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2 **Isotopic and trace elements evolution of the Naica aquifer (Chihuahua,**  
3 **Mexico) over the past 60,000 years revealed by speleothems**

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27 **ABSTRACT**

28

29 The “espada” speleothems of Cueva de las Espadas (Naica Mine, Chihuahua, Mexico)  
30 comprise a high-purity selenite core overlain by successive deposits of calcite, gypsum  
31 and aragonite. We reveal how these speleothems serve as a new proxy that provide a  
32 record of palaeohydrogeochemical changes as a response of the Naica aquifer to Late  
33 Glacial-Holocene climate conditions. Gypsum precipitated under water from a  
34 hydrothermal solution ( $\approx 55^{\circ}\text{C}$ ) when the water table was above the cave level over the  
35 Late Glacial and some intervals of the deglaciation and the Holocene. Aragonite layers  
36 formed at lower temperature ( $\approx 26^{\circ}\text{C}$ ) in a perched lake that occupied the lower cave  
37 level when the water table fell below the cave depth, in consequence to decreased  
38 aquifer recharge during brief dry intervals that occurred over the last deglaciation (14.5  
39 ka BP) and the Early Holocene (7.9 ka BP). The isotopic composition of gypsum  
40 hydration water shows that the deglaciation-Early Holocene aquifer water was enriched  
41 in deuterium by 12.8 – 8.7‰ relative to the Last Glacial stage as a consequence of  
42 increased contributions of relative moisture source from the Gulf of Mexico over the  
43 Holocene compared to the Late Glacial. These results suggest wetter conditions  
44 occurred in the Naica setting at around 57 ka BP than during the Holocene.  
45 Furthermore, trace element contents in gypsum have served to track the regimen of  
46 circulation of the Naica aquifer over the past 60,000 years, also suggesting higher  
47 aquifer recharge over the Late Glacial period.

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49 **Keywords:** cave minerals, gypsum hydration water, gypsum speleothems, Naica caves,  
50 palaeogroundwater, selenite.

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### 53 **Introduction and geological setting**

54

55 Since the middle of the nineteenth century the Naica mining district, located in  
56 Chihuahua State, Northern Mexico, has been one of the most important lead and silver  
57 exploitations in the World (Fig. 1A). At the Naica mine, zinc and lead sulfides enriched  
58 in silver are extracted (Alva-Valdivia et al., 2003). The regional stratigraphy comprises  
59 limestone and dolostone with interbedded clays and silts (Albian and Cenomanian)  
60 (Franco-Rubio, 1978). Intrusive magmatic activity during the Tertiary is evidenced by  
61 felsic dikes in the carbonate series (Megaw et al., 1988) (Fig. 1A). In fact, this part of  
62 the North American subcontinent is characterized by felsic dikes some 26.0-30.2 Myr  
63 old occurring within the carbonate sequences (Alva-Valdivia et al., 2003). In the case of  
64 the Sierra de Naica, the intrusions penetrate an old northwest-southeast fracture. The  
65 dikes consist of both calc-silicates with disseminated sulfides and massive sulfides with  
66 sparse calc-silicates (Ruiz et al., 1985).

67 The contact between the groundwater and these igneous bodies created a hydrothermal  
68 system containing brines, which flowed along the alignment of the dikes that follow  
69 lines of weakness (Ruiz et al., 1985). The oxidation of sulfide minerals gave rise to  
70 sulfates and metals in solution. Meanwhile, acidification due to this mechanism  
71 produced corrosion of the carbonate sequence and the genesis of cave (Forti, 2010).

72 The early conditions of ore deposition were estimated by using fluid inclusion  
73 constraints to be about 400–500 °C and 100–270 MPa (Megaw et al., 1988), whereas  
74 the current temperature of the aquifer is 52-54 °C. The gradual cooling of the aquifer  
75 resulting from the progressive decrease of the magmatic activity under the Sierra de  
76 Naica, produced the precipitation of low-temperature hydrothermal minerals in  
77 subaqueous conditions such as quartz, calcite, aragonite, anhydrite, and eventually  
78 gypsum (Erwood et al., 1979; Marín-Herrera et al., 2006).

79 From a hydrogeological point of view, the Naica aquifer consists of a subhorizontal  
80 carbonate sequence up to 3,000 m deep, which thickness decrease toward the nearby  
81 mountains of Pajarillos (south), Camargo (south-east) and el Alamillo (north), all of  
82 them around 20 km far from the Sierra de Naica (Giulivo et al., 2007). Previous  
83 hydrogeological works suggest that allogenic feeding to the Naica aquifer from the  
84 nearby Rio Conchos and Rio San Pedro, 40 km far from the Sierra de Naica are  
85 presumably low (Giulivo et al., 2007). The current water table at the Naica mine is  
86 below 800 m deep, as a result of the depression cone induced by the mine dewatering,  
87 necessary for the exploitation of the deep ore bodies, whilst the natural groundwater  
88 (without water pumping) would be around 130-140 m deep below the mine entrance  
89 (Fig. 1A) (Giulivo et al., 2007).

90 Highly interesting speleothems occur in many caves within this hypogenic karst system,  
91 such as in “Cueva de los Cristales” (Crystals Cave) (Marín-Herrera et al., 2006; García-  
92 Ruiz et al., 2007; Forti, 2010), “Ojo de la Reina” (Queen’s Eye Cave) (Forti, 2010;  
93 Badino et al., 2011) and “Cueva de las Velas” (Sails Cave) (Bernabei et al., 2007) (Fig.  
94 2) all of them -290 m level below the mine entrance (170 m below the current natural  
95 groundwater level; Fig. 1A) . The “Cueva de los Palacios” (Palace Cave) was the last  
96 cave discovered in the Naica mine, at -90 m below the mine entrance (40 m above the  
97 natural groundwater level; Beverly and Forti, 2010). In this cave, there is no trace of  
98 euhedral gypsum crystals; however gypsum crust flowers and gypsum-hair do occur.  
99 This is evidence that this cave lay only a few meters above the water table, thus  
100 allowing capillary uplift and evaporation of water into its atmosphere.

101 The Cueva de las Espadas (Cave of the Swords), lying at -120 m below the mine  
102 entrance (Foshag, 1927; Rickwood, 1981; Gázquez et al., 2012), hosts a rare kind of  
103 speleothem, the *espadas* (Fig. 1B, C and Fig. 2A), which are the focus of this paper.

104 The entrance to the Cueva de las Espadas follows a subvertical fractures connected to  
105 the Mountain Fault. The difference in height between the cave entrance and its bottom  
106 is 20 m; when it was discovered in 1910, the cave entrance was completely covered by  
107 selenite crystals up to 2 meters long (Foshag, 1927; Rickwood, 1981). Uncontrolled  
108 visits and pillaging mean that, today, many of these crystals are held in private  
109 collections or in museum exhibits.

110 The presence of water in the Cueva de las Espadas is currently quite scarce and limited  
111 to condensation water on the walls and surfaces of the speleothems. Nonetheless, the  
112 presence of euhedral selenite crystals and subaqueous aragonite concretions in the  
113 deepest part of the cave is clear evidence of phreatic conditions that occurred in the past  
114 as suggested by Forti (2010) and Gázquez et al. (2012), and also discussed in the current  
115 paper. In fact, Gázquez et al. (2012) proposed a model addressing the genesis of these  
116 speleothems in which gypsum precipitated in phreatic conditions, when the cave was  
117 totally below the water table. On the contrary, during certain periods vadose conditions  
118 took place in the upper part of the cavity as a result of the fall of the water table below  
119 the cave level. In such circumstances, subaqueous aragonite precipitation occurred in a  
120 cave pool that occupied the lower level of Cueva de las Espadas.

121 In the current article, the mineralogy and the geochemistry (stable isotopes and trace  
122 elements) of the espada speleothems have been examined in order to shed light on their  
123 origin. In addition, geochemical data provide a discontinuous record of changes in the  
124 characteristics (temperature and salinity) of the Naica aquifer water over the past 60 ka,  
125 linked to climate changes that took place in northern Mexico over the Late Glacial-  
126 Holocene boundary.

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## 130 **Methodology**

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### 132 *Sampling method*

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134 Subsamples for mineralogical and geochemical analyses were extracted from an espada  
135 speleothem that was already broken and which was collected from the floor of the  
136 Cueva de las Espadas. No speleothem was taken from the cave walls for conservation  
137 purposes. Therefore, preservation of this unique cave and its speleothems was  
138 considered as mandatory throughout our investigation.

139 A slice of the espada speleothem was cut perpendicular to its principal growth axis  
140 (plane 010) and perpendicular to the exfoliation plane of gypsum, 10 cm from its upper  
141 tip. The rest of the *espada* was cut longitudinally to the main crystallographic axis of  
142 the gypsum crystal. Powdered subsamples were then drilled using a Dremel drill with a  
143 0.8 mm diameter bit, as displayed in Fig. 3.

144 19 carbonate subsamples were analyzed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , in addition to 33 gypsiferous  
145 subsamples in which  $\delta\text{D}$  of hydration water and trace element content were determined.

146 Two powdered subsamples of the aragonite layers of the espada speleothem were dated  
147 by means of U-Th dating method. Furthermore, one powdered gypsum subsample was  
148 extracted from selenite core of the speleothem. Note that up to 10 g of gypsum were  
149 necessary for the U-Th analysis. To obtain such a gypsum amount, the crushing of  
150 practically the whole gypsum core was necessary (Fig. 3).

151

### 152 *Raman spectroscopy and EDX mapping*

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154 The mineralogy of the espada speleothems was determined by micro-Raman  
155 spectroscopy on a polished lamina (100  $\mu\text{m}$ ) longitudinal to the main crystallographic

156 axis of the inner gypsum crystal (Fig. 4A). This technique has enabled thin mineral  
157 layers of the speleothems to be analyzed. The spectrometer used was a KOSI HoloSpec  
158 f/1.8i model from Kaiser. Microanalyses up to a 5  $\mu\text{m}$  diameter spot were undertaken  
159 with a Nikon Eclipse E600 microscope (Gázquez et al., 2012). The Raman vibration  
160 bands overlap with those identified in previous work on gypsum (Berenblut et al.,  
161 1971), calcite (Rutt and Nicola, 1974) and aragonite (Frech et al., 1980). Raman  
162 analyses were performed at the Unidad Asociada UVA-CSIC-CAB of the University of  
163 Valladolid (Spain). EDX (Energy-Dispersive X-ray spectroscopy) was used for sulfur  
164 mapping acquisition on the same polished lamina as described by Gázquez et al. (2012).

165

#### 166 *Isotope analyses methods*

167

168  $\delta\text{D}$  of gypsum hydration water

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170 Powdered gypsum subsamples (0.6 mg) were analyzed for  $\delta\text{D}$  of hydration water using  
171 the silver encapsulation method (Sauer et al., 2009), consisting of high-temperature  
172 pyrolysis (1450  $^{\circ}\text{C}$ ) of the samples in a graphite reactor, and isotopic measurement of  
173 the  $\text{H}_2$  generated. Previous to the analysis, hygroscopic water was removed by pumping  
174 on the sample in vacuum for three hours at room temperature with a liquid nitrogen trap  
175 fitted on the pumping line to remove absorbed water from the gypsum. This low-  
176 vacuum pumping ( $10^{-3}$  mbars) was found to be effective at removing absorbed water  
177 with no detectable loss of hydration water (Playa et al., 2005). The  $\delta\text{D}$  values of the  
178 gypsum samples were measured using a TC/EA coupled to an IRMS (*Isotopic Ratio*  
179 *Mass Spectrometer*) Delta Plus XL (Thermo Finnigan). Samples were prepared and  
180 analyzed in triplicate. This method, unlike others previously utilized to analyze isotopes

181 in gypsum hydration water (Sofer, 1978; Pradhananga and Matsuo, 1985; Hodell et al.,  
182 2012) allows for the analysis of small gypsum samples in order to obtain higher spatial  
183 sampling resolution.

184 The internal standards used were hexatriacontane (EEZ-24;  $\delta D = -207\text{‰}$ ), polyethylene  
185 foil (PEF;  $\delta D = -100.3\text{‰}$ ) and coumarin (CUM;  $\delta D = 65\text{‰}$ ). These standards were  
186 utilized to estimate analytical reproducibility, and their  $\delta D$  values are relative to the  
187 international V-SMOW (*Vienna-Standard Mean Ocean Water*) standard. Analytical  
188 reproducibility of  $\delta D$  was better than  $\pm 1.5\text{‰}$ , relative to the standard measurements.  
189 The analyses were performed in the Stable Isotope Biogeochemistry Laboratory at the  
190 CSIC Experimental Station at Zaidín (Granada, Spain).

191

192  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in carbonate

193

194 The carbonate bands of the speleothem were analyzed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . This was done  
195 by reacting 1.2 mg of sample with high-purity anhydrous  $\text{H}_3\text{PO}_4$  at a constant  
196 temperature of  $50^\circ\text{C}$  for 5 hours. Carbonate analysis used Gas Bench II coupled to an  
197 IRMS Delta Plus XL (Thermo Finnigan). This instrumentation allowed  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$   
198 (V-PDB) to be measured simultaneously with a reproducibility of  $\pm 0.2\text{‰}$  in both cases,  
199 bases on the standard measurements. Values of the standards (EEZ-1, EEZ-5 and EEZ-  
200 10, all pure carbonate and repeatedly calibrated with respect the international standards  
201 NBS-19 and Carrara), varied from  $-2.57\text{‰}$  to  $-21.57\text{‰}$  for  $\delta^{18}\text{O}$  and  $2.59\text{‰}$  to  $-37.21\text{‰}$   
202 for  $\delta^{13}\text{C}$ , compared to the international V-PDB (*Vienna-PeeDee Belemnite*) standard.  
203 The analyses were performed in the Stable Isotope Biogeochemistry Laboratory at the  
204 CSIC Experimental Station at Zaidín (Granada, Spain).

205



206 *Trace element analyses*

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208 Trace elements in powdered gypsum samples were analyzed using a Thermo iCAP  
209 DUO 6300 Inductively Coupled Plasma Atomic Emission Spectrometer installed in the  
210 Department of Geology at the University of Oviedo (Spain). The powdered samples (1  
211 mg) were dissolved in high-purity 2% HNO<sub>3</sub>. Major elements were measured in radial  
212 mode and trace elements in axial mode. Calibration employed international standards  
213 prepared to match typical ratios of trace and major elements in samples, and was  
214 conducted offline using the intensity ratio method described in previous work (de  
215 Villiers et al., 2007). The representative wavelength recommended by the fabricant of  
216 the instrument was utilized to calculate the concentration of each element in the  
217 samples. All trace elements data are reported in mmol trace/mol Ca. Analytical errors  
218 based on repeated measurements of the standards ranged between 1% for Sr/Ca and 11  
219 % for Cu/Ca.

220

221 *<sup>230</sup>Th -<sup>234</sup>U dating method*

222

223 The age of the espada speleothems was revealed using <sup>230</sup>Th -<sup>234</sup>U dating. 10 g of  
224 gypsum and 0.1 g of aragonite were dissolved in 600 ml and 15 ml of ultrapure 1M  
225 HNO<sub>3</sub>, respectively. Actinides are selectively retained using Eichrom TRU resin,  
226 directly from solution. **Further information about the analytical method for actinides**  
227 **separation of these samples can be found in Sanna et al. (2010).**

228 Isotopic measurements were performed on a Nu Plasma HR multicollector ICP-MS  
229 with a U-Pb collector block at the Department of Geology, University of Oslo. Analyses  
230 were done in dry plasma using a DSN-100 desolvating nebuliser. The reproducibility of  
231 each measured <sup>234</sup>U/<sup>238</sup>U ratio was 0.11% (2σ) (Sanna et al., 2010). Data reduction,

232 error optimization and propagation were done using tailored software (Lauritzen and  
233 Lundberg, 1997) which has been rewritten for the Windows environment. Correction  
234 for detrital  $^{230}\text{Th}$  contamination was needed due to the relatively low  $^{230}\text{Th}/^{232}\text{Th}$  ratios  
235 found in the samples. Correction was done assuming “world mean” initial  $^{230}\text{Th}/^{232}\text{Th}$  of  
236 1.5 (Richards and Dorale, 2003).

237

## 238 **Results**

239

240 Within Cueva de las Espadas, gypsum crystals cover the cave walls, in particular at the  
241 lower level, from the cave bottom to approximately the height of 6 meters (-140 to -135  
242 m below the mine entrance). Meanwhile, at the upper cave level (at the depth between -  
243 135 m and -120 m) there are evidences of gypsum crystals dissolution and carbonate  
244 walls corrosion by condensation water. Currently, dissolution of gypsum speleothems is  
245 still active, particularly close to the cave entrance.

246 It is worth noting that the gypsum crystals placed at the lower level appear covered by  
247 whitish and brownish carbonate concretions, whilst the crystals displayed above 2 m  
248 from the cave bottom are totally clear and transparent.

249 Examination of a longitudinal polished section of the espada speleothem indicated up to  
250 seven distinct phases of mineral growth, both by micro-Raman and EDX mapping (Fig.  
251 4A). The speleothem core consists of a high-purity euhedral selenite crystal ( $G_1$ ) as  
252 revealed by typical Raman signals for gypsum. The selenite crystal is overgrown by  
253 several alternating layers of carbonate and microcrystalline gypsum. First, a one-  
254 millimeter-thick layer of aragonite appears on the selenite core ( $A_1$ ). Subsequent  
255 alternating layers are composed of gypsum ( $G_2$  and  $G_3$ ) and aragonite ( $A_2$ ), whereas the  
256 final brownish layer is made of calcite and cemented clay ( $C_1$ ). The sulfur concentration  
257 in the EDX images also reveals this gypsum-carbonate alternation (Fig. 4A). In

258 addition, solid Zn-Mn-Pb inclusions in aragonite have been observed in the *espada*  
259 speleothems, at the junction between the gypsum and aragonite layers.  
260  $^{230}\text{Th}/^{234}\text{U}$  dating method suggests that the innermost aragonite layer ( $A_1$ ) of the  
261 *espadas* dates back  $14.5 \pm 4$  ka BP, whilst the outermost aragonite layer ( $A_2$ ) is  $7.9 \pm$   
262  $0.1$  ka old (Table 1). The selenite crystal core ( $G_1$ ) is dated to  $57 \pm 1.8$  ka BP (Sanna et  
263 al., 2010). Note that this data represents the average age of a large part of the gypsum  
264 crystals as a consequence of the large gypsum amount necessary for the U-Th analysis  
265 (Fig. 3) (Sanna et al., 2010).

266 With regards to isotopes in carbonate samples,  $\delta^{13}\text{C}$  (V-PDB) ranged between  $-2.7$  and -  
267  $1.0$  ‰, whilst its mean value was  $-1.6 \pm 0.5$  ‰ ( $n=19$ ). As for oxygen isotopes, the  $\delta^{18}\text{O}$   
268 values of the carbonate layers ranged between  $-7.0$  ‰ and  $-10.9$  ‰, with a mean of  $-9.5$   
269  $\pm 1.4$  (Table 2). No correlation has been observed between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ( $R^2= 0.1$ ).

270 Hydrogen isotopes ( $\delta\text{D}$ ) of gypsum samples were also studied and three groups were  
271 identified (Fig. 4C and Table 3). The first corresponds to the selenite core of the *espada*  
272 ( $G_1$ ), with a  $\delta\text{D}$  of  $-73\text{‰} \pm 2.5$  ( $n=18$ ). The second gypsum group corresponds to layer  
273  $G_2$  and has a mean  $\delta\text{D}$  of  $-60.1\text{‰} \pm 2.2$  ( $n=5$ ). The third group corresponds to the  
274 outermost gypsum layer of the speleothem ( $G_3$ ), and has an intermediate isotope value of -  
275  $64.6\text{‰} \pm 0.9$  ( $n=8$ ). Regarding the trace elements contained in the gypsum, two different  
276 groups of samples were distinguished. The first group of samples, taken from the  
277 selenite core ( $G_1$ ), is enriched in trace elements (Table 3), in contrast to those extracted  
278 from the external gypsum layers ( $G_2$  and  $G_3$ ). The depletion ranges between  $1.7\%$  for  
279  $\text{Na}/\text{Ca}$  and  $-84.7\%$  for  $\text{Cd}/\text{Ca}$  (Fig. 8). The detailed results of the trace element analysis  
280 in the gypsum layers have been reported in Table 3.

281

282 **Discussion**

283

284 *Mineralogy and genesis of the espada speleothems*

285

286 The precipitation of selenite speleothems in the hypogenic caves of Naica is a  
287 consequence of upward flow of thermal water in the system (García-Ruiz et al., 2007).  
288 During the first hypogenic stages, oxidation of metal sulfides enriched the groundwater  
289 in sulfates, resulting in precipitation of anhydrite at high temperature. In later phases,  
290 anhydrite started to dissolve as the aquifer temperature gradually decreased to around 58  
291 °C, as revealed by fluid inclusion analyses (Garofalo et al., 2010). At this temperature,  
292 the solubility of anhydrite and gypsum are the same, whereas at lower temperatures,  
293 gypsum is the predominant mineral phase (Hardie, 1967) and so it precipitates as  
294 selenite crystals.

295 The incredible size of the speleothems in the Naica mine is a consequence of the  
296 extremely slow nucleation and growth rate resulting from the constantly low level of  
297 saturation over a long period (García-Ruiz et al., 2007). In fact, the selenite crystals of  
298 the Naica caves have been recently identified as the natural crystals with the slowest  
299 growth rate so far described to date ( $1.4 \pm 0.2 \times 10^{-5}$  nm/s, by Van Driessche et al.,  
300 2011).

301 The espada speleothems of Cueva de las Espadas comprise a high-purity selenite core  
302 overlain by successive deposits of calcite, gypsum and aragonite. While the  
303 precipitation of the selenite crystals in this shallower cave was similar to the generation  
304 of the huge selenite crystals in Cueva de los Cristales (García-Ruiz et al., 2007; Forti,  
305 2010) (Fig. 5A and 6A), the outer alternating gypsum and carbonate layers require a  
306 more complex explanation.

307 These thin mineral layers appear covering the selenite crystals precipitated during  
308 previous stages, but only overlay the speleothems placed at the cave bottom, below the

309 height of 2 m from the floor. This fact suggests that during certain phases the cave was  
310 intercepted by the water table of the Naica aquifer and a cave pool, which surface lay  
311 around two meters from the cave bottom, occupied the lower level of the Cueva de las  
312 Espadas. Consequently, the upper part of the caves was in vadose conditions and the  
313 subaqueous precipitation of gypsum was interrupted. Nevertheless, mechanisms of  
314 minerals precipitation, in this case carbonate, continued to occur in the lake placed at  
315 the cave bottom (Fig. 5B).

316 When vadose and oxic conditions prevailed in the upper part of the cave, the  
317 precipitation of polymetallic oxyhydroxides also took place in the lake, that in the  
318 espada speleothems is revealed by the presence of polymetallic inclusion observed in  
319 the aragonite layers (Fig. 4A and Fig. 6B) (Gázquez et al., 2012).

320 As described above, in the Cueva de las Espadas carbonate minerals (aragonite and  
321 calcite) were deposited during certain phases, in addition to gypsum (Fig. 1C). In this  
322 case, the presence of aragonite layers covering selenite crystals only at the lower cave  
323 levels strongly suggests that aragonite ( $A_1$ ) precipitated underwater, when the upper part  
324 of the cave was in vadose conditions and a cave pool occupied the cave bottom, as a  
325 result of the drop in the water table (Fig. 5B and 6C).

326 During this vadose stage, the upper part of the cave, unconnected to the thermal water,  
327 started cooling more rapidly, while the lake maintained a slightly higher temperature.  
328 As a consequence, considerable evaporation from the lake surface took place and  
329 condensation occurred on the cooler cave walls and roof (Fig. 5B). Nevertheless, the  
330 cavity was practically sealed and condensation water laden with  $CO_2$  was returned to  
331 the cave lake. Dissolution of the gypsum crystals placed at upper cave levels occurred,  
332 producing supersaturation of the water lake in calcium carbonate.

333 Accordingly, it can be deduced that at  $14.5 \pm 4$  ka BP, and later at  $7.9 \pm 0.1$  ka BP,  
334 when the aragonite layers precipitated (Sanna et al., 2010; 2011), the bottom of the

335 Cueva de las Espadas became a perched underground lake, **unconnected to the thermal**  
336 **aquifer** as a result of the water table fall (Fig. 5B and 6C). This assertion is also  
337 supported by the temperature at **which** aragonite precipitation occurred in the Cueva de  
338 las Espadas, which was lower than for gypsum generation, as it will see below.  
339 During this period, due to partial disconnection of the main phreatic level, no CO<sub>2</sub> could  
340 reach the lake carried by the aquifer water and the only possible source of additional  
341 CO<sub>2</sub> was the cave atmosphere, where a continuous CO<sub>2</sub> supply was assured from the  
342 vapors rising through conduits that link the cave to deep thermal reservoirs (Gázquez et  
343 al., 2012). Deposition of calcium carbonate was induced by direct diffusion of carbon  
344 dioxide present in the cave atmosphere into the lake water or, more probably, by  
345 solution of CO<sub>2</sub> in the cave atmosphere into the condensing water that later dripped into  
346 the lake. **In such circumstances of high Ca<sup>2+</sup> concentration in lake water and alkaline**  
347 **environment (regarding that the cave is placed in a marine carbonate), aragonite could**  
348 **easily precipitate, only conditioned by the pH of the solution.** Although the CO<sub>2</sub> input  
349 into the Cueva de las Espadas lake should cause slight acidification of the water, this  
350 could have been controlled by the buffering effect of the dolomite host rock that also  
351 supplied Ca<sup>2+</sup> and Mg<sup>2+</sup> to the solution. Precipitation of aragonite is typical of solutions  
352 with high Mg/Ca ratio, because the Mg<sup>2+</sup> ion inhibits the crystallization of calcite and  
353 favors the precipitation of its polymorph (Burton and Walter, 1987).  
354 This mechanism of carbonate precipitation arising from diffusion of CO<sub>2</sub> in saturated  
355 gypsum-rich waters has been reported previously in gypsiferous environments (Forti,  
356 2003) and also in a carbonate environment (Onac and Forti, 2011). This mechanism was  
357 proved to be currently active at the -590 m level in the Naica mine (Forti et al., 2008),  
358 and was the cause of aragonite and calcite precipitation in the Ojo de la Reina Cave  
359 (Badino et al., 2011) at the -290 m level.

360 Subsequently, the water table rose resulting in further phreatic conditions, in which the  
361 cave was totally underwater, thus gypsum started precipitating again but in a different  
362 framework. The degree of saturation of the lake water with respect to gypsum was  
363 higher than during the previous selenite precipitation stage, so the precipitation of  
364 microcrystalline gypsum occurred (Fig. 5C and 6D). This stage of faster gypsum  
365 precipitation ( $G_2$ ) was probably resulted of the enhanced dissolution of the older  
366 gypsum crystals on the walls and roof of the cave by the condensing water during the  
367 previous vadose stage at the upper part of the cave in which the crystals were exposed to  
368 the cave atmosphere. In fact, partial dissolution of gypsum crystals by condensation  
369 water was proved to induce opening of the large fluid inclusions inside selenite crystals  
370 in other cavities of the Naica Mine, such as Ojo de la Reina Cave, which produced high  
371 to extremely high saline content in the drip water (Badino et al., 2011).  
372 Speleological evidence, such as the corroded and dissolved selenite crystals in the upper  
373 part of the cave (Forti and Sanna, 2010) also suggest this part of the cavity was in the  
374 vadose zone above the water table during some periods.  
375 Another source of calcium sulfate was the widespread presence of anhydrite in the host  
376 rock, which provided an additional supply of calcium sulfate into solution, given to the  
377 solubility disequilibrium with respect to gypsum (García-Ruiz et al., 2007). As a result,  
378 when the phreatic conditions were restored, gypsum saturation was high enough for  
379 gypsum deposition to restart immediately in Cueva de las Espadas, whilst aragonite  
380 precipitation stopped (Fig. 5C).  
381 The relatively high salinity of the fluid inclusions in the gypsum layer that were  
382 precipitated during this stage ( $G_2$ ) (7.7 eq. wt.% NaCl) and higher than those analyzed  
383 in the gypsum core ( $G_1$ ) (5.3 eq. wt.% NaCl) (Garofalo et al., 2010) provide clear  
384 evidence that the above-mentioned key mechanism which led to higher saturation in

385 gypsum of the solution than in previous stages is correct, producing the precipitation of  
386 microcrystalline gypsum in Cueva de las Espadas (Fig. 5C).  
387 After this stage, a further lowering of the water table led again **the upper part of the cave**  
388 to **vadose conditions** and a cave pool occupied the lower part of the cavity. In this  
389 situation, gypsum precipitation ceased and aragonite (A<sub>2</sub>) precipitation began again,  
390 caused by CO<sub>2</sub> diffusion from the cave atmosphere into the lake water (Fig. 6E). Later,  
391 the water table rose again and allowed precipitation of a new gypsum layer (G<sub>3</sub>) (Fig.  
392 6F). Finally, a thin calcite layer was precipitated, probably at cooler temperature (C<sub>1</sub>)  
393 after the main phreatic level had abandoned the cave, during a more recent period (Fig.  
394 6G). Finally, when the cave was intercepted by mining operations, mining activity  
395 generated particles in suspension that were deposited over the *espadas* (Fig. 6H).

396

### 397 *Palaeohydrogeochemical evolution of the Naica aquifer*

398

399 In the previous section we showed how variations in groundwater characteristics led to  
400 precipitation of gypsum, aragonite or calcite depending on each situation. In this section  
401 we deduce the palaeohydrochemistry of the Naica groundwater from the *espada*  
402 speleothem geochemistry. Stable isotopes of gypsum ( $\delta D$ ) and carbonates ( $\delta^{18}O$  and  
403  $\delta^{13}C$ ) were studied, as well as trace element content in gypsum.

404 Classic studies of light isotopes in gypsum demonstrate that the  $\delta D$  of gypsum water is  
405 around 19‰ lower than the solution water from which it derives (Fontes and  
406 Gonfiantini, 1967; Pradhananga and Matsuo, 1985). Isotope fractionation of hydrogen  
407 isotopes ( $\alpha_{D_{gyp-H_2O}}=0.985$ ) is virtually independent of temperatures below 58 °C  
408 (Fontes and Gonfiantini, 1967; Hodell et al., 2012). By using this fractionation

409 coefficient we found that the  $\delta D$  of the aquifer water, **which we assume to be equal to**  
410 **the solution from which gypsum precipitated in Cueva de las Espadas**, ranged between -



411 43.5 and -65.3‰ (Fig. 4B) from the  $\delta D$  of gypsum (Table 3). These values are typical  
412 of meteoric water at the Naica setting (Cortés et al., 1997), and suggest that the saline  
413 solution that generated the *espadas* consisted of meteoric water that infiltrated in the  
414 Naica aquifer and underwent changes in chemical composition and temperature.

415 The isotopic value of deuterium in the current Naica groundwater ( $\delta D = -57.5 \pm 0.7$  ‰,  
416 according to García-Ruiz et al., (2007)) is within the range obtained in our study (-65.3  
417 to -43.5‰). On the other hand, the estimated  $\delta^{18}O$  values from the LMWL in  
418 Chihuahua ( $\delta D = 7 \delta^{18}O + 1.9$  by Cortés et al., (1997)) using the  $\delta D$  data inferred from  
419 gypsum are between -9.6 ‰ and -6.8 ‰, respectively. These values accord with those  
420 reported by García-Ruiz et al. (2007) ( $\delta^{18}O = -7.65 \pm 0.15$  ‰) for current aquifer water.

421 In particular, the isotopic composition ( $\delta D$ ) of the Naica aquifer at around 57 ka BP  
422 (from  $G_1$ ) was around -58.6 ‰, whilst the value for  $\delta^{18}O$  was -8.6 ‰, estimated from  
423 the LMWL in this area. Meanwhile, the inferred mean values of  $\delta D$  and  $\delta^{18}O$  of the  
424 aquifer over the deglaciation and the Holocene (from  $G_2$  and  $G_3$ ) was around -48.6 ‰  
425 and -7.2 ‰, respectively (Fig. 4B and C).

426 The  $\delta^{18}O$  and  $\delta^{13}C$  values in carbonate speleothems usually record the oxygen isotope  
427 composition of water and the carbon isotope composition of dissolved inorganic carbon  
428 species, respectively (Fairchild et al., 2006). In particular, the  $\delta^{13}C$  value of precipitated  
429 carbonate in caves usually depends on the provenience of  $CO_2$  as well as the intensity of  
430 the  $CO_2$  degassing into the cave atmosphere. The  $\delta^{13}C$  values ( $-1.59 \pm 0.51$  ‰) found in  
431 the espada speleothem are relatively elevated with respect to the typical values of  
432 carbonate speleothems placed in other caves (Fairchild et al., 2006) in which soil and  
433 vegetation are the main sources of  $CO_2$ . The extremely weak correlation between  $\delta^{13}C$   
434 and  $\delta^{18}O$  in carbonate of the *espadas* ( $R^2 = 0.1$ ) points to intense  $CO_2$  degassing  
435 accompanied by high evaporation rate did not play a main role during the aragonite

436 precipitation, unlike the mechanism of isotopic enrichment observed in speleothems of  
437 other caves (e.i. Baker et al. 1997). This suggests that CO<sub>2</sub> coming from dissolution of  
438 the marine limestone in the hypogenic aquifer of Naica is the main carbon source. <sup>13</sup>C  
439 contribution from host rock has been also proposed as cause of high δ<sup>13</sup>C values in  
440 speleothems of other caves (Spötl and Mangini, 2007).

441 In regard to oxygen isotopes in carbonate, Patterson et al. (1993) calculated δ<sup>18</sup>O  
442 fractionation during aragonite precipitation from dissolved inorganic carbon in water:  
443

$$444 \Delta\delta^{18}\text{O}_{\text{A-W}} = 18.56 (\pm 0.319) \cdot 10^3 \times T^{-1} - 33.49 (\pm 0.307)$$

445

446 Where Δδ<sup>18</sup>O<sub>A-W</sub> is the isotopic fractionation between aragonite and the inorganic  
447 carbonate species dissolved in water during precipitation (V-SMOW) and T (K) is the  
448 water temperature at equilibrium.

449 Regarding the δ<sup>18</sup>O data and applying this equation, the δ<sup>18</sup>O of the aragonite layers of  
450 the *espadas* (≈ -7 to -10 ‰ V-PDB) (Table 2) suggests that the values of δ<sup>18</sup>O in the  
451 aquifer water were similar to those expected for carbonate precipitation from meteoric  
452 water in this area (≈ -7 to -8 V-SMOW according to Cortés et al. (1997)) and also to the  
453 current aquifer water (-7.6 ± 0.1 ‰ V-SMOW according to García-Ruiz et al., (2007)).

454 This is considering that the aragonite precipitation occurred in a perched lake  
455 unconnected to the aquifer when the water table was below the Cueva de las Espadas, so  
456 the water temperature had to be lower than during gypsum precipitation. Isotopic  
457 equilibrium has been also assumed.

458 In contrast, the influence of juvenile water during the genesis of the espada speleothems  
459 was almost minimized, since magmatic water could have negative δD values but not  
460 negative δ<sup>18</sup>O values (Hoefs, 2004).

461 Once the isotopic composition of the Naica aquifer over the deglaciation and the  
462 Holocene had been inferred for gypsum hydration water, these  $\delta^{18}\text{O}$  values could be  
463 utilized to estimate the temperature at which carbonate precipitated in the Cueva de las  
464 Espadas by means of the equation obtained by Patterson et al. (1993) for isotopic  
465 fractionation during aragonite precipitation.

466 The mean  $\delta^{18}\text{O}$  value of aragonite ( $-9.5 \pm 1.4$  ‰ V-PDB) was used to calculate the  
467 water temperature during the precipitation under two different settings for  $\delta^{18}\text{O}$  of  
468 water: (1) the  $\delta^{18}\text{O}$  of the aquifer water estimated from hydration water gypsum younger  
469 than  $14.5 \pm 4$  ka BP ( $G_2$  and  $G_3$ ) ( $-7.2 \pm 0.4$  ‰ V-SMOW) and (2) the current aquifer  
470 water ( $-7.6 \pm 0.1$  ‰ V-SMOW). Due to such similar  $\delta^{18}\text{O}$  values observed between the  
471 palaeogroundwater estimated from gypsum and the current aquifer water we assume  
472 that  $\delta^{18}\text{O}$  of the solution from which aragonite precipitation did not differ too much  
473 from these isotopic values.

474 The water temperature obtained for the deglaciation and the Holocene at the lake of  
475 Cueva de las Espadas was  $27.8 \pm 6.2$  °C, whereas the calculations based on current  
476 aquifer yields a temperature of around  $25.7 \pm 5.9$  °C (Fig. 7). In both cases, the water  
477 temperature deduced was considerably lower than during the phase of selenite crystal  
478 precipitation, which was estimated from fluid inclusion analyses ( $\approx 55$  °C; Garofalo et  
479 al., 2010). These data strongly support the assertion that the Cueva de la Espadas was a  
480 perched lake located above the water table and unconnected from the deep thermal  
481 circulation of the Naica aquifer during the phases of carbonate precipitation at around  
482  $14.5 \pm 4$  ka BP and  $7.9 \pm 0.1$  ka BP.

483 On the other hand, in this study, the  $\delta\text{D}$  of gypsum hydration water and the trace  
484 elements coprecipitated in gypsum have been useful indicators of different  
485 hydrogeological regimens occurred in the Naica aquifer during the formation of the

486 espada speleothems. The **negative** covariation of  $\delta D$  composition and Pb/Ca ratios in  
487 gypsum during the formation of successive stages of the *espadas* (Fig. 4C) suggests  
488 changes in the source of meteoric water (Pacific Ocean/Gulf of Mexico), which were  
489 coupled to changes in the circulation of the Naica aquifer (**deeper aquifer circulation/  
490 shallower aquifer circulation**).

491 Water-rock interaction under thermohaline conditions extracts higher concentrations of  
492 heavy and transition metals due to the highly stable  $Cl^-$  and  $SO_4^{2-}$  complexes (Irving and  
493 William, 1953; Gardner and Nancollas, 1970; Sherman, 2010). **Therefore, the Pb/Ca  
494 ratio in the gypsum of the espada speleothems might have been higher when  
495 precipitation occurred from deeper thermal water placed at the Naica aquifer over the  
496 Last Glacial. During this period, groundwater circulation in the aquifer increased as a  
497 result of higher recharge of the aquifer, and extraction of metals from the ore bodies  
498 placed in the host rock was enhanced, as revealed by higher trace elements content in  
499 the gypsum core of the *espadas* ( $\approx 57$  ka BP). On the contrary, gypsum formed during  
500 later stages ( $14.5 \pm 4$  to  $7.9 \pm 0.1$  ka BP and after  $7.9 \pm 0.1$  ka BP) formed from shallower  
501 water, depleted in dissolved metals, as a result of limited groundwater circulation in the  
502 aquifer due to lower recharge conditions occurred during the deglaciation and the Early  
503 Holocene (Fig. 4C).**

504 Like Pb, a broad array of heavy and transition metals reveal strong enrichment in the  
505 selenite core compared to the subsequent gypsum layer, confirming the greater  
506 **influence of the deeper aquifer circulation** in the earliest phase of the *espada* growth  
507 (Fig. 8).

508 The depletion in trace elements of the first gypsum layer ( $G_2$ ) compared to the gypsum  
509 core ( $G_1$ ) varied between 1.7% for Na and -84.7% for Cd (Fig. 8). **Earlier works of Lu  
510 et al., (1997) demonstrated that the presence of fluid inclusions might affect the  
511 determination of trace elements in gypsum, in particular Na and Mg which**

512 concentrations are usually high in fluid inclusions. On the contrary, these authors found  
513 that other elements which are present in low concentration in fluid inclusions are not  
514 affected by the proportion of fluid inclusions in gypsum. Thus, enrichment of the fluid  
515 in transition and heavy metals (Pb, Cd, As, Fe, Zn) compared to lighter metals (K, Sr)  
516 reflects the greater complexation affinity of the heavy and transition metals with  $\text{Cl}^-$  and  
517  $\text{SO}_4^-$ , which significantly increases their solubility in saline thermal waters (Irving and  
518 William, 1953). This mechanism of metal mobilization was more effective under  
519 greater and deeper circulation of the Naica aquifer occurred over the Late Glacial than  
520 during the deglaciation-Holocene period, when the aquifer circulation was lower.

521

522 *Palaeoenvironmental record of the espada speleothems*

523

524 On the basis of the age of the central gypsum core of the speleothems (around 57 ka BP  
525 of  $G_1$ ) we can assert that greater recharge conditions prevailed in the Naica aquifer  
526 during the Last Glacial stage suggesting wet climate. During this period, the water table  
527 level lay below -90 m (Cueva de los Palacios, where no traces of euhedral gypsum  
528 crystals have been found and only gypsum speleothems formed in vadose conditions  
529 have been described), and above 120 m depth, where the Cueva de las Espadas is  
530 located. The selenite core of the *espadas* formed from a  $\delta\text{D}$  depleted solution (-58.6 ‰  
531 on average), when the cave was affected by the deep circulation of the Naica aquifer  
532 over the Late Glacial.

533 The deglaciation-Early Holocene was a period of intermediate to lower aquifer recharge  
534 when the water table fell, during some intervals below the cave level, and a perched  
535 lake occupied the lower part of the cavity, whereas vadose conditions took place at the  
536 upper levels. Conditions of lowest recharge of the aquifer due to a dryer period  
537 prevailed for brief intervals during the deglaciation and the Holocene which, within the

538 band of certainty of the U-Th ages of the aragonite layers ( $A_1$  and  $A_2$ ), could be  
539 coincident with the beginning of the Bolling/Allerod transition ( $14.5 \pm 4$  ka BP) and the  
540 8.2 ka event ( $7.9 \pm 0.1$  ka BP).

541 When gypsum precipitation resumed (14.5 to 7.9 ka BP and after 7.9 ka BP) due to the  
542 water table rising and the cave was totally underwater, the gypsum layers ( $G_2$  and  $G_3$ ) of  
543 the *espadas* precipitated but, in this case, the hydration water of gypsum enriched in  
544 deuterium ( $-45.7$  ‰ and  $-49.9$  ‰ on average). The cave was influenced by the  
545 shallower aquifer circulation, as a result of lower effective recharge of the aquifer in a  
546 dryer and probably warmer climate occurred during these intervals than over the Late  
547 Glacial.

548 Broadly speaking, the gypsum growth stages of the *espadas* indicate rising levels of  
549 thermal water coinciding with relatively humid period in Northern Mexico, particularly  
550 around 60 ka BP, as revealed by the maximum speleothem growth periods recorded in  
551 other caves in nearby Texas (Musgrove et al., 2001) and New Mexico (Brook et al.,  
552 2006). Recent studies on lacustrine sediments of the Babicora paleolake (also in the  
553 Chihuahua State) argue this area of Northern Mexico received more than average  
554 precipitation during 79-58 cal ka BP (Metcalf et al., 2002; Roy et al., 2012). Chávez-  
555 Lara et al. (2012) also found wetter climate prevailed at 57 cal ka BP in the Chihuahua  
556 Desert by studying lacustrine ostracods, so corroborating the assertion increased  
557 recharge to the Naica aquifer during this stage of the Late Glacial.

558 On the other hand, the isotope record of the *espadas* shows that the aquifer water during  
559 the deglaciation-Holocene was enriched in deuterium by  $12.8 - 8.7$  ‰ relative to the  
560 Last Glacial stage. Such isotopic shift in the Naica's groundwater responded to  
561 variations in the moisture source (Pacific Ocean/Gulf of Mexico) contributions to  
562 precipitation, which have been demonstrated to have an effect on the isotopic  
563 composition of rainfall in Northern Mexico. The oxygen and deuterium composition of

564 modern summer monsoon precipitation in the Gulf of Mexico are isotopically higher  
565 than winter Pacific precipitation (Hoy and Gross, 1982; Yapp, 1985; Higgins, 1997;  
566 Asmerom et al., 2010).

567 In this area, recharge responds most strongly to changing precipitation delivery from the  
568 North American summer monsoon. Currently the region receives precipitation from  
569 Pacific winter cyclones, but the majority (>70%) is derived from the summer monsoon  
570 system in the Gulf of Mexico (Hoy and Gross, 1982; Yapp, 1985; Douglas et al., 1993).

571 Thus, the observed shift towards higher  $\delta D$  values in the Holocene portion of our  
572 *espada* sample is consistent with the greater importance of summer monsoon  
573 precipitation, which strongly indicates warmer and probably drier conditions compared  
574 to the Late Glacial that was wetter and likely colder. Such circumstances played a main  
575 role in effective moisture in this area of North America. Probably, lower temperatures  
576 during the Last Glacial resulted in less evaporation, and even if annual precipitation was  
577 the same for the Last Glacial and the Holocene, the effective precipitation would be  
578 greater during the Glacial period, as also revealed by paleohydrological studies in lakes  
579 of central New Mexico (Allen and Anderson, 2000).

580 During deglaciation and the Holocene, summer monsoon precipitation is documented to  
581 have been significantly reduced by cold North Atlantic sea surface temperatures at  
582 several times, such as the 8.2 ka event and the Bølling/Allerød transition (Lachniet et  
583 al., 2004; Rohling and Pällke, 2005; Kageyama et al., 2005). These intervals were  
584 characterized by a significantly reduced thermohaline circulation in the North Atlantic  
585 and were potentially dry period in the North Atlantic region.

586 These dry events or others with similar characteristics in the Naica setting could  
587 produced a declining water table at around  $7.9 \pm 0.1$  ka and  $14.5 \pm 4$  ka BP in the Naica  
588 aquifer, resulting in the upper part of the Cueva de las Espadas was in vadose conditions  
589 and a perched lake occupied the lower part of the cave where aragonite precipitated.

## 590 **Conclusions**

591

592 The complex gypsum-carbonate espada speleothems from Cueva de las Espadas at  
593 Naica are a compelling new palaeoenvironmental proxy which, by offering information  
594 on relative water table position, recharge rates of the aquifer and moisture sources,  
595 complement existing palaeoclimate records from carbonate speleothems. Alternations of  
596 gypsum and carbonate layer in the espada speleothem are linked to water table  
597 oscillation of the Naica aquifer over the Last Glacial and the Holocene. Meanwhile, the  
598 differences observed in the trace element content between gypsum precipitated at  
599 around 57 ka BP and gypsum younger than 20 ka BP reveal that the circulation of the  
600 aquifer was more active during the Last Glacial than during the deglaciation and the  
601 Holocene, as a result of wetter conditions and greater aquifer recharge occurred over the  
602 Late Glacial stage in the Naica setting. In addition, the stable isotopic composition of  
603 deuterium in the gypsum provides information on the moisture source of past  
604 precipitation, without the temperature effects on isotopic partitioning that occur with  
605 oxygen isotopes in carbonate speleothems. The record from the espada speleothems  
606 distinguishes a relatively humid glacial period dominated by Pacific winter precipitation  
607 and a drier Early Holocene dominated by summer monsoon precipitation from the Gulf  
608 of Mexico. By the early deglaciation, the summer monsoon was the dominant source of  
609 precipitation, and this appears to have increased the vulnerability to drought, as the only  
610 exceptionally and probably brief arid intervals occurred during the deglaciation ( $14.5 \pm$   
611  $4$  ka BP) and the Early Holocene ( $7.9 \pm 0.1$  ka BP). In consequence, the aquifer  
612 recharge decreased during these dry periods, the water table fell below the Cueva de las  
613 Espadas level, giving rise to vadose conditions in the upper part of the cave, whilst a  
614 cave pool occupied the cave bottom, in which the precipitation of carbonate took place.



615 On the basis of these results, it can be hypothesized that the isotopic composition of  
616 other phreatic gypsum speleothems over the World such as those from the Giant Pulpí  
617 Geode (Spain) (García-Guinea et al., 2002), the El Teniente Mine (Chile) (Klemm et al.,  
618 2007) or the Cupp-Coutunn Cave (Turkmenistan) (Maltsev, 1997; Bottrell et al., 2001)  
619 might be used to reconstruct the geochemical characteristics of aquifer  
620 palaeogroundwater. Gypsum speleothems in hypogenic caves like those of Naica are  
621 very limited worldwide. These places must be conserved due to their natural  
622 environmental value as well as for their potential for use in future palaeoclimatic  
623 research.

624

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626

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638

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850

## 851 **FIGURE CAPTIONS**

852

853 **Fig. 1. Location of Cueva de las Espadas within the Naica mine complex.** **A.** Sketch  
854 of the Naica mine with the locations of the main natural caves discovered. **The natural**  
855 **groundwater level of the Naica aquifer (130-140 m below the mine entrance) and that**  
856 **induced by the mine dewatering at the current time (800 m below the mine entrance)**  
857 **have been represented;** **B.** The *espadas* consist of a prismatic gypsum crystal covered by  
858 several layers of carbonates and microcrystalline gypsum; **C.** The speleothem, already  
859 broken through vandalism, was taken from the floor of Cueva de las Espadas.

860

861 **Fig. 2. The three main caves in the Naica mine.** **A.** Cueva de las Espadas (-120 m),  
862 gallery from which the speleothems were sampled; **B.** Cueva de los Cristales (-290 m)  
863 with selenite crystals up to 11 meters in length (Photo by La Venta Exploring Team); **C.**  
864 Cueva del Ojo de la Reina (-290 m) which houses gypsum crystals with hydromagnesite  
865 and calcite alteration crusts (Note: depths relative to the mine entrance level).

866

867 **Fig. 3.** Sampling along a longitudinal section to the axis of an espada speleothem (A),  
868 and along a perpendicular section (B). The composition in trace elements was analyzed,

869 as well as the isotope composition ( $\delta D$ ) in each spot. Spatial resolution of the samples  
870 was 5 mm. The samples shown in red indicate gypsum; those in blue indicate carbonate,  
871 and those in yellow, a mixture of both minerals. Red squares indicate the place where  
872 U-Th dates were obtained (G: in gypsum, A: in aragonite).

873

874 **Fig. 4. Mineralogical and geochemical composition and longitudinal section of an**  
875 **espada speleothem A.** Photograph and micro-stratigraphical scheme showing the  
876 selenite core ( $G_1$ ), two layers of microcrystalline gypsum ( $G_2$  and  $G_3$ ) and two layers of  
877 aragonite intercalations ( $A_1$  and  $A_2$ ). The outer layer is of cemented clays ( $C_1$ ). sulfur  
878 content mapping was elaborated by microprobe EDX analysis and revealed the  
879 aragonite-gypsum contact; **B.** Isotopic evolution ( $\delta D$ ) of the water from which the  
880 gypsum of the *espada* was precipitated, obtained from the isotope composition of the  
881 hydrogen in the water of crystallization of gypsum from gypsiferous samples (extracted  
882 from a 5 cm longitudinal segment taken along the main growth axis of the speleothem).  
883 Question marks represents the growth hiatuses of unknown age (re-dissolution or no  
884 precipitation) that could have occurred between gypsum and aragonite precipitation  
885 stages; **C.**  $\delta D$  ‰ (V-SMOW) and Pb/Ca ratio (mmol/mol) of the gypsiferous samples  
886 extracted from a 5 cm longitudinal segment taken from along the main growth axis of  
887 the speleothem. Analytical reproducibility of Pb/Ca was  $\pm 7$  % and is smaller than the  
888 symbol. Note the logarithmic scale of the X axis.

889

890 **Fig. 5. Evolutionary diagram of the water table position in the Cueva de las**  
891 **Espadas. A. Precipitation of gypsum crystals when the cave was totally under water**  
892 **conditions and deeper circulation of the Naica aquifer; B. Precipitation of aragonite in a**  
893 **pool that occupied the cave bottom as a result of the drop of the water table. The upper**  
894 **part of the caves was under vadose conditions and condensation on the cave walls took**

895 place, giving rise to dissolution of gypsum precipitated during previous stages and  
896 carbonate host rock corrosion; C. Precipitation of microcrystalline gypsum under  
897 phreatic conditions and shallower circulation of the Naica aquifer. Less stable  
898 conditions took place than during the previous stages of selenite crystals precipitation  
899 (topography provided by La Venta Exploring Team).

900

901 **Fig. 6. Evolutionary diagram of an espada speleothem in the Cueva de las Espadas.**

902 **A.** Precipitation of the selenite core ( $G_1$ ) under phreatic conditions and deeper  
903 circulation of the aquifer during the Last Glacial stage (see Fig. 5A); **B.** Precipitation of  
904 Zn-Mn-Pb solid inclusions under oxygenic conditions; **C.** Precipitation of the first layer  
905 of aragonite ( $A_1$ ) in a pool placed at the cave bottom at intermediate temperature, when  
906 vadose conditions prevailed in the upper part of the cave due to the drop of the water  
907 table during brief periods of the deglaciation and the Early Holocene (see Fig. 5B); **D.**  
908 Precipitation of microcrystalline gypsum ( $G_2$ ) when the cave was totally under phreatic  
909 conditions and shallower circulation of the Naica aquifer during periods of the  
910 deglaciation and the Early Holocene (see Fig. 5C); **E.** Precipitation of a second  
911 aragonite layer ( $A_2$ ) under lowest recharge conditions at intermediate temperature; **F.**  
912 Precipitation of a second microcrystalline gypsum layer ( $G_3$ ) under phreatic conditions  
913 during the Holocene; **G.** Precipitation of calcite ( $C_1$ ) under vadose conditions with  
914 falling temperature; **H.** Mining aerosols and cemented clays deposition under  
915 atmospheric cave conditions in a recent period.

916

917

918 **Fig. 7.** Estimated water temperature during aragonite precipitation obtained from the  
919 mean  $\delta^{18}\text{O}$  value of aragonite (V-PDB) and the mean  $\delta^{18}\text{O}$  of the aquifer water in two  
920 different frameworks: (1) inferred mean  $\delta^{18}\text{O}$  value from hydration water of gypsum

921 precipitated during the deglaciation and the Holocene ( $G_1$  and  $G_2$ ) and (2) the current  
922 mean  $\delta^{18}\text{O}$  value of the groundwater in the Naica Mine (García-Ruiz et al., 2007). The  
923 geothermometric equation obtained by Patterson et al. (1993) has been used. The STD  
924 of the estimated water temperature was calculated on the basis of the STD of  $\delta^{18}\text{O}$  in  
925 carbonate obtained from the *espadas* ( $\pm 1.4\%$ ), as well as the STD of the current water  
926 of the Naica aquifer ( $\pm 0.15\%$ , García-Ruiz et al., 2007) and the STD of the estimated  
927 water of the Holocene ( $\pm 0.4\%$ ).

928

929 **Fig. 8.** Depletion (%) of several trace elements ( $((\text{Tr}/\text{Ca}_{\text{gyp core}} - \text{Tr}/\text{Ca}_{\text{inner gyp layer}})/\text{Tr}/\text{Ca}_{\text{gyp}}$   
930  $\text{core}) \times 100$ ) for  $G_2$  compared to  $G_1$ . This factor was calculated for the mean of the ratio  
931  $\text{Tr}/\text{Ca}$  for each element in samples of the selenite core ( $G_1$ ) and the inner gypsum layer  
932 ( $G_2$ ). They are represented as a function of the atomic weight of each trace element.

933

934

935 **Table 1.** Uranium concentration, measured U and Th activity ratios and ages of  
936 subsamples from the espada speleothem of Cueva de las Espadas.

937

938 **Table 2.** Results of isotopic analysis in the carbonate samples represented in Fig. 3.

939

940 **Table 3.**  $\delta\text{D}$  in gypsum hydration water and trace elements composition ( $\text{Tr}/\text{Ca}$  in  
941  $\text{mmol/mol}$ ) of the gypsum samples. The  $\delta\text{D}$  of the original water from which gypsum  
942 derived have been also calculated. Nomenclature of the samples refers to Fig. 3.

943