- and flange-like morphologies (Figures 1, 2). The Beehive vent is a \sim 1-m high, cone-like parasitic structure 151 that vents the hottest fluid (up to 96 to 116°C; Table S1) which can be considered the 152 153 primary, unaltered endmember fluid at LCHF (Aquino et al., 2022; Kelley et al., 2005; 154 Ludwig et al., 2006). The structure itself was no longer present during our sampling in 2018, 155 but we were able to collect chimney samples from a venting orifice, presumably representing the interior of the former structure (Table S2, Figure 2b). Marker C and Marker 2 (also called 156 157 IMAX flange), are parasitic flanges on the Poseidon structure which include horizontally growing structures that trap warm vent fluids (Figure 2c, d). In some cases, chimney spires 158 159 grow on the top of these flanges. We also sampled Marker 8 (Figure 2e), another parasitic 160 flange west of Poseidon, as well as several veins or fissure filling carbonate-brucite deposits 161 located west of Marker 8 (Figure 2f).

162 The eastern wall is a steep escarpment where carbonate veins and morphologically 163 diverse chimney structures (Figure 2g) grow directly along faults or subhorizontal foliations 164 in the serpentinites (Kelley et al., 2005). It is located along a ridge extending towards the 165 northeast from the main vent field (Figure 1). We sampled several structures, including actively venting spires such as Calypso (Figure 2h), and others that showed no evidence of 166 167 venting at the time of sampling. Veins that crosscut the relatively flat-lying, carbonate-cap 168 sedimentary sequences at the top of the southern Atlantis Massif (Kelley et al., 2005) were 169 also sampled. Marker 6 and Sombrero are two sites located east of Poseidon and close to the 170 eastern wall. Sombrero is an actively venting spire with fresh growth at the top of the 171 structure (Figure 2i). The venting structure on Marker 6 on the other hand is a small, delicate, 172 actively venting spire that grew atop rubble of inactive chimneys (Figure 2j). Despite their 173 location away from Poseidon at the center of the field, these vents are thought to share a 174 common flow path with Beehive (Figure 1c; Aquino et al., 2022; Seyfried et al., 2015).

175 **3 Materials and Methods**

176 **3.1 Samples**

177 Grab and suction (slurp) samples of hydrothermal chimneys and fissure-filling veins were collected with the remotely operated vehicle (ROV) Jason during the Lost City 2018 178 179 Return expedition (*R/V Atlantis* cruise AT42-01). Chimney samples were mostly obtained in 180 sites where active venting, recognized primarily by shimmering water and increased water 181 temperatures, was observed. During six dives (Dives 1107 to 1112), we sampled sites that 182 had been previously investigated (Figure 1), such as Beehive and sites named after field 183 markers laid out in 2003 (e.g., Marker 2, Marker C; Kelley et al., 2005). Most of these vents 184 are associated with the massive Poseidon structure at the center of the field (Figure 1). Other 185 active vents along the eastern wall were sampled for the first time in 2018. A total of 31 186 chimneys and 6 vein samples were collected and described macroscopically. These samples were assigned a unique ID including the Jason dive number, the date and time of collection, 187 188 and the sample type (e.g., J.1109.19Sep.0756 CHIM for a chimney sample collected on 189 September 19, 2018, 07:56 GMT during Jason Dive 1109). In this paper, we use a shortened 190 version of the sample ID which includes the dive number and time of collection (e.g., 1109-191 0756). Each sample was subdivided onboard into aliquots and distributed among the science 192 party members. Each of these samples were assigned a unique cruise ID (e.g., sample 1109-193 0756 is further subdivided into samples with cruise ID LC01349, LC01353, etc.). Specimens 194 that exhibited heterogeneities such as distinct colors, textures, or layers were subsampled to

analyze their mineralogy and geochemistry (e.g., LC01349a, LC01349b). Samples

representing a general average or bulk composition of a chimney or vein were also analyzed

197 separately. Mineral separation via hand picking was carried out on selected samples to

198 determine texture- and/or mineralogy-specific isotopic compositions.

199 3.2 Analytical methods

A total of 76 samples from 31 chimeys and 6 carbonate veins were analysed for 200 mineralogy, chemistry, and stable C and O isotope compositions, 33 for ⁸⁷Sr/⁸⁶Sr ratios, and 201 24 for carbonate clumped isotopes (Δ_{47}). 14 and 12 mineral separates were also measured for 202 their ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and Δ_{47} values, respectively. For major and trace element analyses, powdered 203 samples were washed with distilled water and centrifuged several times to remove salt and 204 205 dirt, and subsequently freeze dried. 300 μ g of sample material were then dissolved in 300 μ l 206 of 2% HNO₃ and measured on an Agilent 8800 Triple Quadrupole inductively coupled 207 plasma mass spectrometer (ICP-MS) at the Geological Institute, ETH Zürich. The 208 reproducibility of the analyses is better than \sim 5% (RSD) based on repeated analyses of 209 standards.

210 C and O isotope analyses were conducted on 90 to 140 µg of carbonates (powdered 211 and washed) using a GasBench II system coupled with a Delta V isotope ratio mass 212 spectrometer (IRMS, Thermo Fischer Scientific, Bremen, Germany) at the Geological 213 Institute, ETH Zürich following the methodology of Breitenbach & Bernasconi (2011). 214 Results are reported in the conventional delta notation relative to the Vienna Pee-Dee Belemnite (VPDB). The average standard deviation of repeated measurements of standards 215 during different sessions is less than 0.1% for both δ^{18} O and δ^{13} C. δ^{18} O-based precipitation 216 temperatures were calculated using the calibration of O'Neil et al. (1969) as recalculated by 217 218 Friedman & O'Neil (1977).

Carbonate clumped isotope analyses were performed with a Kiel IV carbonate device coupled to a 253Plus isotope ratio mass spectrometer (IRMS) (both Thermo Fisher Scientific) at the Geological Institute, ETH Zürich as described by Müller et al. (2017) and Meckler (2014). The carbonate samples were reacted with three drops of 104% H₃PO₄ at 70°C via the Kiel IV device. The CO₂ gas released from this reaction was then purified in a custom-built Porapak Q resin held at -40°C to remove potential isobaric contaminations. Samples were measured with a maximum of three replicate measurements per sample and session, which 226 generally consists of 24 measurements of 100-120 μg sample carbonate interspersed with 5

replicates each of the carbonate standards ETH-1, ETH-2 and 10 replicates of ETH-3

(Bernasconi et al., 2018, 2021). The samples were analysed in LIDI mode with 400 seconds

of integration of sample and reference gas. Raw data processing and background corrections

were performed using the Easotope software (John & Bowen, 2016). Sample compositions

are reported as the excess abundance of the CO₂ isotopologue with mass 47 relative to the

abundance expected from a random distribution of isotopes:

$$\Delta_{47} = \frac{R^{47}}{R^{47*} - 1,}$$
[3]

where R^{47} is the ratio of the abundance of the CO₂ isotopologue with mass 47 relative to the 233 abundance of the most common CO_2 isotopologue with mass 44 and R^{47*} is the ratio expected 234 from a random distribution calculated from the measured δ^{13} C and δ^{18} O values. Sample Δ_{47} 235 measurements were converted to the Δ_{47} Intercarb-Carbon Dioxide Equilibrium Scale 236 237 (ICDES) (Bernasconi et al., 2021) using the ETH-1, ETH-2 and ETH-3 carbonate standards 238 described previously by Bernasconi et al. (2018); Meckler et al. (2014); Müller et al. (2017) 239 with the community-derived Δ_{47} values reported by Bernasconi et al. (2021). Δ_{47} based temperatures were calculated using the calibration of Anderson et al. (2021). 240

241 Radiogenic Sr isotope and Sr concentration analysis were performed at the Institute of 242 Geochemistry and Petrology, ETH Zürich. Twenty to thirty mg of powdered carbonate (bulk 243 samples, separated aragonite or calcite) were first reacted in 5 ml of ammonium acetate 244 buffered to pH 5 to leach the carbonate fraction. Leached sample fractions were subsequently 245 dried down and measured dilute for Sr concentrations by ICP-MS (Element XR, Thermo 246 Fisher Scientific). 200 to 500 ng of Sr were separated from the carbonate matrix using Sr spec resin following the methods of Deniel & Pin (2001) and de Souza et al. (2010). 247 Strontium isotope ratios (87 Sr/ 86 Sr) were measured at Sr concentrations of ~100 ppb on a 248 multicollector ICP-MS (Neptune Plus, Thermo Fischer Scientific). Instrumental mass 249 fractionation was corrected for using the exponential law and ⁸⁶Sr/⁸⁸Sr of 0.11940 (Nier, 250 251 1938). The uncertainty of the measurements estimated from repeated measurements of Nist SRM 987 is < 24 ppm (2 SD, n = 15 per session). Sample 87 Sr/ 86 Sr values were renormalized 252 to the accepted value of Nist SRM 987 (87 Sr/ 86 Sr = 0.710248, Thirlwall, 1991). 253

254 **4 Results**

The mineralogy of the samples, summarized in Figure 3, is discussed in detail in the 255 256 companion paper (Aquino et al., 2023). The Lost City chimneys are composed of variable 257 mixtures of aragonite, brucite, and calcite (Figure 3a). In general, the interior of these 258 chimneys is composed mostly of brucite and minor calcite/aragonite (Figure 3b), while the exterior is dominated by aragonite (Figure 3c). Scanning electron microscopy of samples 259 260 from the interior of the chimneys highlighted the spatial association between brucite and calcite (Aquino et al., 2023). Several samples from relatively high temperature vents (e.g., 261 262 Beehive and Sombrero) as well as from eastern wall sites (Calypso and carbonate veins), contain significant amounts of calcite (>20%). Many samples exhibit flow textures preserved 263 as brucite mineral membranes upon which aragonite or calcite may precipitate on. In the 264 following we compare the results of our geochemical analyses with previous mineralogical 265 studies (Tables S2 and S3). 266

267

4.1 Major and trace elements

268 The major and trace element compositions of the samples are shown in Figure 4. In 269 general, variations in Ca, Mg, and Sr concentrations (Figure 4a, b) roughly reflect the relative 270 proportion of carbonate and brucite in the chimneys, consistent with previous studies (Ludwig et al., 2006; Vogel, 2016). The brucite-rich chimney interior contains up to 40 wt% 271 Mg whereas the carbonate-rich exterior and inactive chimneys have up to 45 wt% Ca (Figure 272 4a). Brucite does not appear to incorporate significant Sr because the Sr contents of the 273 brucite-rich (>95 wt% brucite, >30 wt% Mg) samples are low (70 to 237 ppm). In 274 275 comparison, the chimney exterior has more than 4000 pm Sr, reflecting a higher proportion 276 of aragonite (Figure 4b). Inactive structures contain even more elevated amounts of Sr (up to 277 about 19,000 ppm). Interestingly, most carbonate veins and samples from the eastern wall 278 and Beehive show elevated Si and Al contents (>6000 ppm and 1000 ppm, respectively) relative to samples from other sites (<5000 ppm Si, < 1000 ppm Al). These values are similar 279 280 to the average marine carbonate sedimentary rock and lower than those of the average marine unlithified carbonate sediments (Figure 4c, d). Most trace element (Cr, Mn, Ni, Fe, Zn, Pb) 281 282 concentrations are significantly lower than those of the average marine carbonate rock and 283 sediments (Figure S1). On the other hand, Sr, Cd, U, P, and Si have similar or slightly higher 284 concentrations relative to the average marine carbonate rock and carbonate sediments (Figure S1). Ba, U, P, and S show a generally increasing trend with decreasing Mg while Zn roughly
increases with Mg (Figure S1).

287 4.2 Oxygen isotopes

The Lost City chimney carbonates are isotopically variable and show within-sample 288 heterogenity at the 100 μ g sample size used for the measurements (Fig. 5). The δ^{18} O of 289 mixed calcite and aragonite bulk samples of active chimneys span a wide isotopic range 290 291 from -12.45 to 4.67 ‰ (111 analyses of 35 samples) whereas the veins have a narrower range from 1.99 to 5.29 ‰ (116 analyses of 10 samples) (Figure 5a; Table S2). Beehive, Sombrero, 292 293 and Marker 6, which belong to the vent group with the lowest dissolved sulfide concentrations of 0.3 to 0.4 mmol/kg (Aquino et al., 2022), have the lowest and most variable 294 bulk δ^{18} O values (-12.45 to +3.49 ‰; 62 replicates of 10 samples). The interior of the 295 chimneys and veins from the same site have similar or lower δ^{18} O than the bulk, whereas 296 samples from the exterior have similar or higher δ^{18} O than the bulk (e.g., Figures 5, S2b, e, f). 297 The δ^{18} O of inactive structures are generally similar to those of the active ones (Figure S2a e, 298 i). The δ^{18} O of calcite crystals and aggregates separated by hand picking ranges 299 between -12.0 and +2.5‰ (n=54) whereas aragonite δ^{18} O values are -3.8 to +4.0‰ (n=85) 300 (Tables S3, S4; Figure 5b, c). Within each site, calcite δ^{18} O values are generally lower than or 301 similar to values of the mixed samples (Figure S2a, b, d, e). δ^{18} O values of separated 302 aragonites are mostly similar to or slightly higher than the bulk compositions (Figure S2a-g). 303 304 Except for a few fissure-filling deposits, the oxygen isotope composition of samples collected in 2018 are similar to those reported previously (Figure 5c) (Früh-Green et al., 2003; Vogel, 305 306 2016).



Figure 4. Major element concentrations vs. Mg of active carbonate chimneys and fissure 308 309 filling veins including data from Ludwig et al. (2006) and Vogel (2016). (a) Variation in Ca 310 and Mg generally reflects the relative proportions of carbonate and brucite in the samples. 311 Note that the interior of the chimneys are generally Mg rich relative to the exterior. (b) Sr contents increase with increasing Ca and decreasing Mg concentrations. Active structures 312 have significantly lower Sr contents than the inactive chimneys. (c-d) Most samples have 313 314 minor amounts of Si and Al except for a few samples from the eastern wall and Beehive. 315 Data for marine carbonate sedimentary rock and unlithified marine carbonate sediments are 316 from Turekian and Wedepohl (1961).



Figure 5. Carbon and oxygen isotope compositions of the Lost City hydrothermal chimneys and veins: (a) bulk samples and (b) mineral separates. Gray fields indicate the range of compositions of calcite and aragonite crystals. (c) Comparison of samples collected in 2018 (mostly active samples) and previous work (active, inactive, fissure filling) (Früh-Green et al., 2003; Vogel, 2016).

4.3 Carbon isotopes 323

The bulk δ^{13} C of the active chimneys (0.15 to 2.46‰; n=101, Figure 5, Table S2) lie 324 within a narrower range than the δ^{18} O. Although the inactive chimneys have generally 325 slightly higher bulk δ^{13} C values (1.52 to 2.26%; n=25), these isotope compositions still lie 326 within the range of active chimneys (Figure S2a, e, i). Most of the veins (0.94 to 2.91%; 327 n=102) have δ^{13} C values very similar to the chimneys except for one vein west of Marker 8 328 (average $\delta^{13}C = -1.06\%$; Table S2, Figures 5a, S2j). As with $\delta^{18}O$, for samples from the same 329 site, subsamples from the interior of the chimneys have similar or slightly lower $\delta^{13}C$ than the 330 bulk, while subsamples from the exterior of the chimneys have similar or slightly higher δ^{13} C 331 values than the bulk (Figure S2b, e, j). Both pure calcite and aragonite have δ^{13} C values that 332 lie in a relatively wide range between -1.1 to +2.0% (n=54) and between -0.3 to +2.0%333 (n=85), respectively. The average δ^{13} C for calcite is lower than for aragonite (Tables S3, S4). 334 The carbon isotope composition of LCHF samples reported in earlier studies span a wider 335 336 range than those of samples collected in 2018 (Figure 5c) (Früh-Green et al., 2003; Vogel, 2016). 337



Figure 6. Carbonate clumped isotope compositions and Sr geochemistry of the Lost City 340 341 chimneys and veins. Δ_{47} values plotted against (a) oxygen isotope compositions and (b) formation fluid oxygen isotope compositions calculated from carbonate clumped isotope 342

compositions. (c) ⁸⁷Sr/⁸⁶Sr values and Sr concentrations of selected Lost City carbonate
samples. Also shown are the range of marine calcite and aragonite from Kinsman (1969).
Note: For bulk samples, carbonate Sr contents plotted here are estimated from measured Sr
concentrations and the relative abundance of carbonates vs. brucite (Table S3).

347 4.4 Clumped isotopes

The bulk Δ_{47} values of the chimneys vary from 0.611 to 0.702‰ which correspond to 348 349 temperatures of -7 to 20°C (Table S2, Figure 6a, b). Aragonite from these samples have Δ_{47} values that lie within a slightly lower but similar range (0.604 to 0.690%; -3 to 22° C). 350 351 Calcite, on the other hand, has generally lower Δ_{47} than the bulk samples and aragonite (0.471 to 0.653‰; 7 to 78°C) (Tables S2, S3, Figure 6a, b). Samples from Beehive have the 352 lowest and most variable Δ_{47} while the carbonate veins have the highest and least variable Δ_{47} 353 values. In samples where both aragonite and calcite could be measured individually, calcite 354 has consistently lower Δ_{47} than aragonite (Table S3, Figure 6a). 355

356 4.5 Sr isotopes

Strontium concentrations and ⁸⁷Sr/⁸⁶Sr ratios of bulk chimney and vein samples are 357 listed in Table S2 and plotted in Figure 6c together with literature data (Ludwig et al., 2006; 358 Vogel, 2016). ⁸⁷Sr/⁸⁶Sr isotope ratios, ranging between 0.70732 and 0.70900, broadly 359 360 increase with Sr concentrations (Figure 6c). Not all samples were analyzed for Sr geochemistry, nevertheless, we observe that samples from the interior have among the lowest 361 and generally have low ⁸⁷Sr/⁸⁶Sr and Sr concentrations (e.g., Sombrero, eastern wall chimney 362 Table S2, Figure 6c). The opposite is true for the exterior of the chimneys, which have among 363 the highest ⁸⁷Sr/⁸⁶Sr and Sr concentrations (e.g., Marker 2, Figure 6c). There is no clear 364 relationship between the Sr geochemistry of chimneys and veins and their location within the 365 LCHF, and samples taken from each of the vent groups have overlapping ranges of ⁸⁷Sr/⁸⁶Sr 366 367 and Sr concentrations. One sample taken further away from the site of active venting at Beehive (LC02454b) has a significantly higher 87 Sr/ 86 Sr and Sr concentration (87 Sr/ 86 Sr = 368 0.70878, 3889 ppm Sr) than the samples collected directly at the vent (87 Sr/ 86 Sr = 0.70732 to 369 0.70785, 808 to 1246 ppm Sr). Aragonite separates generally have higher ⁸⁷Sr/⁸⁶Sr ratios 370 (0.70722 to 0.70899) and Sr concentrations (2131 to 9988 ppm Sr) than calcite separates 371 (0.70661 to 0.70789; 77 to 1552 ppm Sr) (Table S3, S4). 372

373 **5 Discussion**

Our results show that the mineralogy and the isotope and element geochemistry of the Lost City hydrothermal chimneys vary spatially within individual chimneys and among different vent sites. In the following, we first discuss the effect of varying proportions of vent fluid to seawater on the mineralogy of the chimneys and veins. Then, we discuss how rapid, instantaneous precipitation during fluid mixing controls the carbonate carbon, oxygen, and clumped isotope compositions.

380

5.1 Variable mixing of vent fluid and seawater

In general, the interior of the chimneys from active vents is brucite(±calcite 381 382 \pm aragonite)-rich, with our scanning electron microscopy data highlighting a spatial association between brucite and calcite (Aquino et al., 2023). The chimney interior displays 383 lower 87 Sr/ 86 Sr values and Sr concentrations than the aragonite-rich exterior (Figures 3, 6). 384 This gradient in Sr concentrations and isotopic composition reflect the dominant mineral 385 phases and their affinity to incorporate Sr. The Sr partitioning coefficient of calcite is lower 386 than that of aragonite (Kinsman, 1969); therefore, the aragonite-dominated chimney exterior 387 is expected to incorporate more Sr (Figure 6c). Moreover, the ⁸⁷Sr/⁸⁶Sr values of carbonates 388 record the ⁸⁷Sr/⁸⁶Sr of the fluids from which they precipitate (Coggon & Teagle, 2011). 389 Given that both the endmember hydrothermal fluid (87 Sr/ 86 Sr = 0.70650, Aguino, Früh-390 Green, Rickli, et al., 2022; Ludwig et al., 2006) and seawater (87 Sr/ 86 Sr = 0.70917, Palmer & 391 392 Edmond, 1989) compositions are known, the strontium isotope composition of the carbonates can be used to calculate the mixing proportion of these two fluids during mineral 393 precipitation. Since the temperatures of the vents and seawater are also known, the 394 temperature of the mixed fluid can be estimated (see section 5.3.1). ⁸⁷Sr/⁸⁶Sr compositions of 395 bulk chimneys and veins suggest mixing of 13 to 69% vent fluid with seawater (n=22). 396 397 Carbonates from the chimney interior generally formed from higher proportions of vent fluid (32 to 65% vent fluid; n=4) compared to the exterior (6 to 46% vent fluid; n=4). Calcite is 398 399 formed from a solution containing 48 to 96% vent fluid (n=5) while aragonite is formed with a relatively lower vent fluid contribution (7 to 73%; n=9). 400

To investigate the effect of varying proportions of vent fluid and seawater on the chemistry (e.g., Mg/Ca), temperature, pH, and mineral saturation during mixing of seawater and LCHF vent fluids, we calculated a mixing model (Figure 7) using the Geochemist's Workbench® (Bethke et al., 2020). In the model, 1 kg of Beehive endmember fluid with

405 96°C is mixed gradually with seawater at 10°C. The compositions of the vent fluid and 406 seawater used in the calculation are listed in Table S5. The modeling results show that 407 brucite, aragonite, and/or calcite are supersaturated during mixing of up to 3 kg of seawater with 1 kg of Beehive vent fluids (up to 75% seawater). Brucite, whose solubility is highly 408 409 sensitive to pH (Pokrovsky & Schott, 2004), is supersaturated only at <30% seawater where 410 the pH of the solution is predicted to be greater than 8. Note that pH decreases with 411 increasing temperature because of the temperature dependence of the dissociation constant of 412 water (White, 2009). Thus, the actual in-situ pH of Beehive vent fluids is lower (8.9) than the 413 pH measured in the laboratory at 22°C which is the one commonly reported in the literature 414 (10.8, Table S5; Aquino, Früh-Green, Rickli, et al., 2022; Kelley et al., 2005; Lang et al., 415 2012). Calcium carbonates, on the other hand, are supersaturated at higher seawater mixing 416 proportions, 0 to \sim 50% for calcite, and \sim 35 to \sim 75% seawater for aragonite. This calculation 417 yields comparable results to other studies, which predicted the precipitation of brucite at 418 lower seawater fractions and increasing calcium carbonate precipitation with continued 419 seawater admixture (Allen & Seyfried, 2004; Palandri & Reed, 2004).

420

5.2 Carbonate mineralogy

The mixing calculation (Figure 7) is consistent with the observation that brucite is 421 422 generally more abundant in the interior of the structures, while calcium carbonate (Figure 3) 423 is dominant in the exterior. The model cannot be used to determine which carbonate 424 polymorph precipitates, as both calcite and aragonite precipitate when the precipitation of the 425 other mineral is suppressed in the calculations. Our petrographic observations suggest that 426 calcite is an early precipitate. In the companion paper (Aquino et al., 2023), we provide 427 mineralogical and textural evidence that the interior of at least some of the chimneys contain significant calcite whereas their exterior is dominated by aragonite, where a higher proportion 428 429 of seawater is dominant. Calcite is in most cases intimately associated with brucite and 430 occurs as euhedral, well-formed crystals (Aquino et al., 2023). These mineralogical 431 observations are in agreement with the oxygen- and clumped isotope-derived precipitation 432 temperatures for calcite, which are generally higher than those for aragonite (Tables S3, S4). 433 Temperature and fluid Mg/Ca are the main controls on the calcium carbonate polymorph that 434 precipitates from seawater (Berner, 1975; Davis et al., 2000; Morse et al., 1997, 2007; Sun et 435 al., 2015). At 25°C, calcite precipitates when Mg/Ca is below 1.4±0.1 (Morse et al., 1997) 436 while concurrent precipitation of aragonite and calcite is thermodynamically possible at

- 437 Mg/Ca of around 2 (Sun et al., 2015). This threshold Mg/Ca value for calcite precipitation
- 438 decreases to about 1 at temperatures $>30^{\circ}$ C. Based on these considerations, for Beehive, we
- 439 estimate that co-precipitation of the two calcium carbonate polymorphs is possible at Mg/Ca
- 440 ratios between ~1 and 1.5 (Figure 7a). Below this Mg/Ca, at very low vent fluid/seawater
- ratios, calcite can coexist with brucite (Figure 3). With increasing seawater contribution, the
- 442 Mg/Ca ratio of the fluid is higher than the threshold for calcite precipitation and aragonite
- 443 precipitates.



Figure 7. Mixing calculations involving the addition of seawater to 1kg of Beehive vent fluids. (a) Mixing results in the supersaturation of brucite and calcium carbonate. Brucite solubility is highly sensitive to pH and brucite is only saturated at low seawater fractions < 30%. Calcite is thermodynamically stable at lower Mg/Ca ratios whereas aragonite is stable

at higher Mg/Ca ratios. (b) Gradients in temperature, pH, and Mg/Ca ratios during mixing.
Seawater and Beehive endmember fluid compositions are listed in Table S5.

The model results are broadly supported by the lower ⁸⁷Sr/⁸⁶Sr values of calcite 451 (Figure 6c), which imply calcite precipitates from solutions with more vent fluid, and higher 452 temperatures (calculated from δ^{18} O and Δ_{47}) than the solutions leading to aragonite formation 453 (Tables S3, S4). Overall, the geochemistry and of the petrography of calcite in the interior of 454 455 the chimneys (Aquino et al., 2023) are consistent with calcite being the first carbonate 456 mineral to precipitate in the actively venting structures. The occurrence of primary calcite is 457 not uncommon in hydrothermal chimneys and veins. The interior of active hydrothermal 458 chimneys from the Shinkai Seep Field in the southern Mariana forearc have also been 459 reported to contain more calcite than aragonite (Okumura et al., 2016), and brucite-calcite 460 hydrothermal veins were inferred to form in a fluid-mixing zone at a Lost City-type 461 hydrothermal system at the Iberian Margin (Klein et al., 2015). Furthermore, chimneys from 462 the Old City hydrothermal field (southwest Indian Ridge), like those from the LCHF, are 463 composed of variable mixtures of brucite, calcite, and aragonite including a sample from an 464 active structure comprising of brucite and calcite (Lecoeuvre et al., 2020).

Calcite is also abundant in chimneys from the eastern wall and in veins (Figure 3). 465 466 Veins have calcite contents of up to 39% while samples from Calypso and other small chimneys in the eastern wall contain up to 24% and 58% calcite, respectively (Table S2). We 467 468 suggest that the relatively low vent temperatures (~30°C for Calypso, 11°C for the vein on 469 the carbonate cap), may explain the abundance of calcite. Mixing of small amounts of cold 470 seawater with these relatively low temperature vent fluids will bring the fluid temperatures to 471 $<30^{\circ}$ C at which the minimum Mg/Ca ratio for aragonite precipitation is higher (Morse et al., 1997). 472

473 In addition to the effects of the variation in the mixing proportions of seawater and 474 hydrothermal fluid, carbonate mineralogy and Sr geochemistry in the hydrothermal chimneys 475 are also affected by the ageing of the structures. Observations from both active and inactive chimneys indicate that aragonite in young, active chimneys is converted to calcite by reaction 476 477 with seawater over time (Aquino et al., 2023; Ludwig et al., 2006). Ludwig et al. (2006) and Vogel (2016) have shown that active chimneys have generally lower ⁸⁷Sr/⁸⁶Sr and Sr 478 concentrations (average 6328 ppm) than inactive structures where Sr concentrations increase 479 (average 9015 ppm) and ⁸⁷Sr/⁸⁶Sr ratios approach those of seawater. During aging we also 480

observe the addition of carbonate particles (foraminifera and coccoliths) filtered from
seawater circulating through the porous structures.

483 5.3 Multiple controls on δ^{13} C, δ^{18} O, and Δ_{47} values

Dissolved inorganic carbon (DIC) in the carbonate system exists in three main forms: 484 $CO_{2(aq)}$ (aqueous carbon dioxide), HCO_3^- (bicarbonate), and CO_3^{2-} (carbonate ion), with the 485 relative proportion of these species changing with pH (Zeebe & Wolf-Gladrow, 2001). The 486 487 oxygen isotope fractionation between each species and water is different for each DIC species and is dependent on temperature (Figure 8c) (Beck et al., 2005). Therefore, the 488 489 overall oxygen isotope fractionation between the sum of the DIC species (denoted as S, Figure 8c) and water is a function of both pH and temperature (Zeebe, 2007). At Lost City, 490 carbonates are formed during mixing of seawater and vent fluids with different endmember 491 pH, temperature, and chemistry (Kelley et al., 2005; Lang et al., 2012; Ludwig et al., 2006; 492 493 Proskurowski et al., 2006). Therefore, multiple factors, including variable mixing proportions 494 of vent fluid and seawater, and the initial pH, temperature, and stable isotope compositions of the vent fluid is expected to affect the compositions of the carbonates. 495

496

5.3.1 Estimation of the temperature of the mixed fluid

The carbonates show a large range in δ^{18} O and Δ_{47} values (Figures 5, 6). Precipitation 497 temperatures calculated from clumped and oxygen isotope analyses range from -7°C to 78°C 498 and -1°C to 76°C, respectively (Tables S2, S3). These calculated temperatures are below the 499 measured vent fluid temperatures (Table S1) which is expected as the carbonates precipitate 500 from a mixture of vent fluid and seawater (Ludwig et al., 2006; see section 5.1). However, a 501 502 significant number of samples yield precipitation temperatures below that of ambient seawater ($\sim 10^{\circ}$ C) and even below zero, indicating precipitation under disequilibrium 503 504 conditions. We can estimate the temperature of the mixed fluid that produced each carbonate (T_{est}) combining ⁸⁷Sr/⁸⁶Sr derived seawater and vent fluid fractions (see section 5.1) with the 505 measured exit temperatures of the vent fluids and the temperature of ambient seawater 506 507 (Figure 6c, Table S1). For veins and chimneys where venting was not observed, we use the venting temperature of 22°C, measured in an eastern wall vein northeast of Marker 7 (Aquino 508 et al., 2022). Using this approach, we calculate the expected δ^{18} O and Δ_{47} of a carbonate that 509 precipitated in equilibrium with this mixed fluid (black line in Figure 8a, b for Beehive). 510 Beehive carbonates have δ^{18} O and Δ_{47} values that are much higher than expected at 511

- 512 equilibrium (Figure 8a, b). Calcite, however, appears to precipitate closer to equilibrium than
- 513 aragonite and the bulk sample.



Figure 8. Effect of seawater mixing and temperature to the equilibrium oxygen isotope and 515 clumped isotope compositions. Expected (a) δ^{18} O and (b) Δ_{47} values of carbonate produced 516 by mixing of seawater and Beehive vent fluids assuming equilibrium conditions. Also shown 517 are δ^{18} O and Δ_{47} values of aragonite, calcite, and bulk samples from Beehive plotted against 518 the fraction of seawater estimated from 87 Sr/ 86 Sr in the carbonates. Note that for both δ^{18} O 519 and Δ_{47} , samples from Beehive do not appear to have precipitated in equilibrium. (c) Oxygen 520 isotope fractionation (1000lna) between carbonate and water (vent fluid-seawater solution) of 521 522 the Lost City carbonate samples plotted against estimated temperature during carbonate 523 precipitation (Test). Also shown are equilibrium fractionation lines between calcite and various DIC species and water. S refers to the overall oxygen isotope fractionation between 524 the sum of the DIC species and water at the pH and temperature of the background seawater 525 526 at Lost City. (d) Carbonate clumped isotope composition of the Lost City samples plotted

against estimated temperatures (T_{est}). Also shown are Δ_{47} values at equilibrium. Temperature is estimated from ⁸⁷Sr/⁸⁶Sr derived vent fluid fractions and measured vent temperatures (T_{est} , see section 5.3.1). ^cUpper and lower limits for the calcite-water fractionation are from Coplen (2007) and O'Neil et al. (1969), respectively.

531 The oxygen isotope fractionation between the carbonates and water $(1000 \ln \alpha_{(CaCO3-1)})$ _{H2O}; calculated from the δ^{18} O of the vent fluids and background seawater, Aquino et al., 532 2022) and Δ_{47} values vs. T_{est} for the samples with 87 Sr/ 86 Sr data are shown in Figure 8c, d. 533 Also shown are the equilibrium oxygen isotope fractionation curves between water (i.e., 534 535 mixture between seawater and vent fluids) and the different DIC species, the sum of all 536 species (S), calcite, and aragonite. Most samples have oxygen and clumped isotope 537 compositions far from the expected equilibrium values of calcite at their estimated formation temperature (Figure 8c, d). For $1000 \ln\alpha_{(CaCO3-H2O)}$, most of the data fall between the 538 equilibrium HCO_3^- and CO_3^{-2-} compositions at 10°C, the temperature of background seawater 539 at Lost City. Exception to this are several calcite samples from Beehive and Marker C which 540 541 show lower values. A similar observation is made for Δ_{47} , but for fewer samples.

542 5.3.2 Disequilibrium precipitation

Calcium carbonate minerals often precipitate under non-equilibrium conditions in 543 laboratory and most natural settings and thus display δ^{18} O values that deviate from 544 equilibrium (Daëron et al., 2019; Tripati et al., 2015; Watkins et al., 2013). Disequilibrium, 545 kinetic isotope effects are due to crystal growth reactions as well as the slow isotope 546 exchange between DIC species and water relative to mineral precipitation (Daëron et al., 547 548 2019; Watkins et al., 2013; Zeebe et al., 1999). Carbonate minerals at Lost City precipitate 549 very rapidly whereas equilibrium between DIC and H_2O may take hours to several days to be 550 achieved especially at higher pH (Dietzel et al., 2009; Watkins et al., 2013; Zeebe et al., 1999; Zeebe & Wolf-Gladrow, 2001). 551

553 Oxygen atoms that are incorporated into the carbonate minerals at Lost City are 554 sourced from seawater DIC and/or vent fluid-derived $OH_{(aq)}^{-}$:

$$CO_2 + OH^- \leftrightarrows HCO_3^-,$$
 [4]

seawater vent fluid

$$HCO_3^- + OH^- \leftrightarrows CO_3^{2-} + H_2O,$$
 [5]

seawater vent fluid

$$Ca^{2+} + CO_3^{2-} \to CaCO_3.$$
^[6]

As described above, the carbonates record oxygen and clumped isotope compositions that are 555 556 mostly higher than the equilibrium values for calcite (Figure 8c, d). Kinetic isotope effects 557 during CO₂ hydroxylation (equation 4) reported in terrestrial hyperalkaline systems 558 (including natural springs and laboratory experiments) where atmospheric CO_2 is the principal source of carbon produce strong depletions in ¹⁸O and ¹³C (e.g., Clark et al., 1992; 559 560 Schwarzenbach, Lang, et al., 2013) which is the opposite of what we observe at Lost City. In contrast to terrestrial hyperalkaline springs, seawater DIC which is mostly in the form of 561 562 HCO₃⁻ is the principal source of carbon at Lost City.

Quantitative precipitation of seawater DIC at 10° C and pH = 7.8 will produce a 563 564 carbonate with a $1000 \ln \alpha_{(CaCO3-H2O)}$ value of 34.5 (Figure 8c). A number of samples, especially from relatively low temperature vents (e.g., eastern wall, Calypso, Marker 8), seem 565 to record the δ^{18} O of DIC of background seawater with little variability in 1000ln $\alpha_{(CaCO3-H2O)}$ 566 across many vents (Figure 8c). Addition of warm (~20 to 96°C) Ca-OH vent fluids to an 567 isotopically equilibrated seawater at 10°C will increase the temperature and pH of the 568 solution and will promote the forward reaction in equation 5 forming CO_3^{2-} that can be 569 rapidly incorporated into a growing crystal prior to isotope equilibration at the new fluid 570 571 temperature. Our data show, especially for the samples from the lower temperature vents, that 572 seawater DIC behaves as a generally closed system, and that there is no or very limited reaction between DIC and H₂O or OH⁻ preceeding carbonate precipitation. In addition, since 573 Ca concentrations (10 to 40 mmol/kg) are significantly higher than DIC contents (0 to 2 574 mmol/kg), quantitative precipitation of the DIC may occur. Thus, the carbonates may directly 575 record the δ^{18} O and Δ_{47} composition of the starting seawater DIC. 576

577 The samples from the relatively higher temperature vents (e.g., Beehive, Sombrero), 578 on the other hand, display lower values which can be explained by a combination of multiple 579 processes (Figure 8c). Carbonates forming at relatively higher temperatures generally also 580 form at relatively higher pH (Figure 7b). At higher pH, the oxygen isotope fractionation 581 between DIC and water decreases (Zeebe, 2007) and the equilibration time for oxygen 582 isotopes in DIC increases (Figure S3; Watkins et al., 2013; Zeebe, 1999). However, time 583 required for oxygen isotope equilibration also decreases with increasing temperature (Watkins et al., 2013). At 96°C and pH = 8.9 (e.g., Beehive vent fluid), oxygen isotope 584 585 equilibration time is relatively short and may take about 17 seconds (Figure S3). We suggest that the carbonates from higher temperature, higher pH vents have formed at conditions 586 closer to equilibrium, which explains the overall lower δ^{18} O compositions, especially for 587 calcite formed from vent fluid-rich fluids. In contrast, carbonates formed at lower 588 589 temperatures, either because they are from lower temperature vents or they formed from 590 extensive mixing with seawater, need more time to achieve equilibrium (Figure S3).

591 In contrast to oxygen isotopes, carbon isotopes achieve equilibrium at time scales on 592 the order of less than 30 seconds (Zeebe & Wolf-Gladrow, 2001). Serpentinite-hosted 593 systems such as the Lost City are characterized by fluids that are DIC-poor because of precipitation of carbonate minerals along the flow paths at depth due to the increased pH 594 595 and/or reduction to hydrocarbons (Cipolli et al., 2004; Delacour et al., 2008; Kelley et al., 596 2005; Monnin et al., 2014; Proskurowski et al., 2008; Ternieten et al., 2021a, 2021b). Thus, 597 upon mixing with seawater, C is dominantly sourced from seawater DIC. As a result, carbonates collected from actively venting structures at Lost City predominantely record $\delta^{13}C$ 598 599 within the range of marine carbonates (-2% to +2%; Wefer & Berger, 1991) (Table S2; Figure 5). However, δ^{13} C values as low as -7‰ and as high as +13‰ have been previously 600 reported from samples collected near the eastern wall (e.g., active chimney from Wall Marker 601 H; vein near Marker 7; (Früh-Green et al., 2003; Kelley et al., 2005; Vogel, 2016). We did 602 not observe such low δ^{13} C values, instead our samples from the eastern wall generally record 603 the highest δ^{13} C and δ^{18} O values. Low δ^{13} C values observed in the some carbonate samples 604 have been explained by methane oxidation and/or incorporation of mantle-derived carbon 605 (Früh-Green et al., 2003; Vogel, 2016). 606

607 An interesting aspect of the data is the strong correlation between δ^{18} O and Δ_{47} values 608 (R² = 0.75) which indicates a similar control on these isotope systems. As discussed above, 609 most of the samples record the oxygen and carbon isotope composition of seawater DIC. In 610 contrast, most of the samples have Δ_{47} values that are higher than seawater bicarbonate Δ_{47} , 611 dominating the clumped isotope signal. We do not have an explanation for these elevated Δ_{47} .

612 A significantly lower background seawater temperature than what has been measured for 613 more than a decade at Lost City (~10°C, Aquino, Früh-Green, Rickli, et al., 2022; Lang et al., 2012; Ludwig et al., 2006) is unlikely. It is worth noting that the Δ_{47} of the individual DIC 614 615 species, especially HCO₃, are not very well constrained. In particular, experimentally derived 616 Δ_{47} values for HCO₃⁻ determined by Tripati et al. (2015) are 0.03% higher than values 617 predicted from theory in the same study. Other factors may also affect the temperature 618 dependence of the equilibrium Δ_{47} values of the DIC species. For example, the presence of 619 cations may slightly increase equilibrium clumped isotope compositions (Hill et al., 2020). 620 Uchikawa et al. (2021) also noted a discrepancy in Δ_{47} values of up to 0.106‰ and 0.081‰ for HCO_3^{-1} and CO_3^{-2} , respectively, between values derived from *ab initio* calculations by Hill 621 et al. (2020) which consider the presence of Na⁺ in the solution and experimental results of 622 623 Tripati et al. (2015). Overall, despite uncertainties in the clumped isotope composition of 624 DIC, our data indicate that a large number of our samples record a similar Δ_{47} composition which may imply a common DIC source pool for most samples, just like for δ^{18} O and δ^{13} C. 625

626

5.3.3 Other effects

There is no significant difference in δ^{13} C between aragonite and calcite, although 627 calcite tends to be slightly depleted in ¹³C relative to aragonite (Tables S3, S4; Figure 5b). 628 629 This can be attributed to the lower isotopic fractionation between calcite and DIC compared to aragonite (Lécuyer et al., 2012; Romanek et al., 1992). Similarly, calcite records lower 630 δ^{18} O and Δ_{47} values than aragonite (Tables S3, S4, Figure S2a, b, e), reflecting higher 631 temperatures of precipitation. Calcite and aragonite crystals taken from the same sample 632 633 show very heterogeneous isotopic compositions. Individual calcite crystals from Beehive have δ^{18} O ranging from -12.0 to -3.1‰ and δ^{13} C between -1.1 to 2.0‰ (Figure S2a). In 634 general, there is a positive correlation between δ^{18} O and δ^{13} C, especially in calcite (Figure 635 636 S2a, b, d, e). We attribute this correlation to local Rayleigh fractionation during progressive carbonate precipitation. Carbonates generally have a lower δ^{18} O and δ^{13} C than the DIC they 637 638 precipitate from, resulting in a slight enrichment in the isotopic composition of the remaining 639 DIC. Carbonate crystals that subsequently precipitate from this residual mixed fluid are then slightly enriched in δ^{18} O and δ^{13} C relative to the earlier-formed carbonate. However, we 640 observe a significantly larger variation in δ^{18} O relative to δ^{13} C (~9 vs. ~1‰) in calcite. Vent 641 fluids from Beehive have a pH of 10.7 at 25°C which is equivalent to about 0.45 mmol/kg of 642 OH⁻. We estimate that mixing with less than 20% of seawater is enough to consume the vent 643 644 fluid derived OH⁻ and can locally decrease the pH. The oxygen isotope fractionation between

seawater and DIC increases with decreasing pH (Tripati et al., 2015; Zeebe, 2007). Overall,
Rayleigh fractionation combined with a local decrease in pH during progressive carbonate
precipitation may explain the trend we observe in composition of the mineral separates
collected from the same sample.

649 5.4 Relationship between mineralogy and geochemistry of the Lost City chimneys Here, we link our geochemical results with previous mineralogical and textural 650 investigation of the Lost City chimneys (Aquino et al., 2023; Ludwig et al., 2006). The 651 chimneys and veins are characterized by channel wall flow structures which serve as 652 653 paleofluid flow paths. These mineral channel walls have been shown to be initially composed 654 of brucite in young and active chimneys (Figure 9a; Aquino, Früh-Green, Bernasconi, et al., 655 2022; Ludwig et al., 2006). Brucite is stable at relatively higher pH (Pokrovsky & Schott, 656 2004) and precipitates only from solutions dominated by vent fluids predominantly in the 657 interior of the chimneys (Figures 3, 7). With continued addition of seawater, carbonates may 658 precipitate on the pre-existing brucite layer. Calcite will form at lower Mg/Ca ratios, i.e. from high proportions of vent fluid, in the interior of chimney structures and/or channel walls 659 660 (Figures 7, 9). The coprecipitation of brucite and calcite from vent fluid-rich solutions is 661 consistent with the observed association of these minerals at multiple vent locations (Aquino 662 et al., 2023). Aragonite, in contrast, precipitates from solutions with higher Mg/Ca ratios and 663 nucleates more commonly toward the exterior of brucite mineral channel walls from a 664 seawater-dominated fluid (Figure 9a). Our interpretation that primary calcite and aragonite 665 precipitate from distinct solutions is supported by the textural investigation of a fresh spire 666 from the actively venting site Calypso. In this sample, both aragonite and calcite were 667 observed to be present, but they precipitated on opposite sides of the brucite channel walls (Figure 9a). Mineral separates were unavailable for this sample because of the small size of 668 the crystals (<50 μ m). Nevertheless, calcite in most samples has overall lower 87 Sr/ 86 Sr, δ^{18} O, 669 670 and Δ_{47} values, indicating formation from more pristine hydrothermal fluid at higher 671 temperatures, than coexisting aragonite (Figures 5b, 6). Overall, these suggest that the 672 channel walls separate the chimney structure into distinct domains which may allow solutions 673 of different compositions to flow and distinct carbonate minerals to precipitate.



674

Figure 9. Conceptual model of mineral precipitation in young, active chimneys modified from Aquino et al. (2023). (a) Chimneys initially form 675 brucite mineral membranes that bound fluid flow paths. Carbonate minerals precipitate on these channel walls. In vent fluid-dominated zones, 676 calcite is the carbonate mineral that forms, while aragonite precipitates in seawater-dominated zones (b-c) Multiple venting events and mixing 677 with seawater leads to the thickening of the channel wall by the precipitation of brucite on earlier formed aragonite or continued aragonite 678 precipitation, depending on the vent fluid-seawater mixing proportions. Box shows the approximate area drawn in a and b. Lower row shows 679 corresponding from al. (2023). 680 scanning electron images Aquino et

Aquino, Früh-Green, Bernasconi, et al. (2022) also reported brucite minerals that 681 682 nucleated upon earlier formed aragonite or calcite crystals. As brucite is only supersaturated 683 at vent-fluid rich solutions, this brucite may form from a new influx of vent fluid (Figure 9b), 684 showing a dynamic fluid circulation through the chimneys. The mineral channel walls 685 thicken as mineral precipitation continues with the mineral assemblage being controlled by the changing composition of the fluid (Figure 9c). Overtime, as hydrothermal activity wanes, 686 687 brucite and calcite are no longer thermodynamically stable and only aragonite precipitates. After hydrothermal fluid circulation strops, previously formed aragonite is converted to 688 689 secondary calcite (Ludwig et al., 2006).

690 6 Conclusions

691 Hydrothermal chimneys collected from actively venting structures at the LCHF are 692 composed of variable mixtures of brucite, calcite, and aragonite. Brucite is the first mineral to 693 form upon mixing of the hydrothermal fluid with seawater forming an intricate channel 694 system bounded by mineral membrane walls. During continued formation of the chimney, carbonate minerals precipitate on the preexisting channel walls from fluids of varying 695 696 composition that impart a strong inhomogeneity to the mineralogy and isotope geochemistry 697 of the towers. The mineralogy of the carbonate depends on the Mg/Ca ratio of the mixed fluid 698 which is controlled by variation in the amount of vent fluid and seawater in the mixed fluid, which can be estimated using ⁸⁷Sr/⁸⁶Sr. Vent fluid-dominated solutions have low Mg/Ca 699 ratios and primarily precipitate brucite and calcite. In contrast, in seawater-dominated 700 environments, chimney structures are often dominated by aragonite. Most carbonates, 701 especially those from relatively lower temperature vents, record the δ^{18} O of seawater 702 bicarbonate at background seawater temperature (~10°C) and have δ^{13} C compositions within 703 the range of marine carbonates. The clumped isotope compositions, on the other hand, are 704 705 within a narrow range above the composition of seawater bicarbonate. Overall, our stable isotope data suggest that at Lost City, dissolved inorganic carbon (DIC) is often 706 707 quantitatively precipitated during fluid mixing and equilibration between DIC and H₂O or OH⁻ does not occur. As a result, the carbonates record oxygen and clumped isotope 708 709 compositions that do not reflect the temperature of the formation.

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