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Émilie Dassié, Dominique Genty, Aurélie Noret, Xavier Mangenot, Marc Massault, Nicolas Lebas, Maxence Duhamel, Magali Bonifacie, Marta Gasparrini, Bénédicte Minster, et al.

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1 A newly designed analytical line to examine fluid inclusion isotopic compositions in a variety of  
2 carbonate samples

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8

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22 **Key points:**

23 A new fluid inclusion analytical line with a productivity up to ten carbonate isotopic  
24 measurements per working day

25

26 A new reliable and accurate fluid inclusion analytical line for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  fluid inclusion  
27 analyses in carbonates

28

29 Fluid inclusion  $\delta^{18}\text{O}$  of diagenetic cements agree, within 1 ‰, with the  $\delta^{18}\text{O}$  independently  
30 derived from  $\Delta_{47}$  measurements

31

32 **Abstract**

33  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of fluid inclusions in carbonates provide insights into temperatures and fluid  
34 chemical compositions prevailing during the carbonate precipitation, however various analytical  
35 restrictions limit a wider application of this proxy. This paper presents a new fluid inclusions  
36 isotopic analytical line coupled to an online cavity ring-down spectrometer that increased the  
37 analytical productivity up to ten carbonate samples per working day. This efficiency allowed for  
38 the first time to assess the reliability a large set of water samples with size ranging from 0.1 to 1  
39  $\mu\text{L}$ . Good reproducibility ( $\pm 0.5\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 2\text{‰}$   $\delta\text{D}$ ;  $1\sigma$ ) is obtained for water quantity  
40 superior or equal to 0.3  $\mu\text{L}$  and no evidence of memory effect is found. The line is further tested  
41 using two types of natural carbonates: (1) modern speleothems samples from caves for which  
42  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of drip water were measured and (2) diagenetic carbonates for which the  
43  $\delta^{18}\text{O}$  of the parent water were independently back-calculated from carbonate clumped isotope  $\Delta_{47}$   
44 measurements. Speleothem fluid inclusion values despite falling close to the Global Meteoritic  
45 Water Line are not always representative of the isotopic composition of the parent drip water.  
46 Results on diagenetic cements show that the  $\delta^{18}\text{O}_{\text{water}}$  values measured in fluid inclusions agree,  
47 within 1 %, with the  $\delta^{18}\text{O}_{\text{water}}$  independently derived from  $\Delta_{47}$  measurements. Overall, this study  
48 confirms the reliability and accuracy of the developed analytical line for carbonate fluid  
49 inclusion analyses with a good reproducibility obtained for water quantity above 0.3  $\mu\text{L}$ .

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55 **1. Introduction**

56 Fluid inclusions are fluid-filled voids sealed within minerals that represent relicts of the  
57 paleo-water having precipitated the minerals (i.e. parent water).  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses of fluid  
58 inclusions can provide insights into temperatures and chemical conditions prevailing during the  
59 precipitation of carbonate minerals. While temperature, salinity, and pressure conditions at the  
60 time of fluid inclusion trapping can be deduced from micro-thermometric measurements on  
61 diagenetic carbonates (Goldstein and Reynolds 1994),  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of fluid  
62 inclusions is still technically challenging to measure in carbonates, mainly due to the small  
63 quantity of water extractable from the crushing of these minerals. Obtaining  $\delta^{18}\text{O}$  and  $\delta\text{D}$   
64 composition of diagenetic carbonate fluid inclusions would however have major scientific  
65 purposes such as a better characterization of the water origin and evolution in carbonate systems  
66 from both Earth surface (e.g. palaeosols or speleothems) and sub-surface (e.g. groundwaters).  
67 The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses of fluid inclusions in diagenetic carbonates may provide information  
68 about chemical conditions prevailing in sedimentary units over the evolution of sedimentary  
69 basins. This would allow for a better characterization of past basin groundwaters, as well as their  
70 evolution during water/rock interactions over time. In speleothems (cave carbonate concretions),  
71 fluid inclusions preserve information of the isotopic composition of past cave drip waters; they  
72 are relicts of past precipitations averaged over a period of few months to few years (Hendy et al.,  
73 1969; Genty et al., 2014). Combined with speleothem carbonates  $\delta^{18}\text{O}$  analyses,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of  
74 speleothem fluid inclusions can be used as a direct proxy for moisture source, amount history of  
75 precipitation (Schwarcz et al., 1976), and/or cave paleo-temperatures (which is close to the mean  
76 annual temperature outside the cave, assuming that an isotopic equilibrium state is reached  
77 (Mickler et al., 2004)).

78  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compositions of speleothem fluid inclusions have been analyzed since the  
79 pioneering work of Schwarcz et al. (1976), but until recently, technics were imprecise, time-  
80 consuming, and very restrictive in term of sample quantity. Over the last decade, various  
81 analytical lines and set-up were used, all of them unique in their design (i.e. Dallai et al., 2004;  
82 Vonhof et al., 2006, 2007; Dublyansky and Spötl, 2009). Recent studies have presented laser  
83 spectroscopy (Cavity-Ring Down Spectroscopy (CRDS) PICARRO) as a valuable method to  
84 analyze simultaneously  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of speleothem fluid inclusions (Arienzo et al., 2013;  
85 Affolter et al., 2014; Uemura et al., 2016). Arienzo et al. (2013) were the first to develop an on-  
86 line analytical line coupled to a CRDS that allows the direct measurement of both  $\delta^{18}\text{O}$  and  $\delta\text{D}$   
87 on speleothem fluid inclusions. A speleothem calcite chip is crushed into a 115 °C heated line,  
88 which is entirely made of stainless steel. The crusher is a modified Nupro vacuum valve. They  
89 added an injection port to be able to analyse water standards. The water released by injection  
90 and crushing is carried *via* a carrier gas (dry Nitrogen) to an expansion volume. This expansion  
91 volume serves as reservoir to feed the CRDS analyzer. The main advantage of this line is that the  
92 volume, once isolated from the upstream part of the line, provides a continuous stable signal to  
93 be analyzed. For water samples of 0.5  $\mu\text{L}$  or more, the precision of this analytical line is 0.4 ‰  
94 for  $\delta^{18}\text{O}$  and 1.1 ‰ for  $\delta\text{D}$ . The time needed to analyze a speleothem sample is in the range of 1  
95 to 2 hours. The second analytical line, created by Affolter et al. (2014) is constantly under humid  
96 condition. A humid background of set  $\text{H}_2\text{O}$  concentration and known  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values is  
97 constantly flushed through the line and analysed by the CRDS analyser. A humid background  
98 allows for the measurements of fluid inclusion waters to be performed close to the optimal water  
99 vapor concentration range of the PICARRO analyser (17,000 – 23,000 ppmv). Speleothem  
100 calcite chips are crushed using a hydraulic press. This line has the same injection port as Arienzo

101 et al. (2013) to enable manual injections of water samples. Fluid inclusion and injection waters  
102 are measured on top of the background line. This technic allows the PICARRO analyser to be  
103 more stable and gets rid of the memory effect. For water samples of 1  $\mu\text{L}$  or more, the precision  
104 of this analytical line is 0.4 ‰ for  $\delta^{18}\text{O}$  and 1.5 ‰ for  $\delta\text{D}$ , this precision decreases for smaller  
105 quantities of water. The time needed to analyze a speleothem sample is in the range of 2 to 5  
106 hours. Uemura et al. (2016) developed a new highly sophisticated line resembling the Arienzo et  
107 al. (2013) design. They have however custom-made glass devices for the three main units, the  
108 crusher, injection port, and expansion chamber. Another difference with the Arienzo et al. (2013)  
109 line is the use of a cryogenic trap to collect the water released from the speleothem before  
110 diluting it in the expansion chamber. This new design permits low contents of water (50-260 nL)  
111 to be analyzed with a precision of 0.05 to 0.61 ‰ for  $\delta^{18}\text{O}$  and 0 to 2.9 ‰ for  $\delta\text{D}$ . However,  
112 analysis time is 7 hours per sample. Thanks to those recent studies, potential of isotope  
113 measurements of fluid inclusion water is now fully recognized. However, various analytical  
114 limitations such as sample size restrictions or time consuming analysis are still making a wider  
115 application of this climate proxy difficult.

116 In this study we present a new analytical line based on both Arienzo et al. (2013) and  
117 Affolter et al. (2014) designs, named for the rest of the manuscript as the Miami and Bern lines,  
118 respectively. Our goal is to increase the productivity of the analytical line while keeping the  
119 quantity of needed water realized by crushing below 0.5  $\mu\text{L}$ . Sample quantity is a critical  
120 parameter to ensure the possibility of analyzing (1) different types of natural carbonate samples,  
121 (2) carbonates with relatively low water content, and (3) several replicates of a single carbonate  
122 sample. We therefore assessed, for the first time, errors associated with sample sizes ranging  
123 from 0.1 to 1 $\mu\text{l}$ . This manuscript first describes technical aspects and design of this new

124 analytical line. A thorough assessment of the reliability of water sample measurements was then  
125 achieved to calculate the minimum fluid inclusion quantity needed to obtain reliable  $\delta^{18}\text{O}$  and  $\delta\text{D}$   
126 values. At last, we present results from natural carbonates samples: speleothems and diagenetic  
127 carbonates (calcites and dolomites).

128

## 129 **2. Analytical line description**

### 130 ***2.1. Material***

131 A schematic of the line is presented in Figure 1; it includes three main units, a water vapor  
132 background generator section, an injection line permitting both water injections and crushing of  
133 carbonate material, and a bypass line. The entire line is continuously flushed with dry nitrogen  
134 gas and heated at a constant temperature of 130 °C with warming bands. The heated line, that is  
135 controlled at two different locations, is wrapped in aluminum foil to permit homogeneous  
136 heating conditions. The heating ensures the absence of cold spots (<100 °C) which could lead to  
137 the condensation of the water vapor. A layer of insulating cork material is added to protect the  
138 line from external environment and avoid heat loss.

139

#### 140 *Water vapor background generator*

141 The water vapor background generator is similar to the one developed for the Bern line.  
142 The first component of the line is a water reserve containing an in-house water standard named  
143 BAFF. BAFF is a natural fresh water, collected in the Baffin Island (North of Canada). It was  
144 sampled in large enough quantity (about 30 L) to be used as an internal reference water standard  
145 of the GEOPS laboratory. BAFF was calibrated against international standards: Vienna  
146 Standard Mean Ocean Water scale (VSMOW), Greenland Ice Sheet Precipitation (GISP), and

147 Standard Light Antarctic Precipitation (SLAP). Analyses made on a mass spectrometer (IRMS  
148 Thermo Finnigan Delta Plus, equipped with an equilibrating bench), gave the following results:  
149  $\delta^{18}\text{O} = -15.42 \text{ ‰} \pm 0.03 (1\sigma) (n=9)$ ;  $\delta\text{D} = -121.85 \text{ ‰} \pm 0.86 (1\sigma) (n=6)$ .

150         BAFF standard is extracted from the water reserve by a high precision peristaltic pump  
151 with planetary traction (ISMATEC # ISM945D). Water from the peristaltic pump is carried by a  
152 TYGON LMT-55 tubing (SCO0188T; ID: 0.13 mm and wall: 0.91 mm), to a fused silica  
153 capillary (IDEX Heath & Science FS-115; ID: 150  $\mu\text{m}$ ; wall: 360  $\mu\text{m}$ ; length: ~10 cm), to a  
154 vaporizer (an union tee: Swagelok # SS-200-3). The carrier gas arrives to the vaporizer from the  
155 upstream side of the union tee and the BAFF standard arrives through the side. The fused silica  
156 capillary, carrying BAFF standard, slightly touches the wall of the union tee which  
157 instantaneously vaporized it and carried it downstream. A purge is added to the line to evacuate  
158 parts of the vaporized water. This purge consists of a 5 cm stainless steel capillary (1/16")  
159 attached to the line via a union tee (Swagelok # SS-200-3). Downstream of the purge is a mixing  
160 cavity that reduces the water pulses coming from the vaporizer and homogenizes the water vapor  
161 background. This mixing cavity consists of a 150 mL stainless steel cylinder (Swagelok 304L-  
162 HDF4-150-PD). The quantity of water vapor background going through the line is modified by  
163 increasing or decreasing the velocity of the peristaltic pump. A three ways valve (Swagelok SS-  
164 41GXS2) separates the water vapor background generator section from both the injection and  
165 bypass lines.

166

#### 167 *Injection line*

168         The first component of the injection line is the syringe injection unit that is similar to  
169 both the Miami and Bern lines. It consists of a septum injection nut (Cluzeau Info Labo #



170 EN2SI) fixed to the line *via* a union tee (SS-200-3). A 1  $\mu$ L syringe (SGE Analytical Sciences  
171 syringe) is used to inject water standards with quantities ranging from 0.1 to 1  $\mu$ L. The second  
172 component is the crushing device (Figure 2) that consists of a modified vacuum valve (Swagelok  
173 #SS-4BG), in which the valve stern was taken apart from the valve body. The valve body was  
174 milled until obtaining a 1 cm diameter cavity. The stern cap was replaced by a custom-made  
175 stainless steel cylindrical hammer (see Figure 2 for details). To crush the sample, the valve stern  
176 is used as a power hammer, with the valve bellow leading to the crush of the carbonate sample  
177 by vertical pressure and vibrations. Similar to the Miami line, a 0.5  $\mu$ m pore size (Swagelok SS-  
178 4F-05) in-line filter is inserted downstream from the crusher to prevent particles of carbonate to  
179 be transported to the PICARRO analyzer. A 75 ml expansion volume (Swagelok 304L-HDF4-  
180 75-PD) is added to buffer the water coming from injection or crushing. This volume tends to  
181 mimic the PICARRO vaporizer units used in the Bern line, without diluting the signal.

182

### 183 *Bypass line*

184 The bypass line consists of a 1/8" stainless steel tubing. In the Bern line the stabilization  
185 time after opening the line was around three hours. By switching to this bypass line, the  
186 PICARRO analyser remains under continuous humid flow when we open the crusher to insert  
187 carbonate samples which reduce considerably the stabilization time to about 10 min.

188

## 189 **2.2. Protocol for analysis**

190 For each analytical session a similar protocol is followed (1) the PICARRO analyzer is  
191 turned on, (2) the dry nitrogen flushing valve is open, and (3) the peristaltic pump is turned on.  
192 A quiescence time of half an hour is necessary to obtain a stable humid background. The

193 determined conditions for a stable humid background are based on the standard deviation values  
194 over five minutes: H<sub>2</sub>O concentration  $\pm 10$  (1 $\sigma$ ) ppmv,  $\delta^{18}\text{O} \pm 0.2$  (1 $\sigma$ ) ‰ and  $\delta\text{D} \pm 4$  (1 $\sigma$ ) ‰.  
195 Once these conditions are reached, six 0.3  $\mu\text{L}$  injections of a combination of three certified water  
196 standards (-5‰; -8‰, ESKA, and MAZA; Table 1) are made. Those values are used as part of  
197 the daily calibration. Between each injection, a quiescence time of  $\sim 10$  min is necessary to  
198 reach again background stabilization before the next injection. Once these water standard  
199 injections are done, the line set up is switched to the bypass line to insert the carbonate sample in  
200 the crusher unit. Once the carbonate sample is loaded, the incoming flux is switched back to the  
201 injection line. Another quiescence of  $\sim 15$  min is necessary to remove all impurities and  
202 plausible water contamination at the surface of the sample and to obtain a stable humid  
203 background. Finally, the sample is manually crushed, to a fine powder. The water initially  
204 trapped as fluid inclusions is released, vaporized, and carried to the PICARRO analyzer for  
205 direct isotopic measurements. The line is switched to the bypass line to insert another carbonate  
206 sample in the crusher unit. At the end of the day six 0.3  $\mu\text{L}$  injections of the same certified water  
207 standards analyzed at the beginning of the day are ran to complete the daily calibration. This  
208 analytical set up allows to analyze about 10 carbonate samples per day on a regular, 8 hours,  
209 work day (see Figure 3 for details).

210

### 211 **2.3. Data analysis**

212 The data analysis is based on the method developed by Affolter et al. (2014). The signal  
213 is a mix between the background water and the water sample injected or liberated during the  
214 crushing. The shape of the signal for one measure (for all three parameters, water concentration,  
215  $\delta^{18}\text{O}$ , and  $\delta\text{D}$ ) resemble an abrupt peak followed by a slow return to background conditions. We

216 need to integrate the product of the water amount and its isotopic value with regard to the  
 217 background to calculate sample isotopic  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. To reduce the analytical noise, a  
 218 20-points-rolling median is applied to the three variables. This step was not done by Affolter et  
 219 al. (2014) since their PICARRO analyzer (L1102-i) gives one value averaged over twelve  
 220 seconds of measurement while our PICARRO analyzer (L2120) gives one value averaged over  
 221 two seconds. The deconvolution between the signal and the baseline is a simple integration over  
 222 the duration of the mix, with removal of the baseline, following equation (1) and (2):

$$(1) \quad \delta^{18}\text{O} = \frac{\overline{[\text{H}_2\text{O}]} * \frac{\sum_i ([\text{H}_2\text{O}]_i * \delta^{18}\text{O}_i)}{\sum_i [\text{H}_2\text{O}]_i} - ([\text{H}_2\text{O}]_{\text{background}} * \delta^{18}\text{O}_{\text{background}})}{\overline{[\text{H}_2\text{O}]} - [\text{H}_2\text{O}]_{\text{background}}}$$

$$(2) \quad \delta\text{D} = \frac{\overline{[\text{H}_2\text{O}]} * \frac{\sum_i ([\text{H}_2\text{O}]_i * \delta\text{D}_i)}{\sum_i [\text{H}_2\text{O}]_i} - ([\text{H}_2\text{O}]_{\text{background}} * \delta\text{D}_{\text{background}})}{\overline{[\text{H}_2\text{O}]} - [\text{H}_2\text{O}]_{\text{background}}}$$

224  
 225  
 226  
 227  
 228 The trickier part is to select the duration of the integration, by finding an objective sample  
 229 signal beginning and end. To determine the signal inflection point we use an objective criterion  
 230 of  $d\text{H}_2\text{O}(t)/dt \geq 10 \text{ ppmv.s}^{-1}$ . The end of the sample signal is set when  $d\text{H}_2\text{O}(t)/dt \geq 0 \text{ ppmv.s}^{-1}$   
 231 over a period of nine consecutive values. We automated these calculi by developing a VBA  
 232 application (<https://github.com/MaxenceDuhamel/AUTOPEAK-PICARRO.git>).

233

### 234 3. Calibration of the line using water standards

### 3.1. Determination of the optimal water background concentration

To test the optimal water background concentration, the same protocol as in Affolter et al. (2014) was followed. This test was made over the course of eleven different days from three different months (Table 2 and Figure 4). We varied the background water concentration from 2,000 to 24,000 ppmv and analyzed it over a period of three hours. Data acquired over the last 30 minutes were averaged and used as the value for the set background condition (Table 2 and Figure 4). For  $\delta^{18}\text{O}$  values, the standard deviation is high for concentration below 7,000 ppmv and then become stable with a standard deviation of 0.2 ‰. For  $\delta\text{D}$ , the standard deviation also decreases in a nearly exponential profile with the increase in  $\text{H}_2\text{O}$  concentration. The slope of the decrease become smaller around 7,000 ppmv, and the standard deviation of the  $\delta\text{D}$  measurements stays below 4 ‰ until 24,000 ppmv. As for the  $\text{H}_2\text{O}$  concentration, the standard deviation is stable around 10 ppmv until 11,000 ppmv, and then starts to increase. In regards to those results, the water background concentration for routine measures was set to 8,000 ppmv (Figure 4, red squares).

### 3.2. Estimation of sample's water concentration

Various aliquot of water ranging from 0.1 to 1  $\mu\text{L}$  (30 replicates for each aliquot) were injected to define the relationship between the quantity of water injected and the integrated water volume measured on the PICARRO analyzer (see section 2.3 water integration). A significant linear relationship is found between the quantity of water injected and the integrated water volume measured on the PICARRO (Figure 5). The equation derived from this linear regression:  $7.436e-7 (\pm 3.464e^{-9}) x + 8.049 (\pm 2.852e^{-3})$  ( $R^2 = 0.994$ , significant at 99%) is used to determine the quantity of water released during carbonate sample crushing procedure.

258

### 259 **3.3. Calibration of the instrument**

260 Measured raw isotopic data coming from the instrument need to be converted into  
261 VSMOW scale. Four laboratory standards waters (-5‰, -8‰, ESKA, and MAZA see Table 1),  
262 previously calibrated against VSMOW, GISP, and SLAP, are used to perform the isotopic  
263 calibration of the instrument (Table 3 top panel and Figure 6). The range of the calibration is  
264 -1.18 to -13.96 ‰ for  $\delta^{18}\text{O}$  and -100.15 to 1.28 ‰ for  $\delta\text{D}$ , spanning the entire range of isotopic  
265 values measured in fluid inclusions from natural carbonate samples. For each calibration curve  
266 presented in Figure 6, at least three replicates of 0.5  $\mu\text{L}$  of laboratory standards were measured  
267 (Table 3 top panel). The mean calibrations (average of the five daily ones, Table 4) are  $y = 0.979$   
268  $(\pm 0.005) * \text{measured } \delta^{18}\text{O} + 1.371 (\pm 0.049)$  ( $R^2 = 0.999$ , significant at 99%) and  $y = 0.967 (\pm$   
269  $0.004) * \text{measured } \delta\text{D} - 1.535 (\pm 0.261)$  ( $R^2 = 0.999$ , significant at 99%). The 99 % confidence  
270 interval per standards, following a Student t test, range from 0.15 to 0.28 ‰ for  $\delta^{18}\text{O}$  and from  
271 0.79 to 1.71 ‰ for  $\delta\text{D}$  (Figure 6.C. and D.). These mean calibrations are used to correct both  
272 water injections and carbonate fluid inclusion water analyses. Daily calibrations are  
273 systematically compared to these mean calibrations to evaluate a potential drift of the instrument.  
274 Over the period of one year no significant drift was observed.

275 Additional certified laboratory standards waters (-30‰, NAN, DOMEK, and -10‰) were  
276 analyzed and plotted on top of the mean calibration curves to test the validity of these calibration  
277 equations for out of range water standards (Table 3 bottom panel and Figure 6.C. and D.). Each  
278 of these standards fall on the calibration lines, validating the linearity of the regressions which  
279 will allow to correct out of calibration-range sample values. To assess the memory effect of our  
280 line, five samples of MAZA were injected followed by five of DOMEK, two standards with very

281 different isotopic composition (Table 1). The mean values of the first two DOMECC values is not  
282 statistically different than the mean of the last two ones. We therefore concluded that there is no  
283 evidence of memory effect in our system (similar as Affolter et al., 2014).

284

#### 285 **4. Water sample reproducibility test**

286 We document the accuracy and precision of the line by doing replication measurements  
287 of a laboratory water standard named DIDO2. It is a tap water, demineralized, and calibrated  
288 against VSMOW, GISP, and SLAP. DIDO2 analyses made on a mass spectrometer (IRMS  
289 Thermo Finnigan Delta Plus, equipped with an equilibrating bench), gave  $\delta^{18}\text{O} = -7.30 \text{ ‰} \pm 0.04$   
290  $(1\sigma)$ ;  $\delta\text{D} = -49.91 \text{ ‰} \pm 0.64 (1\sigma)$  ( $n=7$ ). 30 replicates of different aliquots of DIDO2 ranging  
291 from 0.1 to 1  $\mu\text{L}$  at a 0.1  $\mu\text{L}$  increment were analysed (Figure 7). This is the first time such  
292 experiment was completed owing to the fact that it has been time consuming on previous  
293 analytical line designs. We used a bootstrap method to calculate the confidence interval of the  
294 mean. For 3% test over 1,000 iterations, mean  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are not statistically different  
295 for injected volumes ranging from 0.3 to 0.8  $\mu\text{L}$ . Standard deviation of the difference between  
296 the certified values and the measured values for a given injected volume are presented in Figure  
297 7 (Bottom). For injection volume above or equal to 0.2  $\mu\text{L}$ , the standard deviation for  $\delta^{18}\text{O}$   
298 reaches the acceptable value of 0.5 ‰. For  $\delta\text{D}$ , acceptable value of 2 ‰ is reached for injected  
299 volumes above or equal to 0.3  $\mu\text{L}$ . This test indicates that our line has a good  $\delta^{18}\text{O}$  and  $\delta\text{D}$   
300 reproducibility for sample size above 0.3  $\mu\text{L}$ .

301

#### 302 **5. Isotopic composition of fluid inclusions from natural carbonate samples**

303 To validate the reliability of our analytical line, two different types of natural carbonate  
304 samples are analyzed: (1) modern speleothem samples from caves for which  $\delta^{18}\text{O}$  and  $\delta\text{D}$   
305 composition of drip water are known. It is commonly assumed that isotopic composition of  
306 speleothem fluid inclusions reflects the isotopic composition of the parent drip water, itself  
307 closely linked to rainfall variability (Genty et al., 2014); and (2) diagenetic carbonates for which  
308 the  $\delta^{18}\text{O}$  of the mineralizing waters were independently back-calculated by combining clumped  
309 isotope ( $\Delta_{47}$ ) temperatures and  $\delta^{18}\text{O}$  values of the carbonate (Mangenot et al., 2017, 2018). All  
310 the fluid inclusion isotopic values from carbonate samples are presented in Table 5.

311

## 312 **5.1. Speleothems**

### 313 *Sample sites description*

314 Speleothems used in this study come from two different locations in Northern Europe:  
315 Sweden (K13) and Belgium (HanGril). No petrography analyses were done due to the small  
316 quantity of calcite available for analyses.

317 K13 stalagmite comes from the Korallgrottan Cave, North West of Sweden, in the  
318 Caledonian mountain range ( $64^{\circ} 53'16'' \text{ N}$ ;  $14^{\circ} 9'30'' \text{ E}$ ) located 540 to 600 m above sea level  
319 (Sundqvist et al. 2007). K13 is a 7.7 cm long stalagmite that grew mainly between 10.6 ky to 6.9  
320 ky, with a last short growth period around 2 ky (K. Holmgren and H. Sundqvist, unpublished  
321 data). Calcite samples for fluid inclusion analyses were taken at the top of the stalagmite (the  
322 first 5 mm). We assume that the isotopic signal of the input water (rainfall and dripping water)  
323 did not change significantly over the last 2 ky, therefore, samples taken at the top of the  
324 stalagmite (from ~2 ky ago) should be representative of modern day values. Korallgrottan cave  
325 stalactite drip water was collected by H. Sunqvist and K. Holmgren during a monitoring

326 campaign between October 2013 and November 2014. Isotopic values of cave drip water feeding  
327 the stalagmite are  $\delta^{18}\text{O} = -11.95 \pm 0.13 \text{ ‰}$  ( $1\sigma$ ) and  $\delta\text{D} = -85.03 \pm 0.77\text{‰}$  ( $1\sigma$ ) ( $n=9$ ) (Sunqvist  
328 et al., 2007; Table 7).

329 HanGril samples come from the Han-sur-Lesse Cave, South of Belgium ( $50^\circ 7'16'' \text{ N}$ ;  $5$   
330  $^\circ 11'46'' \text{ E}$ ) located 160 m above sea level. Both HanGrilA and HanGrilB are modern calcite that  
331 grew between 1995 to 2012. HanGrilB grew on artificial iron shelves positioned on the floor of  
332 the “Salle du Dôme”, and HanGrilA grew on an artificial tile that was positioned on the  
333 horizontal part of the iron shelf. Regular measurements of cave drip water from a dripping site  
334 located nearby HanGrilA and HanGrilB speleothems, were made at a frequency of one sample a  
335 month in 2011 and two samples a month in 2012. Isotopic values of cave drip water are  $\delta^{18}\text{O} = -$   
336  $7.65 \pm 0.07 \text{ ‰}$  ( $1\sigma$ ) and  $\delta\text{D} = -50.10 \pm 0.39 \text{ ‰}$  ( $1\sigma$ ) ( $n = 36$ ) (Van Rampelbergh et al., 2014;  
337 Table 7). A water sample from the drip water feeding HanGrilA/B deposits was collected in July  
338 2012 giving values close to the aforementioned measurements ( $\delta^{18}\text{O} = -7.37 \text{ ‰}$  and  $\delta\text{D} = -49.15$   
339  $\text{‰}$ ). Cave drip water isotopic measurements can therefore be used as reliable source of  
340 information on speleothem parent water.

341

#### 342 *Sample fluid inclusion concentrations*

343 The relationship between the weight of the speleothem sample and the quantity of the  
344 water released during the crushing is examined (Figure 8A., B, and C). The weight of  
345 speleothem chips varies from 0.04 to 0.84 g, with the amount of water released between 0.09 to  
346 1.12  $\mu\text{L}$ . We observe a positive linear relationship between the amount of speleothem crushed  
347 and the quantity of water released for both K13 and HanGrilB samples, with Pearson correlation  
348 values of 0.95 and 0.90, respectively (both significant at 99 %). We find however, no significant



349 relationship between the sample weight and the amount of water released for HanGrilA samples.  
350 This result points to a heterogeneous distribution of fluid inclusions in stalagmite samples as  
351 already presented in Affolter et al. (2014) and Meckler et al. (2015).

352

### 353 *Isotopic measurements*

354 Isotopic fluid inclusion  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values from K13, HanGrilA, and HanGrilB are  
355 presented in Table 5 and Figure 8.D. Most of the fluid inclusion values are closed to the Global  
356 Meteoritic Water Line (GWML; Craig, 1961), which indicates that enclosed fluid inclusions  
357 were not influenced much by evaporation and should therefore reflect isotopic composition of  
358 parent drip water. The only out of range value (Figure 8.D. black circle) is from a sample that  
359 released a water volume below 0.1  $\mu\text{L}$ , and could not be considered as reliable (see section 4).

360 Mean fluid inclusions  $\delta^{18}\text{O}$  and  $\delta\text{D}$  for each speleothem, are plotted with the isotopic  
361 composition of their parent drip water (Figure 8.E). Recent studies found that local drip water  
362 values are slightly offset towards more negative  $\delta^{18}\text{O}$  values relative to the local or global  
363 meteoritic water line (Genty et al., 2014; Meckler et al., 2015). This offset has been attributed to  
364 condensation on cave walls (Genty et al., 2014). In this study, local drip water from both  
365 Korallgrottan and Han-sur-Lesse caves (Figure 8.E.) fall on the GMWL. This demonstrates that  
366 the signals are of meteoric origin and that no fractionation through evaporation has occurred.

367 Isotope ratio in fluid inclusions from K13 samples are similar (within  $1\sigma$ ) to the isotopic  
368 composition of the parent drip water (Figure 8.E). This indicates that no fractionation occurred  
369 and consequently fluid inclusions in this speleothem is reliable and give isotopic values close to  
370 past rainfall. This is not the case for both HanGrilA and HanGrilB samples. Results from both  
371 speleothem (HanGrilA and HanGrilB) fluid inclusions are similar within  $1\sigma$ , but are significantly

372 different from the parent drip water (Figure 8.E.). Both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  fluid inclusion values are  
373 different from the isotopic composition of the parent drip water, cancelling out a hypothetical  
374 exchange between calcite and fluid inclusion water after its formation. Fluid inclusions in both  
375 HanGrilA and HanGrilB samples might not be in equilibrium with their parent drip water.  
376 Another possible reason for the isotopic composition of an inclusion being different from the  
377 parent water is that the inclusion had leaked. Both HanGrilA and HanGrilB are speleothem  
378 deposited on a flat tile. Those samples might not be representative of natural growth conditions  
379 of stalagmites as already suggested by Labuhn et al. (2015), for similar cave deposits.

380 Section 4 determines that good  $\delta^{18}\text{O}$  and  $\delta\text{D}$  reproducibility are achieved for sample size  
381 above 0.3  $\mu\text{L}$ ; it is also the case for crushed speleothem samples. While the mean isotopic values  
382 between all the crushed samples and the samples that released more than 0.3  $\mu\text{L}$  of water are not  
383 statistically different, the standard deviation and therefore the reproducibility varies. For samples  
384 that released more than 0.3  $\mu\text{L}$ , the reproducibility is about 0.5 ‰ for  $\delta^{18}\text{O}$  and 2 ‰ for  $\delta\text{D}$  while  
385 it is much higher for the other ones, validating 0.3 $\mu\text{l}$  as the minimum water quantity to obtain  
386 robust isotopic fluid inclusions measurements.

387

## 388 **5.2. Diagenetic carbonates**

### 389 *Samples description*

390  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of fluid inclusions were analysed in four calcitic and one dolomitic pore-  
391 filling cements, precipitated in a Middle Jurassic carbonate unit of the Paris basin. Most of the  
392 investigated samples (BEBJ8, VPU4, VPU9, and RN21) were collected at 1700-1800 m depth  
393 (basin depocenter) from a mineral paragenetic sequence already established by Mangenot et al.  
394 (2018) that consists of: (1) a first calcite cement named Cal1 (crystals 100  $\mu\text{m}$  to 3mm), (2) a

395 saddle dolomite cement, named Dol1 (crystals 200  $\mu\text{m}$  to 2mm), (3) a second calcite cement,  
396 named Cal2 (crystals 100  $\mu\text{m}$  to 1mm). A fourth sample (BUF4) was collected at the exposed  
397 southern margin of the basin (Burgundy outcrops) and consists of a vein filling Cal3 (crystals  
398 500  $\mu\text{m}$  to 5mm). Except for BUF4, all the cements were previously investigated in term of  
399 petrography, fluid inclusion microthermometry and stable isotope geochemistry ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$ )  
400 by Mangenot et al. (2017) and Mangenot et al. (2018). Petrographic and microthermometric  
401 analyses of fluid inclusions revealed that all samples host primary and co-genetic populations of  
402 fluid inclusions which did not undergo any post-entrapment modifications (e.g. leakage, thermal  
403 re-equilibration, or refilling processes). The range of homogenization temperatures found for  
404 Cal1, Cal2 and Dol1 fluid inclusions are clustered at  $63 \pm 11^\circ\text{C}$ ,  $80 \pm 10^\circ\text{C}$ , and  $98 \pm 5^\circ\text{C}$ ,  
405 respectively (see Mangenot et al., 2017). Complementary stable isotope analyses ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  
406  $\Delta_{47}$ ) confirmed that these three generations of cements precipitated at distinctive temperatures  
407 and from paleo-waters with different geochemistry. Published  $\Delta_{47}$  compositions and associated  
408  $T\Delta_{47}$  temperatures for Cal1, Dol1, and Cal2 samples, calculated using the universal calibration of  
409 Bonifacie et al. (2017) as well as the additional data for BUF4 sample, are compiled in Table 8.  
410 By combining clumped isotopes temperatures ( $T\Delta_{47}$ ) and  $\delta^{18}\text{O}$  values of the carbonate, the  $\delta^{18}\text{O}$   
411 of the parent water ( $\delta^{18}\text{O}_{\text{water}}$ ) can be reconstructed, here using the fractionation value of oxygen  
412 isotopes between the carbonate and water of O'Neil et al. (1969) for calcite and Horita et al.  
413 (2014) for dolomite. Calculated  $\delta^{18}\text{O}_{\text{water}}$  values and their uncertainties are presented in Table 8.

414

#### 415 *Fluid inclusion measurements*

416  $\delta^{18}\text{O}$  composition of fluid inclusions were measured in the same cement specimens in  
417 order to be directly compared to the  $\delta^{18}\text{O}_{\text{water}}$  values deduced from  $\Delta_{47}$  data (Table 8). Fluid

418 inclusion mean  $\delta^{18}\text{O}$  are:  $2.5 \pm 1.1 \text{ ‰}$  ( $n = 4$ ) for BEBJ8,  $2.4 \pm 1.1 \text{ ‰}$  ( $n = 4$ ) for VPU9,  $0.6 \pm 1.6$   
419  $\text{‰}$  ( $n = 2$ ) for VPU4,  $-3.1 \pm 2.8 \text{ ‰}$  ( $n = 2$ ) for RN21, and  $-6.6 \pm 0.5 \text{ ‰}$  ( $n = 3$ ) for BUF4. Fluid  
420 inclusion  $\delta\text{D}$  values are:  $-18.9 \pm 5.4 \text{ ‰}$  ( $n = 4$ ) for BEBJ8,  $-18.6 \pm 3.1 \text{ ‰}$  ( $n = 4$ ) for VPU9,  $-17.4$   
421  $\pm 1.9 \text{ ‰}$  ( $n = 2$ ) for VPU4,  $-44.2 \pm 7.9 \text{ ‰}$  for RN21 ( $n = 2$ ) and  $-31.2 \pm 1.4 \text{ ‰}$  ( $n = 3$ ) for BUF4  
422 (Table 8). Uncertainties, reported as one standard deviation of the mean, are quite variable for  
423  $\delta^{18}\text{O}$  measurements (between 0.5 and 2.8 ‰), and mostly dependant to the carbonate sample size  
424 and fluid inclusion abundance.

425 The cross-plot between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  is not reported for diagenetic samples as we do not  
426 expect their  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition to fall on the GLWL. However, relationships between  
427  $\delta^{18}\text{O}$  values measured in fluid inclusions and  $\delta^{18}\text{O}_{\text{water}}$  back-calculated from  $\Delta_{47}$  data on the same  
428 mineral can be directly compared and evaluated. This relationship is plotted in Figure 9 with the  
429 1:1 line marked.

430 Although each analytical technique comes with their own working hypotheses and  
431 uncertainties, all the results are remarkably consistent for a total range of variation between -6‰  
432 to +2‰. Notably,  $\delta^{18}\text{O}$  values measured in fluid inclusions agree within  $\sim 1\text{‰}$  with  $\delta^{18}\text{O}_{\text{water}}$   
433 values calculated from  $T\Delta_{47}$  and carbonate  $\delta^{18}\text{O}$  data of the host-mineral. This very good  
434 agreement suggests that both methods reproduce realistic  $\delta^{18}\text{O}_{\text{water}}$  values of the water from  
435 which natural carbonates precipitated, and confirms three important points: i) an independent  
436 cross-validation of both methods from natural samples that experienced a complex burial history  
437 (Mangenot et al. 2018), ii) the absence of substantial isotopic water-rock interaction between the  
438 host carbonate and the fluid inclusion water since mineral precipitation. Given the relatively low  
439 water to rock ratio between the microvolumes of fluid inclusion water and the carbonate matrix,  
440 such isotopic exchanges would likely have changed the isotopic composition of the fluid

441 inclusion water, without changing the  $\delta^{18}\text{O}_{\text{water}}$  back-calculated from the mineral, iii) the primary  
442 and co-genetic natures of fluid inclusions within all of the investigated samples which did not  
443 undergo post-entrapment modifications (e.g. no mixing of different fluid inclusions populations  
444 and no leakage, thermal re-equilibration or and/or refilling processes).

445

## 446 **6. Summary and conclusions**

447 This study presents a newly designed analytical line dedicated to the analyze of fluid  
448 inclusion  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in carbonate samples. The design is based on two previously developed  
449 line, the Miami line (Arienzo et al., 2013) and the Bern line (Affolter et al., 2014) and allow to  
450 increase the productivity up to ten carbonate samples per working day, while being able to keep  
451 the sample size yield below 0.5  $\mu\text{L}$ .

452 We assessed for the first time the reliability of such line by analyzing a large set of water  
453 samples of different size ranging from 0.1 to 1.2  $\mu\text{L}$ . The findings indicated that this newly  
454 designed line has a good  $\delta^{18}\text{O}$  and  $\delta\text{D}$  reproducibility for sample size above 0.2  $\mu\text{L}$  and 0.4  $\mu\text{L}$ ,  
455 respectively. We further tested the line using two type of carbonates samples, speleothems and  
456 diagenetic carbonate. For the speleothem samples, we looked at the relationship between the  
457 weight of the sample and the quantity of the water released during the crushing. The result points  
458 to a heterogeneous distribution of fluid inclusions in stalagmite samples as already presented in  
459 Affolter et al. (2014) and Meckler et al. (2015). We compared speleothem fluid inclusion  $\delta^{18}\text{O}$   
460 and  $\delta\text{D}$  obtained on this new analytical line with isotopic composition of the parent drip water.  
461 Results suggest that the analytical line is valid for speleothem fluid inclusion analyses. However,  
462 isotopic composition of fluid inclusion and parent drip water are not always coherent, pointing  
463 out the need of combining both water drip and fluid inclusions analyses to assess the potential of

464 a stalagmite for paleoclimate study. An independent comparison between  $\delta^{18}\text{O}$  water values  
465 directly measured in fluid inclusions and the  $\delta^{18}\text{O}$  water indirectly back-calculated from  $\Delta_{47}$   
466 composition of diagenetic carbonates revealed that both methods reproduce realistic  $\delta^{18}\text{O}_{\text{water}}$   
467 values, with typical uncertainties of  $\pm 1\%$ . Such results are promising for future application of  
468  $\delta^{18}\text{O}$  and  $\delta\text{D}$  measurements of fluid inclusions from diagenetic carbonates aiming to evaluate the  
469 chemical evolution of ancient groundwaters in sedimentary basins.

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507 **Reference List:**

508 Affolter, S., D. Fleitmann, and M. Leuenberger, 2014: New on-line method for water isotope  
509 analysis of speleothem fluid inclusions using laser absorption spectroscopy (WS-CRDS).

510 *Clim. Past Discuss*, **10**, 429–467, doi:10.5194/cpd-10-429-2014.

511 Arienzo, M. M., P. K. Swart, and H. B. Vonhof, 2013: Measurement of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of  
512 fluid inclusion water in speleothems using cavity ring-down spectroscopy compared with  
513 isotope ratio mass spectrometry. *Rapid Commun. Mass Spectrom*, **27**, 2616–2624,  
514 doi:10.1002/rcm.6723.

515 Bonifacie, M., D. Calmels, J. M. Eiler, J. Horita, C. Chaduteau, C. Vasconcelos, P. Agrinier, A.  
516 Katz, B. H., Passey, J. M. Ferry, and J. J. Bourand, 2017: Experimental calibration of the  
517 dolomite clumped isotope thermometer from 25 to 350°C, and implications for the  
518 temperature estimates for all (Ca, Mg, Fe) CO<sub>3</sub> carbonates digested at high temperature.  
519 *Geochimica et Cosmochimica Acta*, **200**, 255-279, doi: 10.1016/j.gca.2016.11.028

520 Craig H., 1961, Isotopic variations in meteoric waters, *Science*, **133**, 1702-1703,  
521 doi:10.1126/science.133.3465.1702

522 Dallai L., L. Lucchini, Z.D. Sharp, 2004: Techniques for stable isotope analysis of fluid and  
523 gaseous inclusions, *Handbook of Stable Isotope Analytical Techniques*, de Groot P. (ed).  
524 Elsevier: Amsterdam, 62-77

525 Dublyansky Y. V., and C. Spötl, 2009: Hydrogen and oxygen isotopes of water from inclusions  
526 in minerals: design of a new crushing system and on-line continuous-flow isotope ratio mass  
527 spectrometric analysis. *Rapid Commun. Mass Spectrom*, **23**, 2605–2613,  
528 doi:10.1002/rcm.4155.

529 Genty, D., I. Labuhna , G. Hoffmann, P. A. Danis, O. Mestre, F. Bourges, K. Wainer, M.  
530 Massault, S. Van Exter, E. Régnier, Ph. Orengo, S. Falourd, and B.Minster, 2014: Rainfall  
531 and cave water isotopic relationships in two South-France sites. *Geochimica et*  
532 *Cosmochimica Acta*, **131**, 323–343, doi:10.1016/j.gca.2014.01.043.



533 Goldstein, R., and J. Reynolds, 1994: Systematics of Fluid Inclusions. SEPM Short Course Notes  
534 31, 188, doi: 10.2110/scn.94.31

535 Hendy, C. H., 1971: The isotopic geochemistry of speleothems—I. The calculation of the effects  
536 of different modes of formation on the isotopic composition of speleothems and their  
537 applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta*, **35**, 801–824,  
538 doi:10.1016/0016-7037(71)90127-x.

539 Henkes, G. A., B. H. Passey, A. D. Wanamaker, E. L. Grossman, W. G. Ambrose, and M. L.  
540 Carroll, 2013: Carbonate clumped isotope compositions of modern marine mollusk and  
541 brachiopod shells. *Geochimica et Cosmochimica Acta*, **106**, 307–325, doi:  
542 10.1016/j.gca.2012.12.020

543 Horita, J., 2014: Oxygen and carbon isotope fractionation in the system dolomite–water–CO<sub>2</sub> to  
544 elevated temperatures. *Geochimica et Cosmochimica Acta*, **129**, 111–124. doi:  
545 10.1016/j.gca.2013.12.027

546 Labuhn, I., D. Genty, H. Vonhof, C. Bourdin, D. Blamart, E. Douville, J. Ruan, H. Cheng, R.  
547 Lawrence Edwards, E. Pons-Branchu, and M. Pierre, 2015: A high-resolution fluid inclusion  
548  $\delta^{18}\text{O}$  record from a stalagmite in SW France: modern calibration and comparison with  
549 multiple proxies. *Quaternary Science Reviews*, **110**, 152–165,  
550 doi:10.1016/j.quascirev.2014.12.021.

551 Mangenot X., M. Bonifacie, M. Gasparri, A. Goetz, C. Chaduteau, M. Ader, and V. Rouchon  
552 (2017). Coupling  $\Delta_{47}$  and fluid inclusion thermometries on carbonate cements to precisely  
553 reconstruct the temperature, salinity and  $\delta^{18}\text{O}$  of circulating paleowater in sedimentary  
554 basins. *Chemical Geology*, 472, 44-57, doi: 10.1016/j.chemgeo.2017.10.01

555 Mangenot X., M. Gasparri, M. Bonifacie, V. Rouchon, M. Bonifacie (2018). Basin scale

556 thermal and fluid-flow histories revealed by carbonate clumped isotopes ( $\Delta_{47}$ ) - Middle  
557 Jurassic of the Paris Basin. *Sedimentology*, **65**, 123-150, doi: 10.1111/sed.12427

558 Meckler A. N., S. Affolter, Y. V. Dublyansky, Y. Krüger, N. Vogel, S. M. Bernasconi, M. Frenz,  
559 R. Kipfer, M. Leuenberger, C. Spötl, S. Carolin, K. M. Cobb, J. Moerman, J. F. Adkins, and  
560 D. Fleitmann, 2015: Glacial-interglacial temperature change in the tropical West Pacific: A  
561 comparison of stalagmite-based paleo-thermometers. *Quaternary Science Reviews*, 1–28,  
562 doi:10.1016/j.quascirev.2015.06.015.

563 Mickler, P. J., J. L. Banner, L. Stern, Y. Asmerom, R. L. Edwards, and E. Ito, 2004: Stable  
564 isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope  
565 effects. *Geochimica et Cosmochimica Acta*, **68**, 4381–4393, doi:10.1016/j.gca.2004.02.012.

566 O'Neil, J.R., 1969: Equilibrium and nonequilibrium oxygen isotope effects in synthetic  
567 carbonates. *Geochimica et Cosmochimica Acta*. **61**, 3461–3475, doi: 10.1016/S0016-  
568 7037(97)00169-5

569 Schwarcz, H. P., R. S. Harmon, and P. Thompson, 1976: Stable isotope studies of fluid  
570 inclusions in speleothems and their paleoclimatic significance. *Geochimica et Cosmochimica*  
571 *Acta*, **40**, 657–665, doi:10.1016/0016-7037(76)90111-3.

572 Sundqvist, H. S., J. Seibert, and K. Holmgren, 2007: Understanding conditions behind  
573 speleothem formation in Korallgrottan, northwestern Sweden. *Journal of Hydrology*, **347**,  
574 13–22, doi:10.1016/j.jhydrol.2007.08.015.

575 Uemura, R., M. Nakamoto, R. Asami, S. Mishima, M. Gibo, K. Masaka, C. Jin-Ping, C-C. Wu,  
576 Y-We. Chang, and C-C. Shen, 2016: Precise oxygen and hydrogen isotope determination in  
577 nanoliter quantities of speleothem inclusion water by cavity ring-down spectroscopic  
578 techniques. *Geochimica et Cosmochimica Acta*, **172**, 159–176,

579 doi:10.1016/j.gca.2015.09.017.

580 Van Rampelbergh, M., S. Verheyden, M. Allan, Y. Quinif, E. Keppens, and P. Claeys, 2014:

581 Monitoring of a fast-growing speleothem site from the Han-sur-Lesse cave, Belgium,

582 indicates equilibrium deposition of the seasonal  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  signals in the calcite. *Climate*

583 *of the Past*, 10, 1871–1885, doi:10.5194/cp-10-1871-2014.

584 Vonhof, H. B., M. R. van Breukelen, O. Postma, P. J. Rowe, T. C. Atkinson, and D. Kroon,

585 2006: A continuous-flow crushing device for on-line  $\delta^2\text{H}$  analysis of fluid inclusion water in

586 speleothems. *Rapid Commun. Mass Spectrom*, **20**, 2553–2558, doi:10.1002/rcm.2618.

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Figure 1.

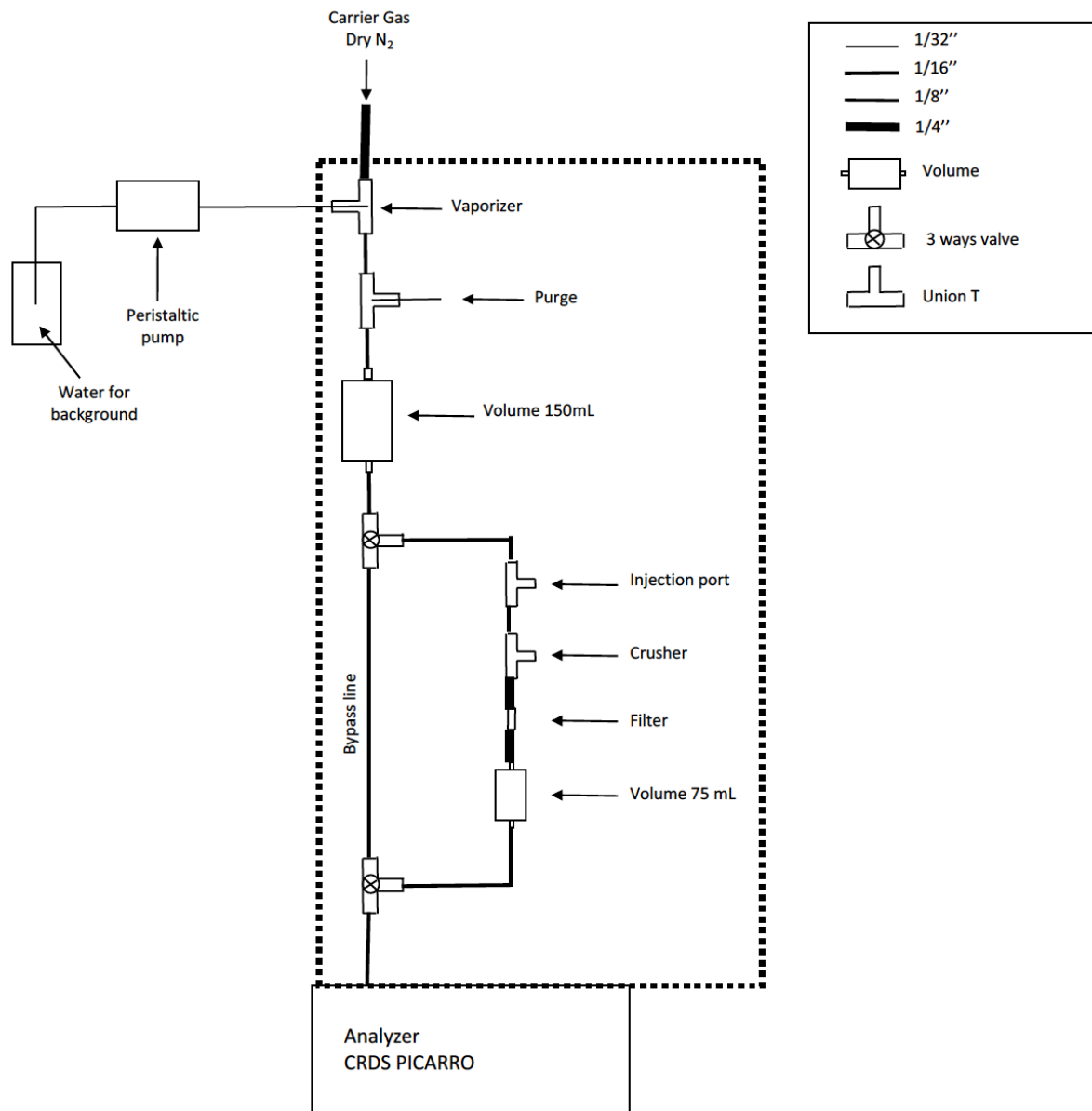


Figure 1: Schematic of the line which includes three main sections: a water vapor background generator section, an injection line permitting both water injections and crushing of carbonate material, and a bypass line. The part of the line heated at 130°C is delimited by the dotted square.

Figure 2.

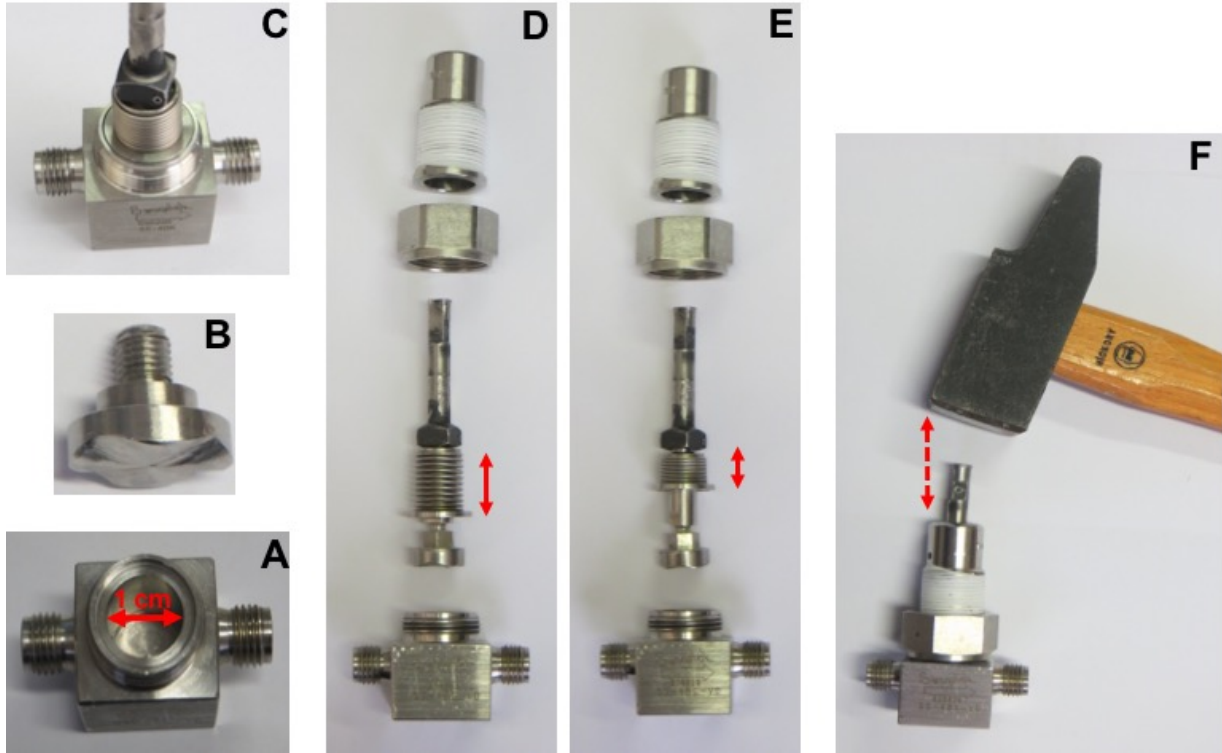


Figure 2: Different sections of the crushing device: A. The modified vacuum valve body milled to obtain a 1 cm diameter cavity, B. The modified valve stern cap used as a power hammer, C. The valve body and valve stem are sealed with airtight metallic-metallic connexion using metallic washer, D. and E. present the valve bellow before (D) and after (E) the crush, F. Picture presenting the vertical movement of the hammer hammering the top of the valve stem.

Figure 3.



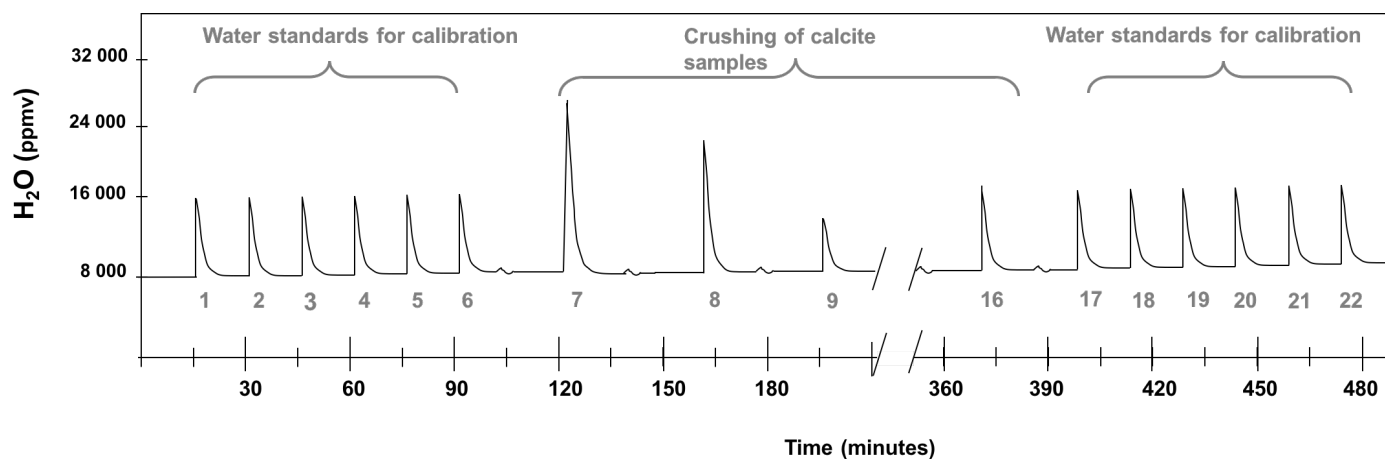


Figure 3: Schematic of water vapour evolution over the course of a regular analysing day. Peaks 1 to 6, are 0.3  $\mu\text{L}$  injections of water standards for calibration MAZA (1, 2), -5‰ (3, 4), and -8‰ (5, 6). Peaks 7 to 16 corresponds to the released fluid inclusion water after calcite crushing. Peaks 17 to 22, are 0.3  $\mu\text{L}$  injections of water standards for calibration MAZA (17, 18), -5‰ (19, 20), and -8‰ (21, 22).

Figure 4.

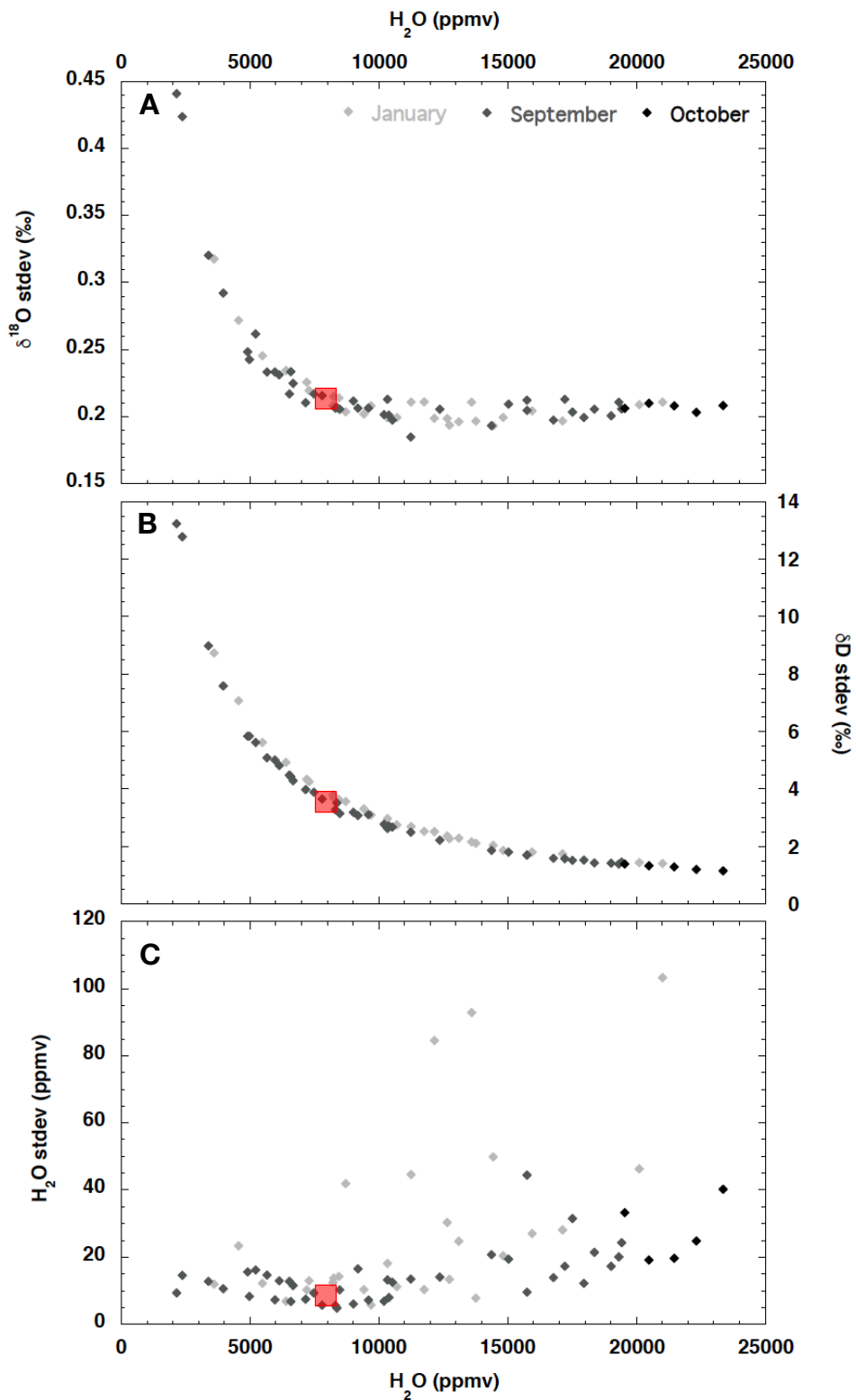


Figure 4: Water background stability. Each point corresponds to the standard deviation of A.  $\delta^{18}O$ , B.  $\delta D$ , and C. the water concentration ( $H_2O$ ). Each set background was analyzed over a period of three hours and we averaged the data over the last 30 minutes. Red squares correspond to the background values chosen.

Figure 5.

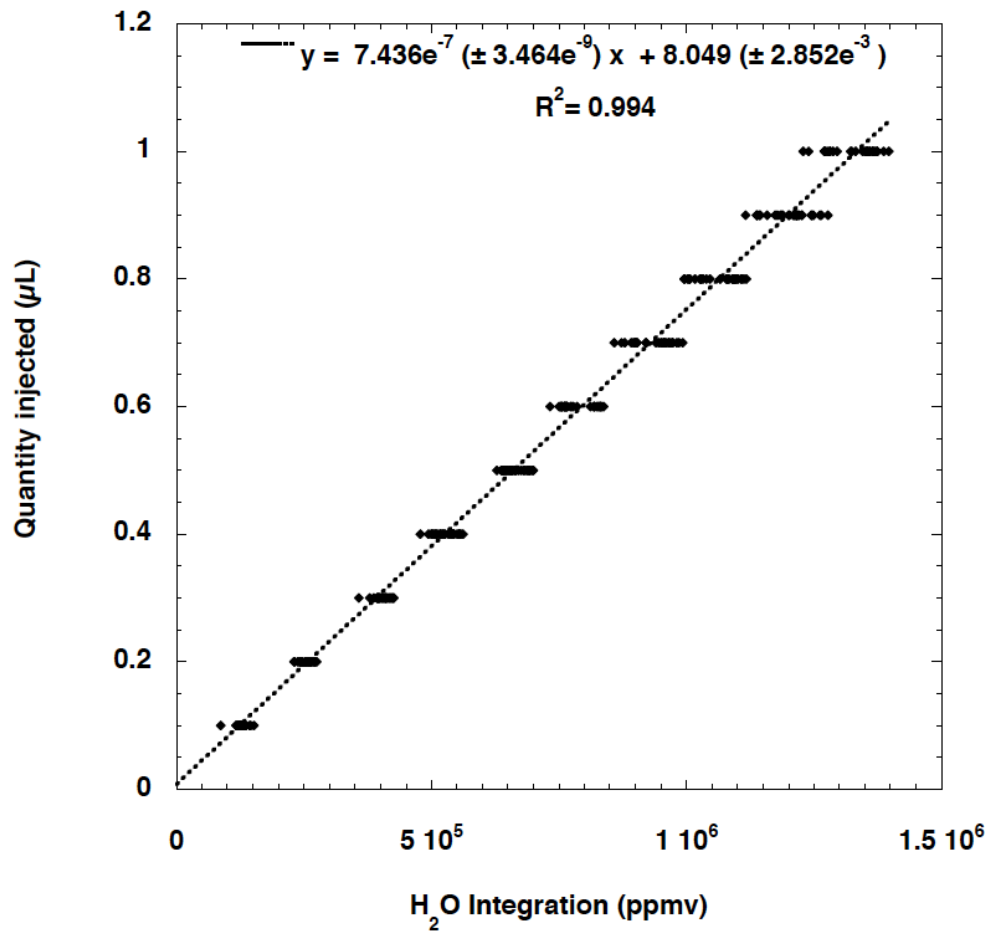


Figure 5: Linear regression between the quantity of water injected and the sample signal water amount integrated over the duration of the water peak.

Figure 6.

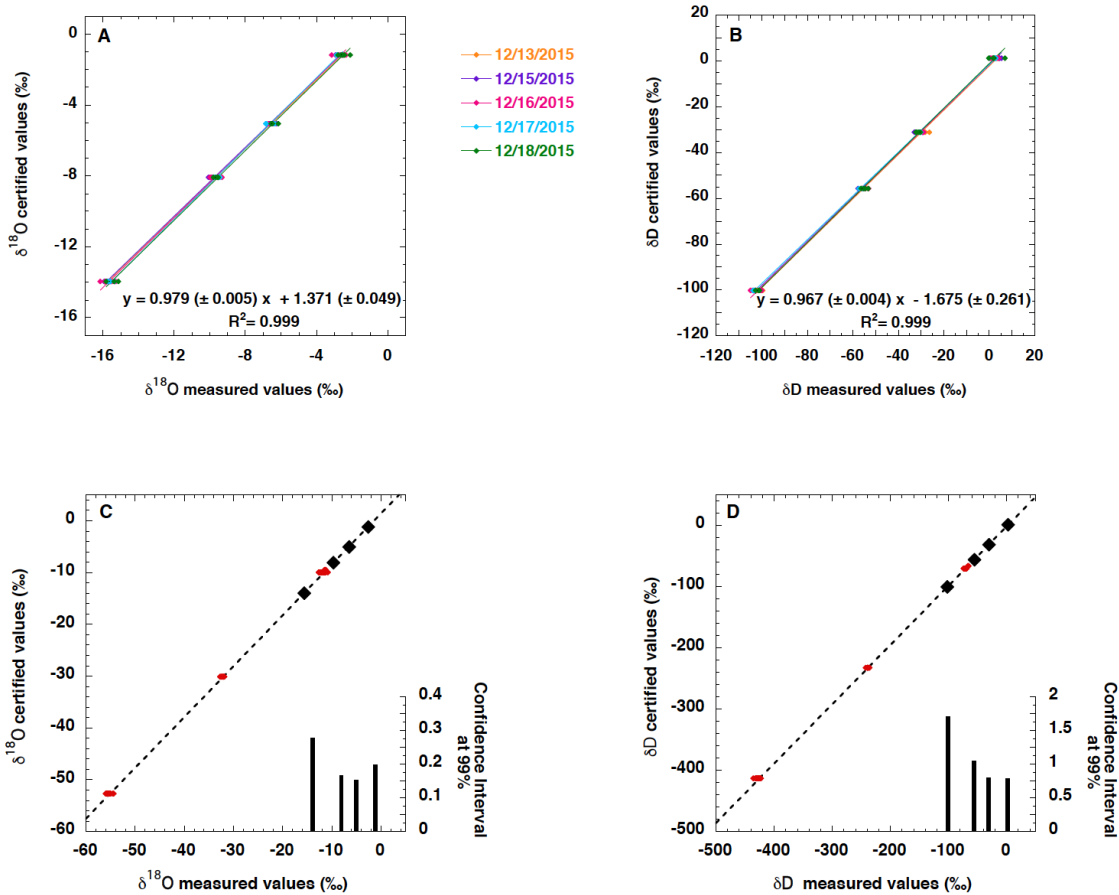


Figure 6: A. and B. Values of four 0.5  $\mu\text{L}$  injections of laboratory standard (-5‰, -8‰, ESKA, and MAZA) over different days. The averaged calibration equation is represented in each plot. C. and D. Mean values for the calibration and confidence interval at 99 % for each point of calibration. The red dots are other laboratory standards (DOMEC; NAN; -10 ‰; -30 ‰; Table 1) analyzed to test the validity of the calibration for out of range water standards.

**Figure 7.**



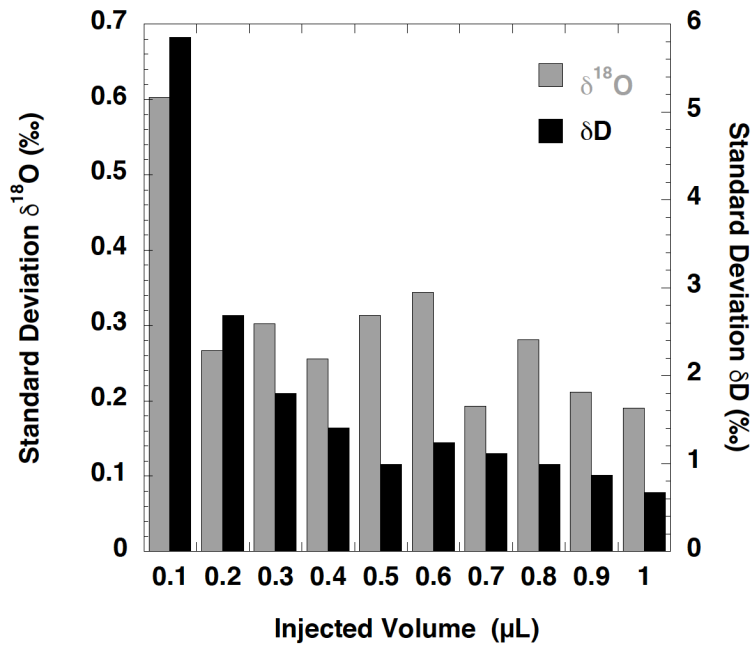
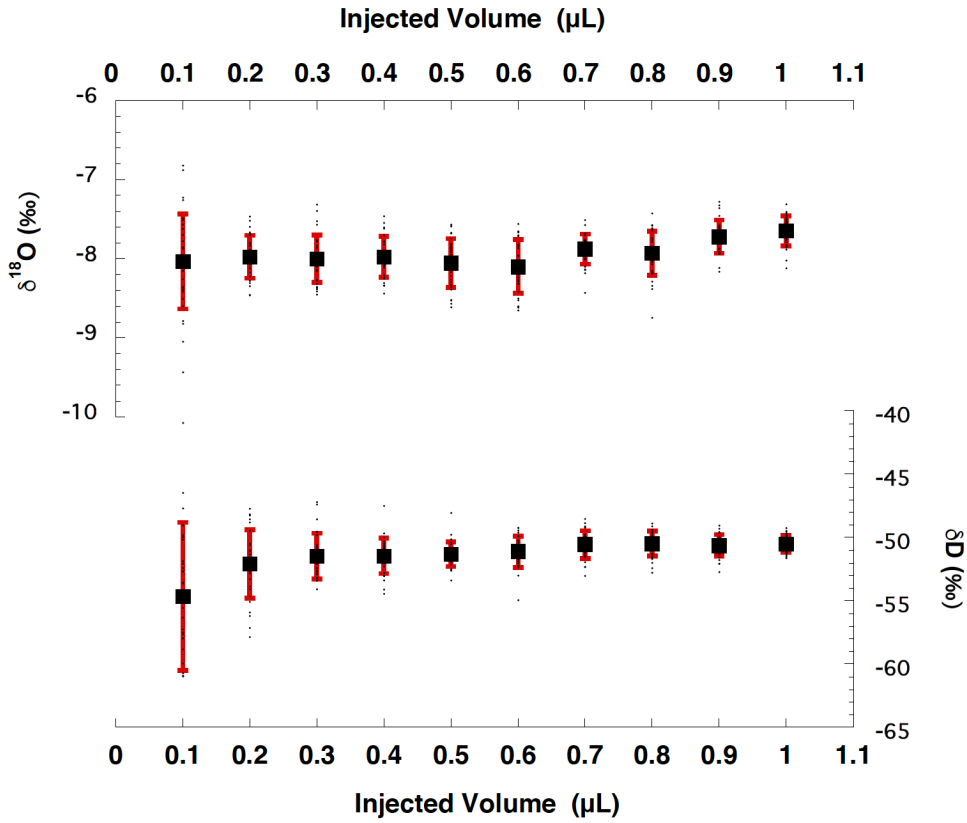


Figure 7: Top panel:  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of 30 injections per injected volumes of DIDO2 (laboratory water standard) are plotted (black dots). Their means (black squares) and standard deviations (red lines) are presented. Bottom panel: Standard deviation of the difference between the certified values and the measured values for given injected volumes for both  $\delta^{18}\text{O}$  (grey) and  $\delta\text{D}$  (black).

Figure 8.

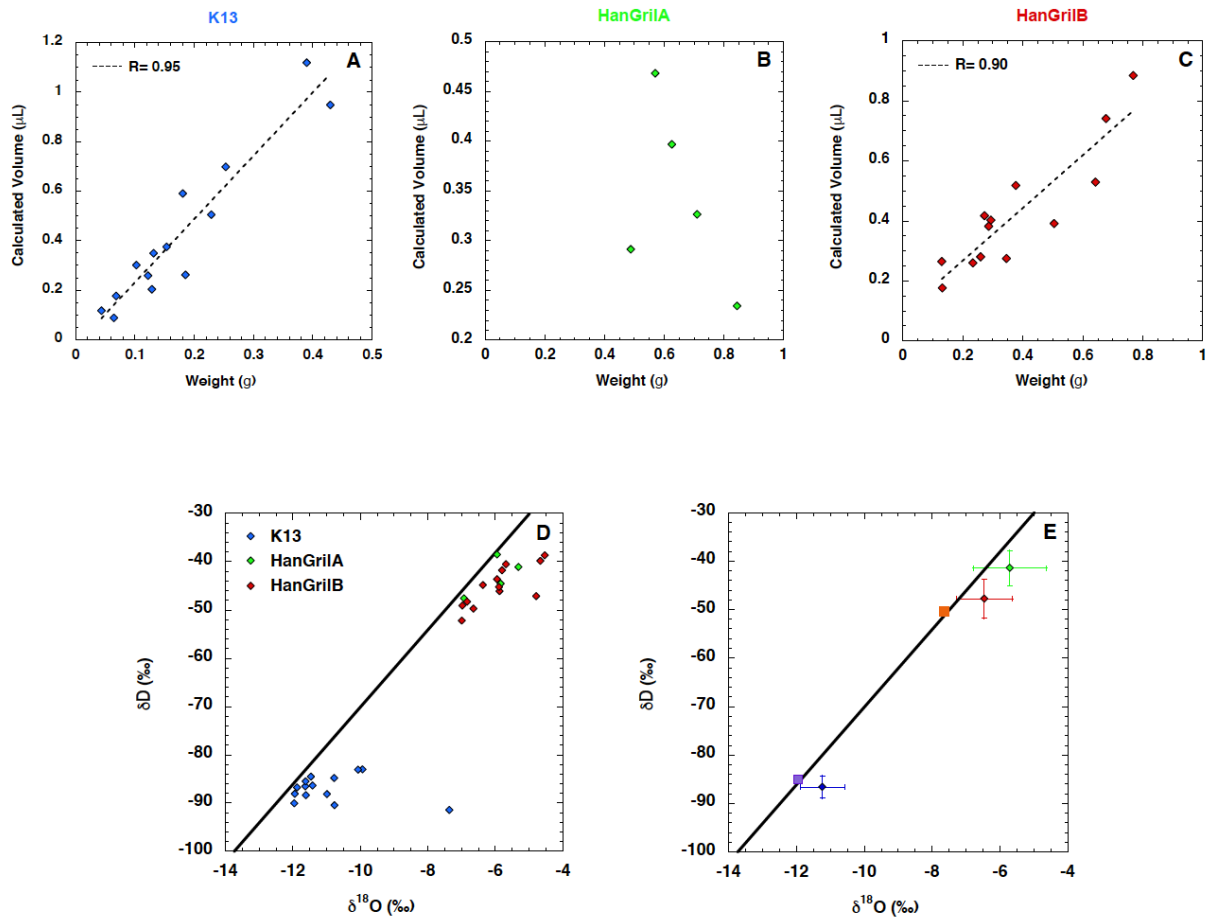


Figure 8: Top panel: relationship between quantity of calcite (in g) and quantity of water released (in  $\mu\text{L}$ ) for the three speleothem samples: K13, HanGrilA, and HanGrilB. Plot D: Relationship between fluid inclusions  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of all three speleothem samples. Plot E: The mean fluid inclusion  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of all the speleothem samples, except the one outlined on plot D, are plotted with their associated error represented by  $1\sigma$ . The black line on plot D. and E. corresponds to the Global Meteoric Water Line (GMWL) (Craig, 1961).

Figure 9.

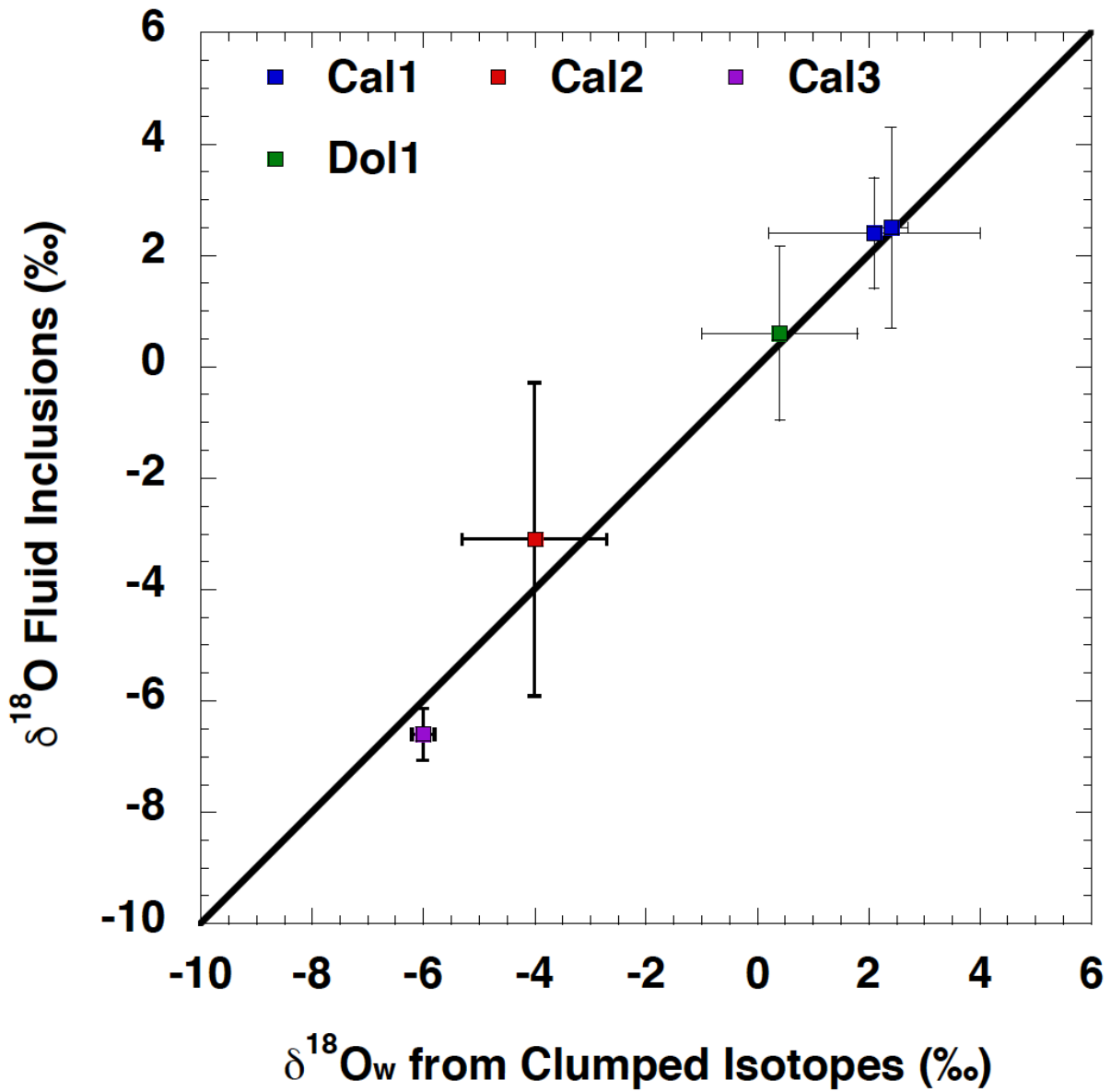


Figure 9: Cross-plot between fluid inclusions  $\delta^{18}\text{O}$  values measured with the analytical line presented in this paper and  $\delta^{18}\text{O}_w$  composition independently calculated from  $\Delta_{47}$  analyses on the host carbonate. The two methods were applied on the same cement specimens. The black line represents the 1:1 relationship. Error bars on the x axis correspond to the associated error of the  $\Delta_{47}$  analyses and error bars on the y axis correspond to one standard deviation of the mean of the fluid inclusion values.