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1 Title: Farmed calcite $\delta^{13}\text{C}$ at Ascunsă Cave, Romania, and its relation with CO_2 outgassing
2 and drip rate

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28

29 **Abstract**

30 When calcite precipitates in caves, its carbon stable isotope signature can be modified by the CO₂
31 outgassing gradient between drip water and cave atmosphere. This effect is modulated by water
32 residence time in the cave, from its emergence in the cave until the deposition of calcite. Moreover,
33 CO₂ solubility, calcite precipitation rate, and isotopic fractionation are controlled by temperature.

34 Here, we present up to date results of an ongoing monitoring study at Ascunsă Cave (Romania),
35 exploring the relationship between farmed calcite $\delta^{13}\text{C}$, drip rate, and CO₂ outgassing. In addition
36 to measuring CO₂ concentration in cave air, we also measured the CO₂ concentration in the
37 headspace of a water-air equilibrator that collects drip water without exposing it to cave
38 atmosphere, preventing outgassing. $\delta^{13}\text{C}$ from calcite farmed at two neighboring stalagmites with
39 different drip rates was also measured.

40 Although caves have generally stable temperatures, we show here that temperature inside Ascunsă
41 and Isverna caves has risen by more than 2°C over the course of a year, bearing important
42 implications for stable isotopic fractionation equations and CO₂ dynamics.

43 Our results show that $\delta^{13}\text{C}$ of farmed calcite has a strong relationship with drip rate at the slow
44 dripping site, but no correlation at the faster dripping site. These two sites are also different when
45 $\delta^{13}\text{C}$ is compared to the outgassing gradient. At the slower drip site, $\delta^{13}\text{C}$ and the outgassing
46 gradient are directly correlated, whereas at the faster drip site their correlation is inverse.

47 Our study brings new light onto speleothem $\delta^{13}\text{C}$ behavior in general, and at Ascunsă Cave in
48 particular, which is crucial for understanding the paleoclimate information captured by speleothems
49 from this cave or elsewhere.

50 **Keywords:** cave monitoring, CO₂, farmed calcite, $\delta^{13}\text{C}$, Ascunsă Cave

51

52 **1. Introduction**

53 Cave monitoring programs specifically designed for speleothem studies are meant to bring
54 information on how speleothems are archiving environmental information. The most used
55 environmental proxies in speleothem studies are $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, but they are influenced by a wide
56 range of processes that act at global, regional and local scale (Fairchild and Baker, 2012; Lachniet,
57 2009; McDermott, 2004). At local scale, not only do these processes vary between caves, but they
58 also vary inside the same cave, having different impacts on different speleothems.

59 One of the local factors that have an important imprint in speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is the
60 outgassing of CO_2 from the groundwater that feeds a speleothem. This process takes place both
61 during the emergence and stagnation of a drop of water around its entry point (e.g., a stalactite tip),
62 but also after the formation of a thin water film on top of a stalagmite (Dreybrodt, 2008).

63 Recently, laboratory experiments were carried out in order to test theoretical models of stable
64 isotope dynamics (Wiedner et al., 2008; Polag et al., 2010; Hansen et al., 2019). Experimental work
65 of Hansen et al. (2013), Hansen et al. (2017) or Dreybrodt (2019) focused on the outgassing and
66 isotopic exchange processes taking place during the presence of a thin water film on top of a
67 stalagmite, from which calcite precipitates. They confirmed previous theoretical studies and
68 identified two outgassing steps. The first takes place by diffusion shortly after the formation of the
69 thin film on the stalagmite tip. Diffusion occurs in a matter of seconds until the aqueous CO_2
70 equilibrates with atmospheric CO_2 , irrespective of the gradient between drip water and atmosphere
71 $p\text{CO}_2$, and without impacting the isotopic composition of the dissolved inorganic carbon (DIC).
72 The second step, that does control the isotopic composition of calcite, takes place during carbonate
73 precipitation from this chemically equilibrated solution, with a duration that is one order of
74 magnitude longer than the first step. Moreover, Dreybrodt et al. (2016) calculated the duration of a
75 third process related to isotopic exchange between drip water CO_2 and cave air CO_2 , which is on
76 the order of thousands of seconds.

77 Apart from water and air chemistry, both CO_2 outgassing and carbonate precipitation are influenced
78 by temperature and this is one of the main parameters recorded during cave monitoring programs.
79 This is important because caves are thought to represent stable environments, with little

80 temperature variability, which allows for speleothem deposition under stable conditions. Moreover,
81 cave air temperature is thought to represent the mean surface temperature (Badino, 2004;
82 Dominguez-Villar, 2012).

83 Our study presents up-to-date measurements of several parameters relevant for speleothem
84 paleoclimatic studies at Ascunsă Cave (Romania), that were first reported by Drăgușin et al.
85 (2017b). We aim to investigate in more detail the relationship between farmed calcite $\delta^{13}\text{C}$ on the
86 one hand, and the CO_2 outgassing gradient between drip water and the atmosphere on the other. We
87 also study the relationship between drip rate and farmed calcite $\delta^{13}\text{C}$, and present the variability of
88 the calcite saturation index calculated based on pH, electrical conductivity and alkalinity of drip
89 water.

90 Our results allow a better understanding of how calcite $\delta^{13}\text{C}$ responds to local factors and will help
91 us refine its paleoenvironmental interpretation in speleothems from this cave. Speleothem stable
92 isotope records from two stalagmites from this cave were already published by Drăgușin et al.
93 (2014) and Staubwasser et al. (2018), but forthcoming studies will benefit from a more thorough
94 understanding of local processes brought by the present work.

95

96 **2. Materials and methods**

97 Ascunsă Cave is located in SW Romania, at an altitude of 1050 m and is part of a larger cave
98 system, of which Isverna Cave is the main groundwater collector and discharge point, at 450 m. In
99 this study we used the field methods detailed in Drăgușin et al. (2017b) and focus on the
100 monitoring point associated with the POM 2 stalagmite, in the Great Chamber, where we measured
101 different parameters at available points, that are a few meters apart from each other (Fig. 1). For
102 example, because the ceiling is about 10 m high, drip water for stable isotope analysis was taken
103 from a more accessible straw stalactite population. The water-air equilibrators were installed at a
104 different stalactite, which ensures enough recharge for the equilibrators to have constantly refreshed
105 water and reduce CO_2 outgassing through the water column.

106 The water-air equilibrator is air-tight by design and there should be no gaseous CO₂ exchange with
107 the atmosphere except through the water column (Fig. 2). The CO₂ inside the headspace, as well as
108 other gasses in the confined atmosphere, should be at equilibrium with the accumulated water.
109 Dripping inside the equilibrator contributes to the perturbation of the water surface, ensuring fast
110 equilibration. Thus, any change in drip water chemistry should be reflected in the chemistry of the
111 headspace in a relatively short time. The only way for CO₂ to escape the headspace is by being
112 dissolved and carried away through the syphon formed at the bottom of the equilibrator and
113 discharged into the cave. We note that we discontinued the use of a second equilibrator that was
114 described in Drăgușin et al. (2017b), because it was behaving as a rhythmic spring and was purging
115 all the water by syphoning.

116 CO₂ measurements were performed using a Vaisala GMP222 probe with an accuracy expressed as
117 the sum of 1.5% of measurement range of the probe (in the case of our probe, calibrated for 0 to
118 10,000 ppmv, this a priori value translates to 150 ppmv) plus an additional 2% of the measured
119 value. For example, for an 8000 ppmv measurement, the error would be 310 ppmv. The CO₂ values
120 are reported at ambient temperature and pressure. Atmospheric pressure, was measured with a
121 Sunartis BKT381 barometer. Headspace CO₂ (CO_{2 HS}) is considered to be in equilibrium with
122 dissolved CO₂, while CO₂ dissolved in water exposed to the atmosphere is considered to be in
123 equilibrium with atmospheric CO₂. For the purpose of this study, we consider the values of CO_{2 HS}
124 as reflecting those of dissolved CO₂ in drip water before entering the cave, while CO_{2 ATM} reflects
125 dissolved CO₂ after equilibration with cave atmosphere values.

126 Air temperature and relative humidity were measured using Tinytag Plus2 data loggers. Due to
127 condensation on the RH sensor, this parameter could not be measured reliably and will be further
128 assumed to be close to 100%.

129 We installed Stalagmate drip loggers at the site of the POM 2 stalagmite described by Drăgușin et
130 al. (2014) and at the site of stalagmite POM 10, a few meters away. The drip loggers at POM 2 and
131 POM 10 were topped by glass plates on which water dripped and deposited calcite. We also

132 installed a glass plate on the nearby active stalagmite POM X. The observed drip rate at POM X is
133 much slower than at POM 2, but similar to that at POM 10.

134 Stable carbon isotope ratios of farmed calcite ($\delta^{13}\text{C}$) that were not yet reported in Drăguşin et al.
135 (2017b) were measured at Northumbria University (UK) on a Thermo Delta V Advantage IRMS
136 coupled to a GasBench II sample preparation and introduction system. Typical measurement errors
137 are $\pm 0.1\%$, and stable isotope values are reported on the VPDB scale.

138 Drip water was sampled from several drip sites, pools and water-air equilibrators in the cave and
139 preliminary results were presented in Drăguşin et al. (2017b). In this study we focus on the samples
140 taken from the drip site that fed the POM 2 stalagmite, and from the nearby water-air equilibrator.
141 Water pH, as well as temperature, were measured using a WTW Sentix 41 probe, after the pH
142 electrode was calibrated against two buffer solutions (7 and 10) that were left to equilibrate with
143 the cave temperature. Electrical conductivity (EC) was measured using a WTW Tetra-Con 325 EC
144 electrode. Alkalinity was determined in the field by titration using a Merck MColorTest carbonate
145 hardness test, whose semiquantitative determination could have an uncertainty as high as 30%
146 (Vatca C., Merck, pers. comm.)

147 Before the installation of the drip logger at POM 2, drip water was left to accumulate in a plastic
148 bottle from one visit to the next. After the drip logger was installed in August 2014, water could be
149 left to accumulate in a plastic bottle only during the visit to the cave, a process that could take
150 several hours depending on the drip rate. Due to such time constraints, in 2015 we discontinued the
151 direct sampling of this drip point. Nevertheless, we continued to sample water from the equilibrator
152 that is readily available and measured physical and chemical parameters until September 2017.
153 Regarding the similarity of samples left to accumulate for long periods of time compared to those
154 accumulated over several hours, we note that at the POM Entrance drip site, two such samples
155 showed almost identical values for pH, alkalinity, EC and chemical composition (unpublished data).
156 This seems to indicate that water is refreshed in the plastic bottle over the course of hours and
157 should not be considered representative for longer periods of time.

158 Water from the equilibrator was sampled using a tube and allowed to fill the bottle by avoiding
159 turbulent flow as much as possible, in order to reduce CO₂ outgassing during the procedure.

160 Based on field measurements, we calculated the calcite saturation index following the equation
161 derived from Langelier (1936):

162 $SI = pH - pH_s$,

163 where pH is the measured pH and pH_s is the saturation pH, calculated as

164 $pH_s = \{9.3 + [(\log_{10}TDS - 1) / 10] + [-13.12 \times \log_{10}(T+273) + 34.55]\} - [(\log_{10}Ca^{2+} - 0.4) +$
165 $\log_{10}ANC]$, where TDS (mg/L) = 0.55 x EC (μS/cm), T(°C) is the water temperature, Ca²⁺ is
166 expressed as CaCO₃ (mg/L) and is calculated as ANC (mmol/L) x 50.04 mg/L.

167

168 **3. Results and discussion**

169 **3.1. Air temperature.** The temperature logger closest to the cave entrance (POM Entrance)
170 records seasonal cycles related to the chimney effect circulation, but during 2019 a sharp 4°C rise
171 can be seen during the warm season in comparison to previous years (Fig. 3). At POM A, air
172 temperature increased by almost 2°C since January 2019 after experiencing a slight multi annual
173 increase trend of about 0.2°C. One can also distinguish subdued seasonal cycles of about 0.2°C,
174 similar in timing to those at POM Entrance, and probably linked to cave ventilation regimes. On
175 short time scales on the order of ten of hours, temperature at POM A was shown to be very stable
176 and is influenced by atmospheric thermal tides (Drăgușin et al., 2018).

177 More dramatically, at POM2 temperature rose by about 2.5°C in 2019, from ~8°C to >10.5°C,
178 where it seems to have stabilized. By comparison, the nearby Isverna Cave experienced a similar
179 2°C dramatic warming over 2016-2017, from ~10°C to ~12°C (Drăgușin et al., 2017b), followed by
180 two years when temperature remained high. Over the summer of 2019, temperature returned
181 abruptly to a value closer to 10°C.

182 At this point there is no clear indication to explain the rapid increase in temperature inside Ascunsă
183 Cave during 2019. We cannot completely rule out a delay in heat transfer through bedrock, if the
184 temperature rise in both Isverna and Ascunsă caves was produced by a warming episode of surface
185 temperature in 2016 or earlier. Nevertheless, this is less probable, as all three points inside Ascunsă
186 Cave start warming at the same time, even though the overburden is about 20 m at POM Entrance,
187 40 m at POM A and 100 m at POM 2. At Isverna Cave, the overburden is around 30 m, implying
188 that a common surface warming would be observed roughly at the same time at Isverna and POM
189 A (which is more stable than POM Entrance). Neither of the two caves are open to the public and
190 are seldomly visited.

191 In the vadose zone of karst systems, water and air flow can alter the geothermal gradient, acting as
192 cooling liquids (Luetscher and Jeannin, 2004; Badino, 2005; Dominguez-Villar, 2012). We can thus
193 hypothesize that geothermalism is better expressed following the overall reduction in groundwater
194 flux to the cave, that we measured as a general decrease in drip rate. It seems that during 2019, a
195 threshold was crossed at Ascunsă Cave, where infiltrating water decreased so much that it lost its
196 ability to counteract the thermal effect of rock temperature on cave air.

197 **3.2. Drip rate** at POM 2 shows a generally decreasing trend since 2014 when it stood at about
198 30 drips/min, punctuated by fast drip periods linked to rainfall or snow melt events (Fig. 4). The
199 aquifer feeding the drip site reached baseline in the second half of 2017 due to lack of recharge in
200 spring and summer, recording values of 1-2 drips/min. Higher snowmelt and spring rainfall in early
201 2018 recharged the aquifer, but drip rates indicate a return towards baseline in early 2019. This
202 pattern repeated in the spring of 2019, with values decreasing later in the year. The quick response
203 of drip rates to rainfall and snow melt indicates that the aquifer is fed via fractures, possibly mixed
204 with seepage flow that would be responsible for maintaining baseline conditions (Baker et al.,
205 1997).

206 The drip logger on the POM 10 stalagmite recorded very low values since its placement in 2016.
207 The maximum value recorded was 1.2 drips/min in November 2019, but values did seldomly
208 surpass 0.6 drips/min, possibly indicating a seepage flow regime. Overall, the POM 10 record

209 mirrors the POM 2, although at such slow drip rates even small increases appear to stand out from
210 the generally low background.

211 **3.3. CO₂ concentration** in the headspace of the water-air equilibrator (CO_{2HS}) is several times
212 higher than the one in the cave atmosphere (CO_{2ATM}). While the headspace values were between
213 6000 ppmv and 8000 ppmv, the ones in the cave atmosphere did not exceed 4000 ppmv (Fig. 5 and
214 Table 1). CO_{2 HS} values were generally around 8000 ppmv between the summer of 2015 and the
215 summer of 2017, but decreased to a level below 6000 ppmv by the end of 2019. Drăgușin et al.
216 (2017b) suggested that such high values throughout the year indicate the presence of an organic
217 matter reservoir deep inside the epikarst that continues to decompose and to produce CO₂ over the
218 winter.

219 Both CO_{2 HS} and CO_{2 ATM} records show a decreasing trend over the five years of monitoring, that is
220 steeper in the headspace values. The overall decrease in CO_{2 ATM} is very small and the trend in our
221 data is imposed by two high values recorded at the end of 2015 and beginning of 2016. The full
222 record sits mostly around 2000 ppmv, and it might indicate a possible modulation by other factors.

223 The correlation coefficient between CO_{2 ATM} and drip rate is 0.7, p-value = 0.02 (Table 2),
224 suggesting that either CO₂ is introduced to the cave atmosphere mostly via drip water or that they
225 might have a common process behind their covariance. At Chauvet Cave in France, Bourges et al.
226 (2020) too, identified a link between atmospheric CO₂ and drip rates, but with an inverse
227 correlation that was imposed by a combination of external processes that include outside air
228 temperature and water excess. We have no estimation of CO₂ transport to the cave via open
229 fractures as identified for example in Gibraltar by Matthey et al. (2016).

230 The difference between CO_{2 HS} and CO_{2 ATM}, ΔCO₂, is used to describe the gradient between the
231 CO₂ concentration in equilibrium with drip water before entering the cave, and the CO₂
232 concentration in water that is at equilibrium with the cave atmosphere. The correlation between
233 CO_{2HS} and ΔCO₂ (r = 0.8, p-value = 0.01) indicates that ΔCO₂ is imposed by CO_{2 HS}. This has
234 relevance for the outgassing of CO₂ from drip water, as higher CO_{2 HS} values would impose a
235 higher ΔCO₂. As we will see further, this is important for defining isotopic fractionation conditions.

236 **Water chemistry.** The pH of the POM 2 drip point ranges between 7.5 and 8.1 (Fig. 6, Table 3)
237 and shows a negative correlation with CO_2_{ATM} ($r = -0.8$, $p\text{-value} = 0.005$). This inverse correlation
238 could indicate that the pH of drip water reached equilibrium with CO_2_{ATM} . If the pH of drip water
239 equilibrates with cave air CO_2 , it does so in a short time, on the order of seconds as suggested by
240 laboratory experiments (Hansen et al., 2017; Dreybrodt, 2019). Moreover, the strong correlation
241 along all the record indicates no influence of water sampling method, with no difference in
242 behavior between plastic bottles left to accumulate drip water on the order of hours compared to
243 those on the order of weeks. Inside the equilibrator, pH values are lower and more stable, between
244 7.3 and 7.7., and show no significant correlation with neither CO_2_{HS} nor CO_2_{ATM} . Lower values
245 could be explained by the higher concentration of dissolved CO_2 in drip water prior to outgassing.

246 Alkalinity was relatively stable at the drip site, with values between 4.7 and 5.7 mg/L H^+ (Table 3).
247 Inside the equilibrator, values varied between 4.6 and 5.8 mg/L H^+ , and the longer dataset allows
248 one to distinguish more variability.

249 Electrical conductivity of the drip site was stable in the first part of the record, around $\sim 445 \mu\text{S}/\text{cm}$,
250 but rose to values of $\sim 480 \mu\text{S}/\text{cm}$ at the end of the measurement period. Water sampled from the
251 equilibrator shows values above $\sim 465 \mu\text{S}/\text{cm}$ for the whole period and a generally rising trend, up
252 to $\sim 490 \mu\text{S}/\text{cm}$. One might also distinguish slight reductions in values during the late autumn (at
253 the beginning and end of the record) and, more clearly, during the winters of 2015-2016 and 2016-
254 2017.

255 The calcite saturation index is positive at the POM 2 drip site, with values ranging from 0.1 to 0.6.
256 Its variability closely resembles that of pH ($r = 0.9$), indicating the strong control that pH has in
257 defining the saturation index. Inside the equilibrator, the saturation index shows periods with
258 fluctuating positive and negative values, between -0.2 and 0.3, varying in step with pH values.

259 If the saturation index follows cave air CO_2 evolution (mediated by the evolution of pH), it should
260 also be influenced by the residence time of drip water at the stalactite tip and as a water film on top
261 of the stalagmite. At high drip rates (e.g. 60 drips/min), water might not have enough time to outgas

262 and equilibrate with air CO₂, thus retaining a lower pH and saturation index, leading to less calcite
263 deposition. This is obvious at POM 2, where calcite deposited on glass plates almost continuously
264 since January 2017, when drip rate reached baseline at 1-2 drips/min, which translates to a
265 residence time of 30-60 seconds. This might explain why there are more periods with calcite
266 deposition at POM X, where the drip rate is similar to that recorded at POM 10, below 1 drip/min.

267 **3.4. δ¹³C values of farmed calcite** are discussed here as being representative for the whole
268 period the glass plates spent under the drip point. Nevertheless, we need to acknowledge that
269 calcite deposition might not take place continuously, being ultimately controlled by the calcite
270 saturation index of the drip water, that could itself vary during the several weeks of glass plate
271 emplacement. Moreover, we compare isotopic values of farmed calcite to average values of CO₂
272 measured at the beginning and end of the deposition period, lacking a high-resolution record that
273 could be available by using CO₂ data loggers for both CO₂_{ATM} and CO₂_{HS}. We also lack data on the
274 isotopic composition of the dissolved inorganic carbon (DIC) as a crucial parameter in calcite δ¹³C
275 dynamics.

276 POM 2 δ¹³C shows 1‰ trend towards lower values between 2012 and 2017, from ~ -10.5‰ to ~ -
277 11.5‰, followed by a return to almost -10.5‰ in 2019 (Fig. 7). POM X values are much more
278 variable, with more than 2‰ amplitude.

279 δ¹³C values at POM 2 and POM X are not correlated ($r = -0.1$). The difference between them, Δ¹³C,
280 is important for comparisons between speleothems formed beneath relatively fast and slow drip
281 sites, such as POM 2 on one side and POM X and POM 10 on the other side.

282 POM X δ¹³C has a very good correlation with Δ¹³C ($r = 0.9$, p-value = 0.0001), while POM 2 δ¹³C
283 and Δ¹³C are inversely, and only moderately correlated ($r = -0.5$, p-value = 0.18). This strongly
284 suggests that the difference between POM 2 and POM X stalagmites is controlled by the variability
285 of the latter.

286 The correlation between drip rate and POM X δ¹³C is inverse ($r = -0.6$, p-value = 0.04), with two
287 outlier values corresponding to the periods between October 2017 to January 2018, and August

288 2018 to October 2018. If the two POM X outliers are omitted from the calculation, r becomes 0.96
289 (p-value = 6E-6). There is no apparent correlation between $\delta^{13}\text{C}$ and drip rate at POM 2 (Fig. 7A).

290 As lower drip rates translate into longer residence times of drip water, this inverse correlation can
291 be explained by a longer precipitation time of CaCO_3 , resulting in higher calcite $\delta^{13}\text{C}$ (Hansen et al.,
292 2019). Longer carbonate precipitation times can also lead to calcite precipitating at the stalactite tip
293 or upstream of the stalactite tip (prior calcite precipitation - PCP) a process that leads to higher
294 stalagmite $\delta^{13}\text{C}$ (Fairchild et al., 2000). The occurrence of PCP would be indicated by increased
295 ratios of minor or trace elements such as Mg or Sr to Ca (Fairchild and Treble, 2009). Although
296 Drăgușin et al. (2017a) presented Mg/Ca values from four POM X calcite samples and several drip
297 water samples, a forthcoming study will take a more detailed look at the chemical variability of
298 drip water and farmed calcite at Ascunsă Cave.

299 $\Delta^{13}\text{C}$, the isotopic difference between the two stalagmites, is directly correlated with the average
300 outgassing gradient, ΔCO_2 ($r = 0.7$, p-value = 0.03). We envisage this as being the result of a
301 possible series of processes. Following a decrease in drip rate, the contribution of dissolved CO_2 as
302 a source of $\text{CO}_{2\text{ATM}}$ also decreases, leading to an increase in ΔCO_2 if drip water dissolved CO_2 still
303 retains high values. More importantly, slower drip rates translate to longer precipitation times of
304 CaCO_3 . The increase in CO_2 gradient, outgassing time, and carbonate precipitation time lead to
305 higher $\delta^{13}\text{C}$ at POM X which further leads to higher $\Delta^{13}\text{C}$. This dynamic is particularly useful if
306 $\delta^{13}\text{C}$ in the fast and slow drip stalagmites are compared (e.g., POM 2 versus POM 10), as larger
307 differences in $\delta^{13}\text{C}$ between them would reflect decreasing drip rates and decreasing water
308 availability.

309 One of the most intriguing results is that POM 2 $\delta^{13}\text{C}$ is inversely correlated with the average ΔCO_2
310 ($r = -0.7$, p-value = 0.01). This shows that stronger CO_2 gradients do not necessarily lead to
311 isotopic enrichment of calcite at POM 2. Knowing that ΔCO_2 is strongly controlled by $\text{CO}_{2\text{HS}}$, we
312 would expect to see a stronger link between POM 2 $\delta^{13}\text{C}$ and $\text{CO}_{2\text{HS}}$, but the correlation coefficient
313 is rather weak ($r = -0.4$, p-value = 0.19). The correlation with $\text{CO}_{2\text{ATM}}$ is also weak ($r = 0.4$), while
314 there is almost no correlation with drip rate ($r = 0.1$). Thus, it is possible that $\delta^{13}\text{C}$ at POM 2 is

315 controlled by other factors that were not taken into account in this study, such as the isotopic
316 composition of DIC. It is also possible that the effect of drip rate and CO₂ outgassing could be
317 masked or countered by other factors.

318

319 **4. Conclusions**

320 We used drip loggers at two points with highly different drip rates and identified stalagmite POM
321 10 as being fed by a very slow drip site, <1 drip/min, while POM 2 has drip rates ranging from 1
322 drip/min at baseline to 90 drips/min after rain or snow melt events.

323 Since 2015, CO₂ concentration in the cave atmosphere was largely stable around 2000 ppmv, while
324 the concentration measured in the headspace of a stalactite-fed water-air equilibrators was as high as
325 8000 ppmv. The difference between drip water dissolved CO₂ and cave atmospheric CO₂ is
326 controlled by the former, which has constantly higher concentrations.

327 Calcite δ¹³C at the POM X stalagmite varies within 2‰ and is strongly controlled by drip rate,
328 whereas drip rate has no impact on δ¹³C at POM 2. Therefore, the δ¹³C difference between
329 stalagmites from the faster dripping site of POM 2 and the slower dripping sites of POM X and
330 POM 10, could be used in the future to study past hydrological changes.

331 Analysis of drip water sampled at the drip site of stalagmite POM 2 and from inside the water-air
332 equilibrators shows that the water exposed to the cave atmosphere has a higher pH than prior to
333 entering the cave and that its pH value is in equilibrium with the CO₂ content of the cave
334 atmosphere. During the measurement period, drip water calcite saturation index, controlled by pH,
335 was always positive between 0.1 and 0.6. Since 2017 when drip rate values dropped below 10
336 drips/min calcite deposition took place more continuously at POM 2, indicating yet again the
337 control of drip rates on calcite formation and isotopic values.

338 We also observed a dramatic ~2°C rise in cave air temperature over the year 2019, that could have
339 been the result of reduced groundwater cooling of host rock and cave air. This shows that cave air
340 temperature, which controls water-calcite fractionation, is not truly stable for long periods of time

341 but it could be controlled by hydrology, with implications for stable isotope fractionation during
342 calcite deposition.

343

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348

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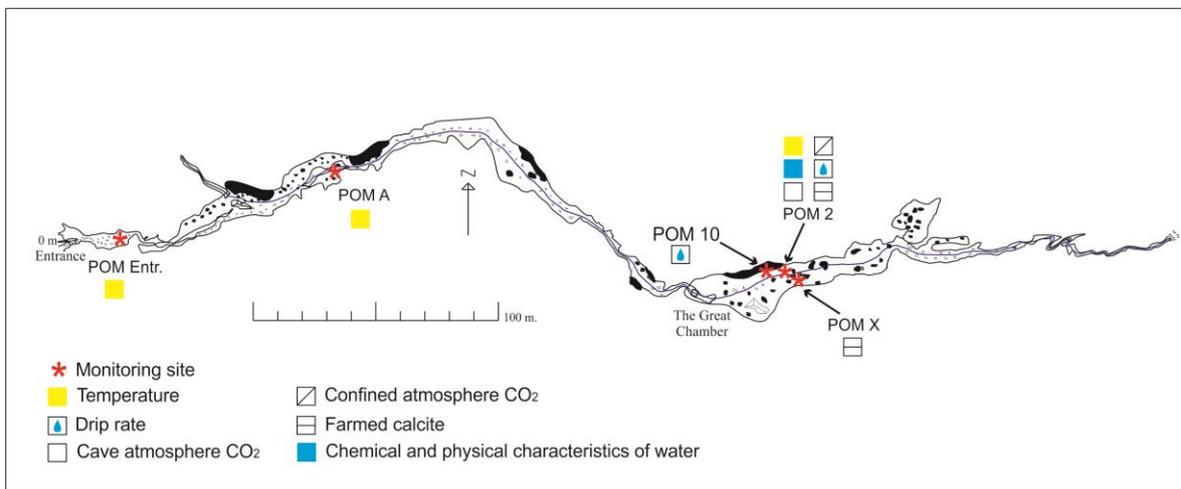
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445 **Figures and tables**

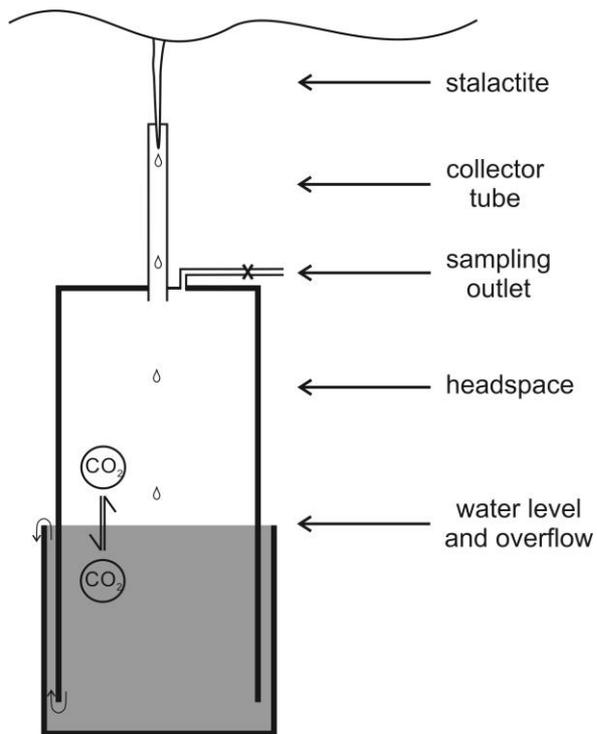
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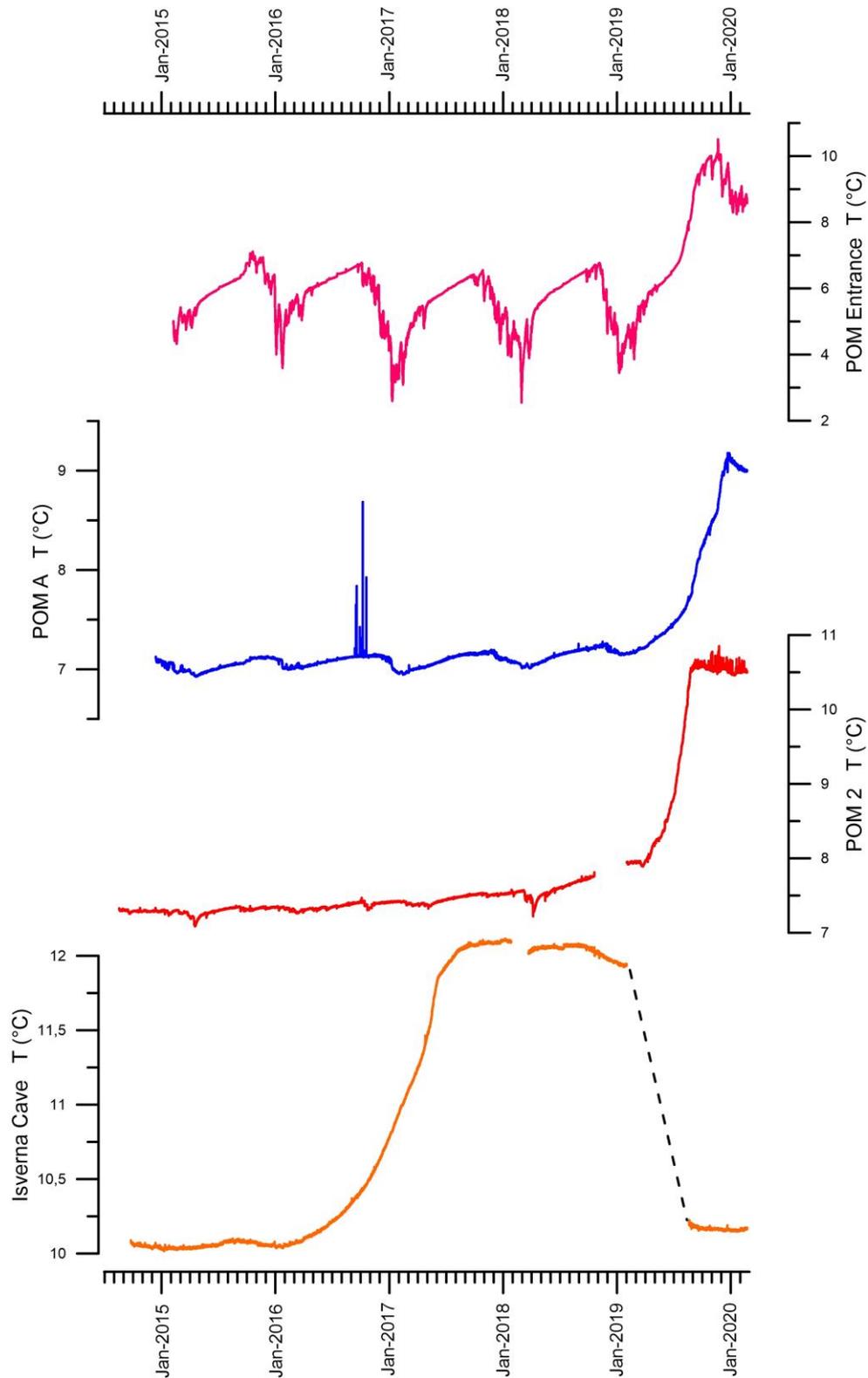
448 Fig. 1 – Cave map with location of monitoring points and measured parameters (modified

449 from Drăgușin et al., 2017a).



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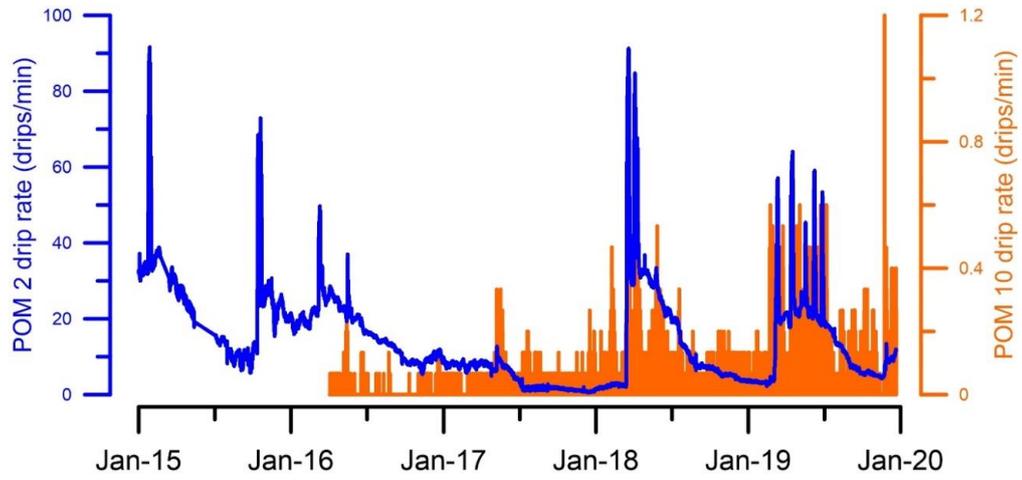
451 Fig. 2 – Functioning scheme of the water-air equilibrator (from Drăgușin et al., 2017a)



452

453 Fig. 3 – Temperature records from POM Entrance, POM A, POM 2, and Isverna Cave. During the
 454 summer of 2016, several events of higher temperature are visible at POM A, which we presume are
 455 due to the presence of bats near the logger.

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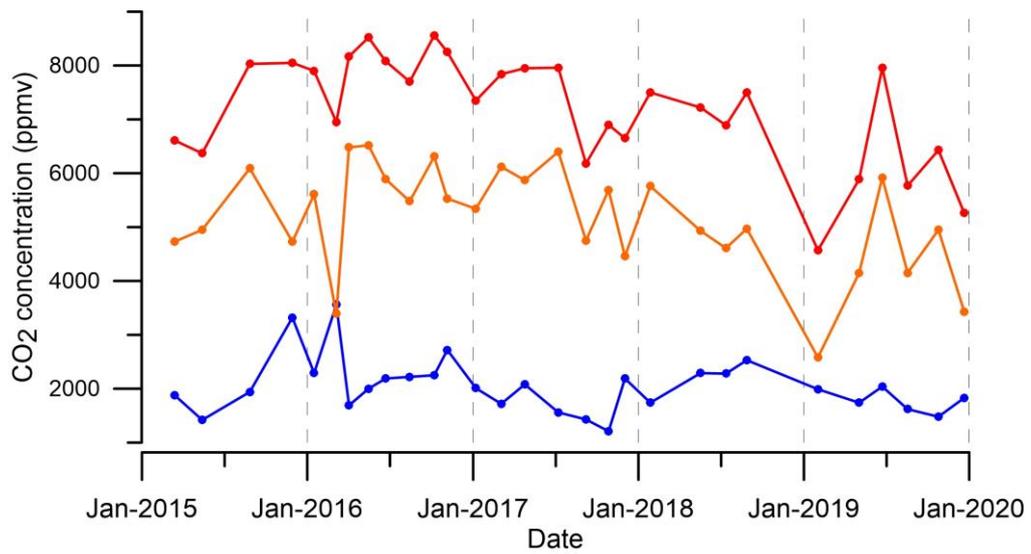


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458 Fig. 4 – Drip rate at POM 2 and POM 10.

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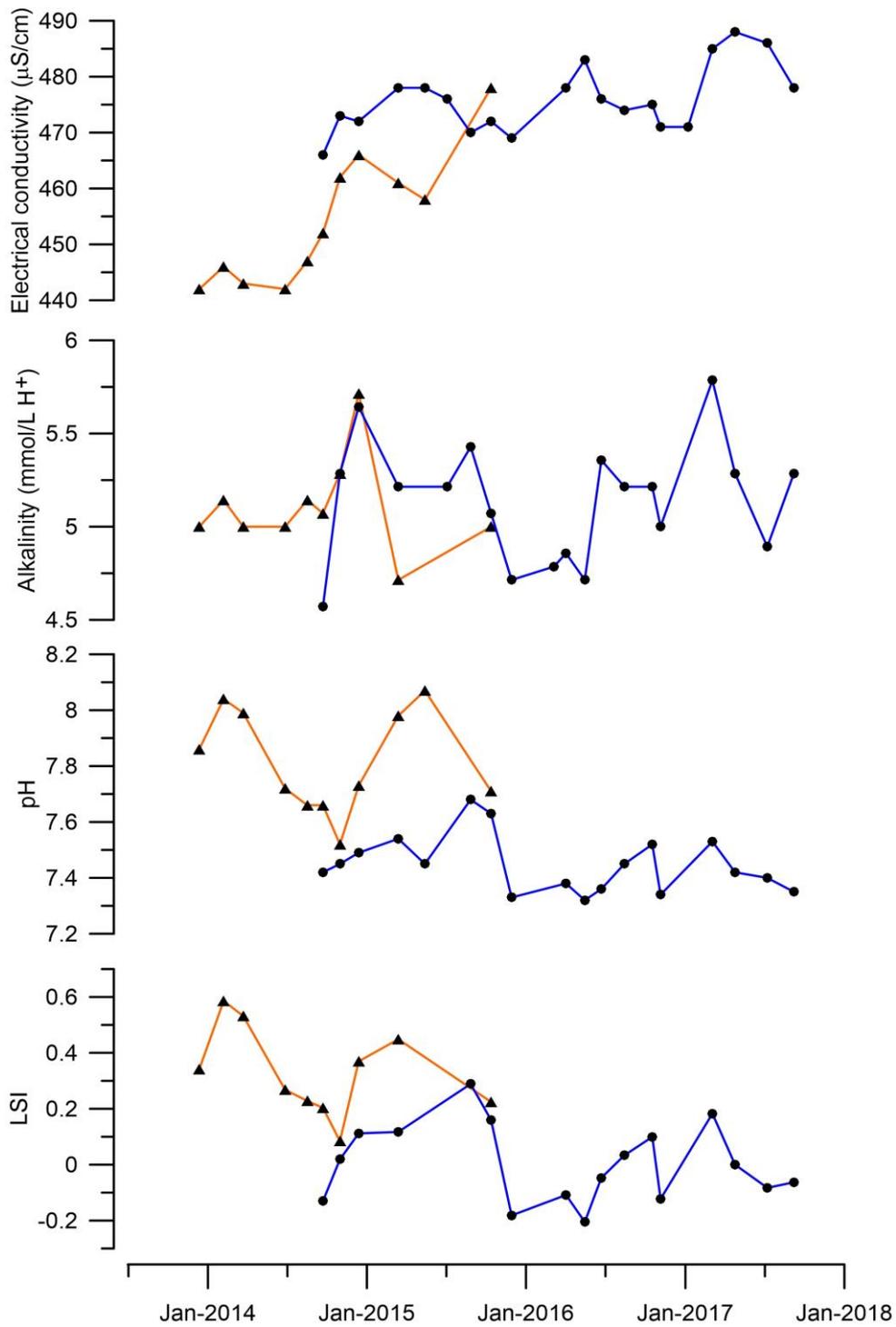
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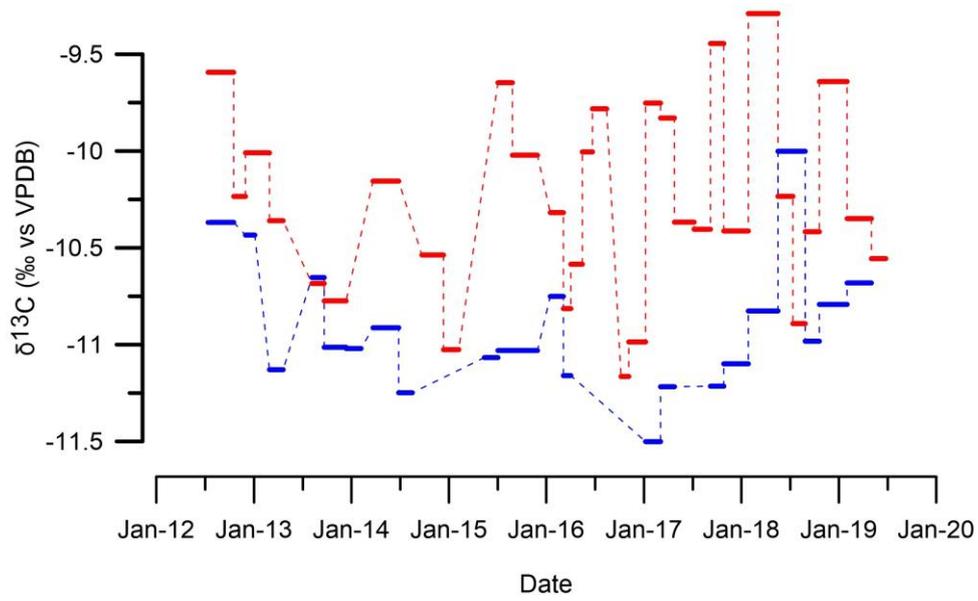
462 Fig. 5 – $CO_{2\text{ATM}}$ (blue), $CO_{2\text{HS}}$ (red), and ΔCO_2 (orange).

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465 Fig. 6 – Electrical conductivity, alkalinity, pH and calcite saturation index of water samples from
 466 the drip site POM 2 (triangles) and the water-air equilibrator (dots).



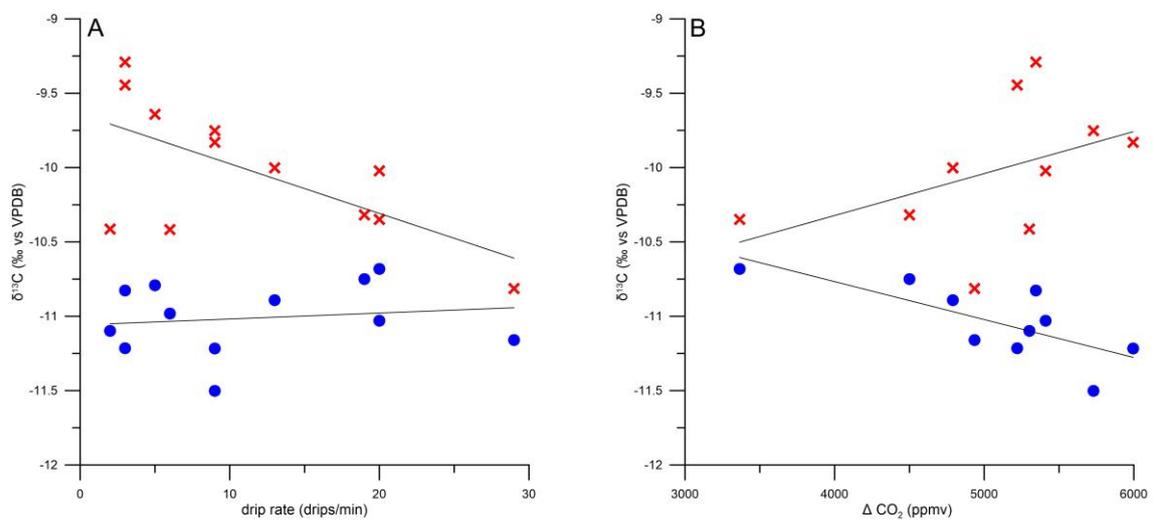
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468 Fig. 7 - $\delta^{13}\text{C}$ of farmed calcite at POM 2 (blue) and POM X (red).

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473 Fig. 8 – A. $\delta^{13}\text{C}$ and drip rate at POM X (red) and POM 2 (blue); B. $\delta^{13}\text{C}$ and ΔCO_2 at POM X (red)

474 and POM 2 (blue).

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Average drip rate (drips/min)	1.0							
POM 2 $\delta^{13}\text{C}$ (‰ vs VPDB)	0.1	1.0						
POM X $\delta^{13}\text{C}$ (‰ vs VPDB)	-0.6	-0.1	1.0					
$\Delta^{13}\text{C}$ (‰ vs VPDB)	-0.6	-0.5	0.9	1.0				
ΔCO_2 (ppmv)	-0.5	-0.7	0.4	0.7	1.0			
Average CO_2 ATM (ppmv)	0.7	0.4	-0.5	-0.6	-0.2	1.0		
Average CO_2 HS (ppmv)	0.0	-0.4	0.1	0.3	0.8	0.4	1.0	

486

487 Table 3. Spot measurements of water samples.

Date	CO_2 ATM (ppmv)	Water T (°C)		pH		EC ($\mu\text{S}/\text{cm}$)		Alcalinity ($\text{mg}/\text{L H}^+$)		LSI	
		Eq.	Drip	Eq.	Drip	Eq.	Drip	Eq.	Drip	Eq.	Drip
12/12/2013	2030		5.2		7.9		442		5.0		0.3
6/2/2014	1550		7.2		8.0		446		5.1		0.6
23/3/2014	960		8.2		8.0		443		5.0		0.5
27/6/2014	1770		8.5		7.7		442		5.0		0.3
17/8/2014	2270		8.3		7.7		447		5.1		0.2
22/9/2014	2470	7.6	7.7	7.4	7.7	466	452	4.6	5.1	-0.1	0.2
31/10/2014	3440	7.3	7.0	7.5	7.5	473	462	5.3	5.3	0.0	0.1
13/12/2014	3319	7.1	7.4	7.5	7.7	472	466	5.6	5.7	0.1	0.4
14/3/2015	1880	8.3	7.2	7.5	8.0	478	461	5.2	4.7	0.1	0.4
14/5/2015	1400	7.8	6.6	7.5	8.1	478	458				
4/7/2015		8.9				476		5.2			
27/8/2015		8.1		7.7		470		5.4		0.3	
13/10/2015		7.1	7.0	7.6	7.7	472	478	5.1	5.0	0.2	0.2
29/11/2015		8.2		7.3		469		4.7		-0.2	
5/3/2016								4.8			
2/4/2016		8.1		7.4		478		4.9		-0.1	
15/5/2016		7.6		7.3		483		4.7		-0.2	
22/6/2016		7.9		7.4		476		5.4		0.0	
14/8/2016		8.6		7.5		474		5.2		0.0	
17/10/2016		8.4		7.5		475		5.2		0.1	
5/11/2016		8.1		7.3		471		5.0		-0.1	
7/1/2017		7.2				471					
4/3/2017		7.6		7.5		485		5.8		0.2	

25/4/2017		7.9		7.4		488		5.3		0.0	
8/7/2017		8.1		7.4		486		4.9		-0.1	
7/9/2017		8.2		7.4		478		5.3		-0.1	

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