

1 **Paleoflood events recorded by speleothems in caves**

2 Fernando Gázquez^{1,2*}, José María Calaforra², Paolo Forti³, Heather Stoll⁴,
3 Bassam Ghaleb⁵, Antonio Delgado-Huertas⁶

4 ¹Unidad Asociada UVA-CSIC al Centro de Astrobiología, University of Valladolid, Parque
5 Tecnológico Boecillo, 47151, Valladolid, Spain (f.gazquez@ual.es) *corresponding author

6 ²Water Resources and Environmental Geology Research Group, Department of Hydrogeology-
7 University of Almería. Ctra. Sacramento s/n, 04120. La Cañada de San Urbano, Almería
8 (Spain) (jmcalaforra@ual.es)

9 ³Italian Institute of Speleology, Department of Biological, Geological and Environmental
10 Sciences, University of Bologna. Via Zamboni, 67, 40126. Bologna, Italy (paolo.forti@unibo.it)

11 ⁴Department of Geology, University of Oviedo, Arias de Velasco s/n. 30005 Oviedo.
12 (hstoll@geol.uniovi.es)

13 ⁵Centre de Recherche en Géochimie et Géodynamique (GÉOTOP-UQAM)-McGill University
14 (Montreal, Canada) (ghaleb.bassam@uqam.ca)

15 ⁶Instituto Andaluz de Ciencias de la Tierra, Camino del Jueves s/n, 18100
16 Armilla, Granada. (antoniodelgado@ugr.es)

17 *corresponding author

18

19 **ABSTRACT**

20 Speleothems are usually composed of thin layers of calcite (or aragonite).
21 However, cemented detrital materials interlayered between laminae of
22 speleothemic carbonate have been also observed in many caves. Flowstones
23 comprising discontinuous carbonate layers form due to flowing water films,

24 whilst flood events introduce fluviokarstic sediments in caves that, on occasion,
25 are recorded as clayey layers inside flowstones and stalagmites. This record
26 provides a potential means of understanding the frequency of palaeofloods
27 using cave records. In this paper, we investigate the origin of this type of detrital
28 deposits in El Soplao Cave (Northern Spain). The age of the lowest aragonite
29 layer of a flowstone reveals that the earliest flood period occurred before 500
30 ka, though most of the flowstone formed between 422 +69/-43 ka and 400 +66/-
31 42 ka. This suggests that the cave was periodically affected by palaeoflood
32 events that introduced detrital sediments from the surface as a result of
33 occasional extreme rainfall events, especially at around 400 ka. The
34 mineralogical data enable an evolutionary model for this flowstone to be
35 generated based on the alternation of flood events with laminar flows and
36 carbonate layers precipitation that can be extrapolated to other caves in which
37 detrital sediments inside speleothems have been found.

38

39 **KEYWORDS:** paleofloods, aragonite speleothems, flowstone, cave sediments,
40 El Soplao Cave.

41

42 **INTRODUCTION**

43 Cave deposits (both clastic and chemical) provide evidence of geological
44 processes and climatic trends that are not preserved at the surface in most
45 karst regions (Ford and Williams, 2007). In particular, clastic sediments from
46 caves have supplied valuable information about the evolution of karstic systems
47 and geomorphological processes (e.g. Bull, 1981; Springer and Kite, 1997;

48 Klimchouk and Andrejchuk, 2002; Quinif et al., 2006; Lisker et al., 2010; Zupan
49 Hajna, 2010; Martini, 2011) and palaeoclimatic events (e.g. Schmidt, 1982;
50 Brook and Nickmann, 1996; Gospodarič, 1998; Šroubek et al., 2001; Sasowsky,
51 2007; White, 2007). In addition, clastic sediments have been used to
52 reconstruct the history of archaeological and palaeontological sites (e.g. Murray,
53 1957; Karkanas, 2000; Farrand, 2001). Recent studies have demonstrated the
54 importance of the role of sediment in transporting contaminants (Mahler et al.,
55 1999; Vesper et al., 2003; Vesper and White, 2003) and microorganisms
56 (Mahler et al., 2000) in karst systems.

57 Clastic cave sediments can be subdivided into two categories (White, 2007)
58 with respect to their origin: autochthonous and allochthonous. Autochthonous
59 clastic sediments are derived locally within the cave from weathering of the
60 bedrock, or from breakdown, whereas allochthonous clastic sediments are
61 transported into the cave from outside. Sediment influx into caves occurs
62 through solutionally-widened fractures of the host rock or via shafts and
63 sinkholes in the karst. The nature of the injected material depends on the rock
64 types in the vicinity of the cave, and is usually a mixture from all these sources.

65 The cave entrances can act as a trap where sediments are unaffected by
66 surface erosion. However, once inside the cave, sediments are transported as
67 suspended load or bedload, depending on the particle size and the velocity of
68 the stream flow (Ford and Williams, 2007). When sediments derive from flood
69 events, the coarse fraction of the load frequently appears on the bed of streams
70 inside the caves, whilst fine-grained materials (clays and silts) usually form the
71 top part of the sedimentary sequence and are deposited when the energy of the
72 flow decreases (Bosch and White, 2004; Van Gundy and White, 2009). In

73 places, clayey sediments can coat the cave walls and ceiling, suggesting that
74 cave passages were once totally filled with muddy sediments.

75 Magnetostratigraphy has been the most common method for dating clastic
76 sediments from caves (Schmidt, 1982; Sasowsky et al., 1995; Šroubek et al.,
77 2001; Chess et al., 2010; Zupan Hajna et al., 2010). As long as the sedimentary
78 sequence has not been altered, the magnetic grains maintain the orientation
79 according to the Earth's magnetic field at the moment of their deposition. Over
80 the past decade, new techniques like OSL dating (optically stimulated
81 luminescence) have been applied to cave sediments (Sanna et al., 2009),
82 providing the absolute date when the sediments were trapped in the cave. On
83 the other hand, the age of cave sediments have also been determined from
84 radiocative decay of cosmogenic ^{26}Al and ^{10}Be (Granger et al., 2001; Stock
85 et al., 2005). In addition to these three above-mentioned dating methods, cave
86 sediments can also be chronologically constraint by means of dating of buried
87 terrestrial shells (Molokov, 2001), charcoal, wood and bone collagen (Boaretto
88 et al., 2009; De Waele et al., 2009).

89 The presence of detrital materials interbedded between chemically precipitated
90 speleothems has been reported in some caves (Dorale et al., 1992; Sasowsky
91 et al., 2007; Stöll et al., 2008; Dasgupta et al., 2010; Pickering et al., 2010;
92 Ballesteros et al., 2012). However, few cases describe clastic materials
93 intercalated with subhorizontal aragonite layers whereby a flowstone is formed
94 due to the degassing (and evaporation) of a water lamina flowing over a
95 surface. Dating the carbonate layers of the speleothem that are sandwiched
96 between clastic materials is an alternative to direct dating of detrital sediments
97 (Pickering et al., 2007; Sanna et al., 2010; Ballesteros et al., 2012).

98 The current article deals with evidence of paleofloods events in caves, as
99 recorded by speleothems, in particular through the study of flowstones recently
100 discovered in El Soplao Cave (Northern Spain), which are composed of
101 aragonite laminae interlayered between successive thin strata of cemented silt
102 and clay. The geochronology of four carbonate layers was determined using the
103 U-Th dating method. These data, together with the mineralogical observations
104 enabled the evolution of this flowstone to be reconstructed and allowed us to
105 identify the flood periods when detrital materials were injected into the cave.
106 Our work shows how dating carbonate layers of speleothems is an accurate
107 method for determining periods in which caves were affected by paleofloods
108 events, what represents an alternative to direct dating of detrital sediments.

109

110 **DESCRIPTION OF THE STUDY AREA**

111 **Geological setting**

112 El Soplao Cave (43°17'45, 42"N - 4°25'45, 76"W) is located in the Sierra de
113 Arnero, in the Escudo de Cabuérniga mountain range (Cantabria, Northern
114 Spain). The Sierra de Arnero mountain chain runs parallel to the Cantabrian
115 Coast, between the Bustriguado and Nansa valleys (municipal districts of
116 Valdáliga, Rionansa and Herrerías) (Fig. 1A). This natural cavity was
117 accidentally discovered in the early-nineteenth century as a result of mining
118 activity in La Florida mine (Carcavilla and Durán, 2011).

119 The cave is developed in the Reocín Formation, shallow platform carbonate
120 rocks of Early Cretaceous (Aptian) age that is inclined 40° N. There is
121 considerable metallogenic interest in the region due to the large patches of

122 dolomitization associated with sulphide deposits that are the result of rising
123 hydrothermal fluids in the carbonates (Quesada et al., 2005; López-Cilla et al.,
124 2009; López-Horgue et al., 2009). In fact, important deposits of lead and zinc
125 sulphides occur in the Florida Mine and in the El Soplao Cave itself, appearing
126 as pre-existing patches of mineralization that were intersected by the cave
127 (Tornos and Velasco, 2011). Tectonic efforts in this area are shown by a fault
128 system that runs parallel to the Sierra de Arnedo mountains and is inclined 50°
129 SE (Jiménez-Sánchez et al., 2011).

130 From a hydrogeological point of view, the Reocín Formation comprises a
131 carbonate sequence 300 m thick on average that is significantly karstified and
132 fractured due to tectonic efforts, which in the El Soplao area gave rise to La
133 Florida aquifer (Meléndez-Ansesio and Rodríguez-González, 2011). The mining
134 activities carried out in the Florida mine since 1900 produced considerable
135 modifications in the hydrogeological regime of the aquifer. In fact, several
136 springs placed few meters below the cave level dried as a result of the drainage
137 of the carbonate formation, in contrast to several artificial artesian pits arisen
138 upon the mining exploration.

139 Recent hydrogeological studies reveal that 21 natural spring plus 6 artificial
140 upwellings supply water to the Nansa River and the Bustriagudo Spring, with
141 flow rates ranging 10 to 120 l/s depending on the time of year (Meléndez-
142 Ansesio and Rodríguez-González, 2011). The present-day water table level in
143 the El Soplao setting is inferred to be at around 150-200 m a.s.l, coinciding with
144 the altitude of these main springs, whilst the base level is given by the bed of
145 the Nansa River, 100 m a.s.l.

147 **Description of El Soplao Cave**

148 The cave entrance lies 540 m a.s.l. and its passages extend over 17 km, with
149 around 200 metres variation in altitude. The total length of the cave, including
150 the mining galleries, is approximately 20 km (Fig. 1B and C). An artificial cave
151 mouth excavated parallel to the Isidra gallery serves as entrance for tourist
152 visits. In addition, there are two natural cave entrances: Torca Ancha and Torca
153 Juñosa, by which access is difficult (González-Hierro, 2011). Preliminary
154 studies inside and outside the cave suggest other entrances may exist,
155 influencing the microclimate dynamics and cave environment.

156 The main passage of the cave is a low-gradient canyon, ~2 km long, developed
157 along the strike of the beds (Fig. 1C). It represents a relict “ideal water table”
158 cave segment (Ford and Williams, 2007), formed when the water table was
159 ~400 m higher than is today. The cave morphology is controlled by a fault
160 running E-W, inclined 50 ° SE (Jiménez-Sánchez et al., 2011) and its passages
161 are oriented following this fault, with a secondary axis running NE-SW. The
162 fault’s displacement controlled the evolution of the cave morphology, and very
163 probably the direction of the vadose water flows in the past. In fact, the external
164 geomorphology of the mountains range in which the cave is developed could
165 differ considerably from its current aspect. Today, the main cave passages
166 describe a horizontal plane that is inclined 1.5 ° to the east (González-Hierro,
167 2011) and the most elevated cave passages lie at 545 m a.s.l, coinciding with
168 the Galería Gorda Chamber, practically at the same level as the natural cave
169 entrances (Fig. 1C). However, the altitude of the entrance sinkholes was

170 probably higher in the past, and was gradually reduced due to erosion and
171 denudation mechanisms, as well as tectonic efforts. Consequently, a part of the
172 detrital sediments produced in this area were introduced by water flows into the
173 cave, in which were stored. Recent speleological surveys revealed that the
174 deepest part of the cave lies just beneath these natural entrances, at a depth of
175 150 m below the surface (450 m a.s.l.). At present, there are no permanent
176 streams flowing in the cave and water flows are limited to dripping water from
177 speleothems.

178 The cave presents much evidence of subaqueous speleogenesis, such as
179 corrosion cupolas and phreatic tubes, whose floors were subsequently eroded
180 by a stream under vadose conditions, as revealed by the presence of several
181 stalagmite pavements at different elevations (Fig. 2B). Up to three “banquettes”
182 or floor levels have been observed in some passages (Jiménez-Sánchez et al.,
183 2011) and there is also evidence of palaeoflood events that introduced fine-
184 grained sediments into the cave. Flood level marks evidenced by silt lines on
185 earlier carbonate speleothems (Fig. 2.E, G and H), mud deposits on the cave
186 floor (Fig. 2A) and layered detrital deposits in several cave passages (Fig. 2A)
187 suggest that flood events have occurred quite recently in El Soplao Cave.

188 El Soplao Cave was opened as a show cave in 2005. Spectacular helictites,
189 anthodites and huge speleothems are the most relevant aesthetic features of
190 this mine show-cave. Other unusual speleothems have also been described in
191 this cave, including the dark amberine speleothems whose colour is related to
192 lixiviates from a carbonaceous stratum located above this speleothem formation
193 (Gázquez et al., 2012), black ferromanganese crusts (Gázquez et al., 2011) and
194 ferromanganese stromatolites (Rossi et al., 2010).

195 The current cave temperature ranges between 9 and 13 °C, depending on the
196 mean annual temperature outside the cave, while its relative humidity is usually
197 around 80-100%. The CO₂ concentration in air is around 440-600 ppm,
198 depending on the number of visitors per day (Calaforra et al., 2011).

199

200 **METHODS**

201 **Sample description and sampling methods**

202 The sample analysed consisted of a fragment of carbonate flowstone, weighing
203 about 3 kg, collected from the Pasillo de los Cubos (also called “Contessa
204 Passage”) of El Soplao Cave (Fig. 1B, C). The speleothem is a horizontal
205 stalagmite pavement up to 20 cm thick that hangs 30 cm above the cave floor
206 (Fig. 2A).

207 The sample was cut using a rock-cutting machine along its main growth axis.
208 Subsequently, the cut surface was manually polished and a high-resolution
209 image of its cross section was scanned. Mineralogical analyses were performed
210 by XRD, using the methodology described by Gázquez et al. (2011). Four
211 powdered samples from the whiter carbonate layers were collected for U-Th
212 dating using a Dremel drill with a 0.8 mm diameter bit. Sampling was done at
213 the lower part of the flowstone (SPL-00), and at 30 mm (SPL-30), 60 mm (SPL-
214 60) and 67 mm (SPL-67) from the speleothem base, following the horizontal
215 aragonite layers.

216

217 **U-Th dating**

218 U/Th dating was carried out at the GEOTOP research centre of the University
219 du Quebec in Montreal. Subsamples of 0.5 g of carbonate (n=4) were weighed
220 and transferred to 250 mL Teflon beakers, into which weighed amounts of a
221 mixed ^{233}U - ^{236}U - ^{229}Th spike had been placed and evaporated. Actinides (Th and
222 U fractions) were selectively retained and subsequently eluted using 0.2 mL U-
223 Teva (Eichrom) resin volume, following the method described in Hillaire-Marcel
224 et al. (1996). The U and Th fractions were deposited on a Re filament between
225 two layers of graphite and measured using a Triton Plus mass spectrometer
226 (TIMS) equipped with an RPQ (retardation potential quadrupole). Mass
227 fractionation for U was corrected by the double spike of $^{236}\text{U}/^{233}\text{U}$ (1.1322),
228 while mass fractionation for Th was considered negligible with respect to
229 analytical error. The overall analytical reproducibility, as estimated from
230 replicate measurements of standards, was generally better than 0.5% for U
231 concentration and $^{234}\text{U}/^{238}\text{U}$ ratios, and ranged from 0.5% to 1% for $^{230}\text{Th}/^{234}\text{U}$
232 ratios (2σ error range).

233 The presence of the non-authigenic ^{230}Th in the carbonate samples was
234 negligible as indicated by the high $^{230}\text{Th}/^{232}\text{Th}$ (up to 5200), thus no correction
235 for detrital contamination was required. U-Th ages were calculated from the
236 isotopic ratios $^{235}\text{U}/^{236}\text{U}$, $^{235}\text{U}/^{234}\text{U}$, $^{236}\text{U}/^{234}\text{U}$, $^{232}\text{Th}/^{229}\text{Th}$ and $^{229}\text{Th}/^{230}\text{Th}$ using
237 ISOPLOT/Ex version 2.0 software (Ludwig, 1999).

238

239 **RESULTS**

240 The carbonate flowstone is 20 cm thick, including white aragonite layers. In
241 addition, up to eleven cemented detrital layers, varying from several microns to

242 centimetres in thickness, were identified (Fig. 3). There were two further dark
243 layers at the upper part of the speleothem, interlayered with clayey and
244 carbonate layers. An incipient stalagmite was presented in the middle of the
245 stratigraphic sequence. The flowstone occurs on a 30 cm thick stratum of non-
246 consolidated sediments that was partially eroded by a stream in more recent
247 times (Fig. 2A). Observations on a polished thin section of the speleothem did
248 not reveal dissolutional or corrosion of carbonate layers to have occurred after
249 precipitation (Gázquez, 2012).

250 U-Th dating of the flowstone revealed that this speleothem grew during a period
251 beginning more than 500 ka. Sample SPL-00 is in secular equilibrium for the U-
252 Th system as suggested by the ratio $^{230}\text{Th}/^{234}\text{U} \approx 1$, thus exceeding the dating
253 limit of the U-Th method (≈ 500 ka).

254 Before 500 ka, a 30 cm-thick layer of sediments beneath the earliest carbonate
255 layer was deposited. In places, these detrital sediments were removed by more
256 recent stream flows, leaving the flowstone hanging above the cave floor (Fig.
257 2A). Subsequent deposition of layers of aragonite “fossilized” these first detrital
258 sediments. Further floods occurred before 500 ka, as suggested by a 2.5 cm-
259 thick layer of cemented detrital materials. The ages of the further aragonite
260 layers analysed, SPL-30 and SPL-60, were $422 \pm 69/-43$ ka and $400 \pm 66/-42$ ka,
261 respectively. Hiatuses represented by thin detrital layers can be observed
262 intercalated with the aragonite layers, in addition to a 1 cm high stalagmite
263 which was “fossilized” by further aragonite laminae (Fig. 3).

264 In the top part of the flowstone, several thin dark layers of polymetallic
265 oxyhydroxides were observed, previously characterized by Gázquez et al.

266 (2011). Above the Fe-Mn-Zn deposits a further aragonite layer was found,
267 which dates to 32.7 ± 0.4 ka (Table 1) constraining the age of the latter.

268 Regarding age uncertainties, relatively high uranium concentrations in the
269 aragonite layer (18 - 47 ppm), meant that the dating error was less than 1.2%
270 for the youngest sample (SPL-67). However, dating errors up to +16/-10% were
271 obtained for the oldest aragonite layers (SPL-30 and SPL-60), which ages are
272 close to the upper dating limit of the U-Th dating method. Additionally, relatively
273 low contamination due to detrital thorium is suggested by $^{230}\text{Th}/^{232}\text{Th}$ ratios that
274 exceeded 500 in the oldest samples and up to 5200 in the youngest aragonite
275 layers. Since $^{230}\text{Th}/^{232}\text{Th}$ ratios were higher than 100, no correction for non-
276 authigenic thorium was needed (Kaufman et al., 1998), because of the low
277 concentration of detrital thorium.

278

279 **DISCUSSION**

280 The flowstones found in El Soplao Cave are an example of complex
281 speleothems consisting of alternating layers of carbonate and cemented detrital
282 materials, similar to others described in a variety of caves (Dorale et al., 1992;
283 Sasowsky et al., 2007; Stöll et al., 2008; Dasgupta et al., 2010; Pickering et al.,
284 2010; Ballesteros et al., 2012). In the upper part of the El Soplao's flowstone, up
285 to 11 layers of clay and silt cemented in a calcite matrix are sandwiched
286 between aragonite layers in just a 7 cm section, followed by several polymetallic
287 oxyhydroxide layers in the upper part of the speleothem.

288 The U-Th dating of four aragonite layers allows confirmation that the flowstone
289 started growing more than 500 ka ago as the basal aragonite lamina is in

290 secular equilibrium in terms of the U-Th system. This fact is consistent with data
291 reported in previous studies by Rossi et al. (2010) in which stalagmites around
292 1 Ma old (983 ka, 896 ka, 1016 ka, 1024 ka and 1075 ka with errors of ± 245 ka
293 obtained by U-Pb dating) were found in other parts of the cave, so suggesting
294 that speleothem precipitation in El Soplao cave has occurred at least since the
295 Middle Pleistocene. On the other hand, recent work has identified stalagmites of
296 Holocene age in El Bosque Gallery, near the Pasillo de los Cubos, whose
297 growth extends to the present day (Carcavilla et al., 2011). Consequently, it can
298 be postulated that speleothems, both dripstones and flowstones, have
299 precipitated intermittently in El Soplao cave over the past million years at least.
300 In addition to vadose stages when dripstones and flowstones were generated,
301 there is ample evidence that the cave was partially flooded in repeated
302 occasions.

303 In fact, before the vadose stage when aragonite laminae began to precipitate in
304 the Pasillo de los Cubos, the cave floor was already covered by a thick layer of
305 fluviokarstic sediments, which underlie the flowstone (Fig. 4A). The
306 granulometry of these sediments corresponds to silts and clays (20 – 200 μm),
307 whilst granulometric gradation has not been observed along the stratigraphic
308 sequence. According to the classification of cave sediments facies proposed by
309 Bosch and White (2004), these materials correspond to the “slackwater facies”,
310 characterized by fine- and medium-grained sediments. Slackwater facies are
311 thin layers of fine-grained silt and clay, usually deposited from muddy water, as
312 also described in other caves (Chess et al., 2010; van Hengstum et al., 2011).
313 They are often found in blind side passages, pockets, and other niches in caves
314 that are unlikely to be reached by flowing water. Rising floodwaters fill all

315 available voids, which are then ponded during some periods. While the passage
316 is filled with water, suspended sediments have time to settle down and form a
317 stratified deposit (Bosch and White, 2004).

318 These kinds of sediments are usually injected into the cave by a water flow
319 coming from outside. In the case of El Soplao cave, sediments entered through
320 the natural cave entrances (Fig. 1C), which in the past were probably at higher
321 altitude and more elevated than the current cave passages, favouring the water
322 and sediments flows into the cave. In fact, the cave's evolution has been
323 controlled by an active fault that surely modified the relative altitude of the cave
324 passage with respect to the main cave entrances in the past.

325 In the Pasillo de los Cubos, the layers of detrital sediments were covered by
326 aragonite layers (Fig. 4A). Aragonite precipitation occurred mainly around 400
327 ka. During this period, the cave was under vadose conditions and water films
328 began to flow over the detrital sediments deposited in earlier periods. CO₂
329 degassing (and probably evaporation) of the solution resulted in precipitation of
330 calcium carbonate as aragonite, a common mineral in dolomite caves like El
331 Soplao. The precipitation of aragonite as flowstone speleothems, however, is
332 not a frequent occurrence (Hill and Forti, 1997), although other cases have
333 recently been described elsewhere (Caddeo et al., 2011). Precipitation of
334 CaCO₃ as aragonite is frequently favoured by a high Mg/Ca ratio in the water, a
335 situation in which calcite precipitation is inhibited (Frisia et al., 2002).

336 Up to eleven flood events alternating with "quiet" periods of carbonate
337 precipitation were repeated between 422 +69/-43 ka and 400 +66/-42 ka in El
338 Soplao Cave. The cave was flooded by muddy water that introduced sediments

339 into the cave (Fig. 4B). When the inflow of water declined, water remained
340 temporally trapped in depressions in the cave as subterranean lakes where
341 suspended clay and silt settled down. CO₂ degassing of ponded water resulted
342 in supersaturation in calcium carbonate, thus a matrix of calcite was precipitated
343 that cemented the silty and clayey materials (Fig. 4C).

344 It is likely that the Mg/Ca of this underground water pool was lower, compared
345 to that of the water film flowing on the flowstone in previous stages, as a result
346 of paleoflood events. This was conditioned by the limited contact time between
347 the water flow and dolomitic host rock during paleofloods. In such situation of
348 low Mg/Ca ration in the water, the precipitation of calcite nucleation was
349 favoured on aragonite (Frisia et al., 2002). There are no evidences of
350 dissolution or corrosion of the carbonate layers on microscopic scale (Gázquez,
351 2012). This indicates that the water floods -subsaturated in calcite- were in
352 contact during a short time with aragonite layers precipitated in previous stages.
353 Otherwise, the earlier aragonite laminae would have been corroded by the
354 subsaturated ponded water. In addition, energy flow was low enough for the
355 sediments load deposition.

356 When the stagnant water disappeared due to evaporation or more probably
357 infiltration to deeper levels in the karst, a further water film flowed over the
358 cemented detrital sediments, so renewing the conditions for aragonite
359 precipitation. During some phases of aragonite precipitation, contributions of
360 water to the flowstone were not exclusively from sheet flows but also came from
361 dripwater from the cave ceiling impacting the speleothem surface. In this
362 situation, aragonite stalagmites formed on the calcareous pavement (Fig. 4D).
363 When the dripping slowed, a water film traversing the flowstone was again

364 dominant over dripwater from the ceiling. Thus, emergent stalagmites that had
365 begun to grow on the flowstone were fossilized inside new deposits of aragonite
366 (Fig. 4E). Subaerial periods, in which aragonite was precipitated were
367 repeatedly interrupted by flood events, when detrital sediments were introduced
368 into the cave, as revealed by the presence of thin brownish layers interbedded
369 in the aragonite lamina up to the 6.6 cm level of the flowstone (Fig. 3).
370 Regarding the uncertainties of the U/Th age of this relatively old speleothems,
371 we can only assert that sediments were introduced into the cave due to extreme
372 rainfall events that took place between MIS 11 and MIS 9. This period
373 comprised major paleoclimatic changes, including two interglacials and one
374 glacial stage. Therefore, it is not possible to attribute the occurrence of
375 paleofloods in El Soplao Cave to specific climatic conditions but to extreme
376 rainfall events, which occurred repeatedly in an unknown climatic framework.

377 Bluish-black layers appear in the upper strata of the flowstone which EDX
378 analysis (Gázquez et al., 2011; Gázquez, 2012) revealed to be oxides of Fe-
379 Mn-Zn, similar to those found in ferromanganese crusts near the Campamento
380 Gallery (Gázquez et al., 2011). The precipitation of these metal oxides in the El
381 Soplao Cave is related to the mobilization of metals (Fe, Mn and Zn) from the
382 host rock probably under phreatic anaerobic conditions (Fig. 4F) and their
383 subsequent precipitation on the walls and floors of the cave as oxides when the
384 water table fell and conditions were again oxygenic (Fig. 4G). In particular, the
385 ferromanganese layers appear on clayey sediment covering the ceiling of the
386 Campamento Gallery (Fig. 2C).

387 The existence of this black crust indicates that the water table was present at
388 that cave level in the past. Oxidation of Mn and Fe could be mediated by

389 microorganisms (as suggested by the presence of fossil bacteria inside
390 ferromanganese stromatolites recently discovered in this cave by Rossi et al.,
391 2010). Although the dark layers observed in the upper strata of the flowstone
392 are younger than 358 ka, precipitation of ferromanganese oxyhydroxides
393 occurred in El Soplao Cave also before 1 Ma BP (the age of the stromatolite
394 studied by Rossi et al., 2010) and these are crowned by carbonate stalagmites
395 with ages around 900 - 1000 ka. This suggests that El Soplao Cave has
396 remained hydrodynamically active, with alternating vadose and
397 phreatic/epiphreatic periods for at least the past 1 Ma.

398 After the period of metal oxide deposition in the Pasillo de los Cubos, conditions
399 for aragonite precipitation were renewed and new carbonate laminae were
400 precipitated, in this case fossilizing the dark layers. Conditions could be
401 phreatic/epiphreatic until at least 33 ka, when a further layer of aragonite was
402 precipitated, as recorded in the flowstone (Fig. 4H). In the period between 358
403 and 33 ka the evolution of the speleothem is uncertain. Most probably,
404 precipitation of carbonate layers alternated with flood events that deposited
405 additional clastic sediments. However, these materials could have been eroded
406 and remobilized by turbulent flows, thus removing some of the paleoclimatic
407 information recorded in the speleothem. This hypothesis is strongly supported
408 by evidence of stream erosion in the cave notches in the lower parts of the cave
409 walls and hanging flowstones (Jiménez-Sánchez et al., 2011), similar to the
410 flowstone studied in the current work. Suspended flowstones appear in several
411 locations in the cave, like in the Organ Chamber (Sala del Órgano) (Fig. 2B). In
412 the False Floor Chamber (Fig. 2F) a stalagmite pavement hangs 3 metres

413 above the cave floor as a result of the erosion of a thick deposit of detrital
414 sediments below it.

415 Finally, muddy coatings frequently cover older speleothems and the cave walls.
416 For instance, in the Campamento Gallery the height of the mud lamina is easily
417 identified on older speleothems (Fig, 2E, G and H), though the absence of mud
418 coatings on younger speleothems (Fig. 2E and H) suggests that flood events
419 did not occur in recent periods.

420

421 **CONCLUSIONS AND PALEOENVIRONMENTAL IMPLICATIONS**

422 Detrital sediments are introduced into caves due to extreme rainfall events, and
423 then are mobilized or stored depending on the particle size, the velocity of the
424 stream flow and the characteristics of the cave passages. If after paleofloods
425 “quite” vadose conditions take place during a long period, fluviokarstic
426 sediments can be covered by chemically precipitated sediments in the form of
427 flowstones or stalagmites. In cases, speleothemic carbonate layers prevent
428 older detrital sediments from being eroded by further energetic water flows.

429 In the present paper, we have demonstrated that dating carbonate layers
430 deposited over detrital sediments represents an alternative to direct dating of
431 clayey materials. In particular, a flowstone comprising aragonite and cemented
432 detrital layers from El Soplao Cave (Cantabria, northern Spain) was dated using
433 the U/Th method, revealing that this speleothem was intermittently formed
434 during the Quaternary, and sediments introduced into the cave mainly around
435 491-358 ka. Remarkably, this flowstone represents one of the few sedimentary
436 records of the period comprised between MIS 11 and MIS 9 discovered in the

437 Cantabrian Mountains to date (Villa et al., 2013), in particular by studying cave
438 sediments, and if so it might yield valuable paleoclimate information.

439 Further geochemical analyses, including stable isotopes and trace element
440 analysis together with a more precise geochronology of detrital sediments in
441 caves, could provide more details about the climatic framework in which
442 subterranean paleofloods took place, not only in El Soplao Cave but also in
443 other cavities where detrital materials interlayered between laminae of
444 speleothemic carbonate have been found.

445

446 **ACKNOWLEDGMENTS**

447 We are grateful to the management of El Soplao S.L. for providing access to the
448 cave and allowing us to use their facilities. Sarah Steines is also acknowledged
449 for revising the English. Financial support was made available through the
450 "PALEOGYP" International Collaboration Project (CGL2006-01707/BTE Ministry
451 of Science and Innovation. Spain), the Spanish Science Grant AP-2007-02799,
452 funds of the Water Resources and Environmental Geology Research Group
453 (University of Almería) and the Project "RLS Exomars Science" (AYA2011-
454 30291-C02-02; funded by the Ministry of Science and Innovation, Spain and
455 FEDER funds of EU). Finally, the authors appreciate the suggestions made by
456 Professors Jo De Waele and S.N. Lane, as well as two anonymous reviewers,
457 which helped to improve the original manuscript.

458

459 **REFERENCES**

460 Ballesteros D, Jiménez-Sánchez M, Giralt S, García-Sansegundo J. 2012.
461 Cartografía geomorfológica de cuevas y dataciones por el método U-Th.
462 Contribución a la espeleogénesis en los Picos de Europa (Norte de España).
463 In: Resúmenes extendidos del VIII Congreso Geológico de España. CD
464 anexo a Geo-Temas 13 (Eds. LP Fernández. A Fernández, A Cuesta, JR
465 Bahamonde): 649-652.

466 Boaretto E, Xiaohong W, Jiarong Y, Bar-Yosef O, Chu V, Pan Yan Liu K, Cohen
467 D, Jiao T, Li S, Gu H, Goldber P, Weiner S. 2009. Radiocarbon dating of
468 charcoal and bone collagen associated with early pottery at Yuchanyan
469 Cave. Hunan Province. China. PNAS 106: 9595-9600.

470 Bosch RF, White WB .2004. Lithofacies and transport of clastic sediments in
471 karstic aquifers. In: Studies of cave sediments (Eds: ID Sasowsky, JE
472 Mylroie), New York. Kluwer Academic/Plenum Publishers: 1–22.

473 Brook GA, Nickmann RJ. 1996. Evidence of late Quaternary environments in
474 northwestern Georgia from sediments preserved in Red Spider Cave.
475 Physical Geography 17: 465-484.

476 Bull PA. 1981. Some fine-grained sedimentation phenomena in caves. Earth
477 Surface Processes and Landforms 6: 11-22.

478 Caddeo GA, De Waele J, Frau F, Railsback LB. 2011. Trace element and
479 stable isotope data from a flowstone in a natural cave of the mining district of
480 SW Sardinia (Italy): evidence for Zn²⁺-induced aragonite precipitation in
481 comparatively wet climatic conditions. International Journal of Speleology 40
482 (2): 181-190.

- 483 Calaforra JM, Fernández-Cortés A, Gázquez-Parra JA, Novas N. 2011.
484 Conservando la cueva de El Soplao para el futuro: control de parámetros
485 ambientales. In: El Soplao: una ventana a la ciencia subterránea (Eds. El
486 Soplao S.L y Conserjería de Cultura. Turismo y Deportes del Gobierno de
487 Cantabria): 52-57.
- 488 Carcavilla L, Durán JJ. 2011. El Soplao como elemento central del patrimonio
489 geológico y minero de Cantabria. In: El Soplao. Una ventana a la ciencia
490 subterránea. (Eds. El Soplao S.L y Conserjería de Cultura, Turismo y
491 Deportes del Gobierno de Cantabria): 30-33.
- 492 Carcavilla L, Castanedo M, Durán JJ, Lozano RP, Robledo PA. 2011. 100
493 preguntas y respuestas sobre El Soplao. Una guía sencilla y divertida de la
494 cueva. (Eds. M^o Ciencia e Innovación. Madrid): 136 pp.
- 495 Chess DL, Chess CA, Sasowsky ID, Schmidt VA, White W. 2010. Clastic
496 sediments in the Butler Cave – sinking creek system, Virginia, USA. *Acta*
497 *Carsologica* 39(1): 11-26.
- 498 Dasgupta S, Saar MO, Edwards RL, Chuan-Chou S, Hai C, Alexander, EC Jr.
499 2010. Three thousand years of extreme rainfall events recorded in
500 stalagmites from Spring Valley Caverns, Minnesota. *Earth and Planetary*
501 *Science Letters* 300: 46–54.
- 502 De Waele J, Forti P, Picotti V, Galli E, Rossi A, Brook G, Zini L, Cucchi F. 2009.
503 Cave deposits in Cordillera de la Sal (Atacama, Chile). In: Rossi P.L. (Ed.),
504 Geological constraints on the onset and evolution of an extreme
505 environment: the Atacama Area, *GeoActa*, Special Publication 2, pp. 97-111.

506 Dorale JA, Gonzalez LA, Reagan MK, Pickett DA, Murrell M, Baker RG. 1992. A
507 High-Resolution Record of Holocene Climate in Speleothem calcite from
508 Cold Water Cave, Northeast Iowa. *Science* 258: 1626-1630.

509 Farrand WR. 2001. Sediments and Stratigraphy in Rock Shelters and Caves.
510 *Geoarcheology* 16: 537–557.

511 Ford DC, Williams PW. 2007. *Karst Hydrology and Geomorphology*. Wiley. 576
512 pp.

513 Frisia S, Borsato A, Fairchild IJ, McDermott F, Selmo EM. 2002. Aragonite–
514 calcite relationships in speleothems (Grotte de Clamouse, France):
515 Environment, fabrics and carbonate geochemistry. *Journal of Sedimentary*
516 *Research* 72: 687–699.

517 Gázquez F, Calaforra JM, Forti P. 2011. Black Mn-Fe Crusts as Markers of
518 Abrupt Palaeoenvironmental Changes in El Soplao Cave (Cantabria, Spain).
519 *International Journal of Speleology* 40: 163-169.

520 Gázquez F. 2012. Registros paleoambientales a partir de espeleotemas
521 yesíferos y carbonáticos. PhD Thesis. University of Almería. (Spain), 381 pp.

522 Gázquez F, Calaforra JM, Rull F, Forti P, García-Casco A. 2012. Organic
523 matter of fossil origin in the amberine speleothems from El Soplao Cave
524 (Cantabria, Northern Spain). *International Journal of Speleology* 41: 113-123.

525 González-Hierro M. 2011. De las primeras exploraciones espeleológicas a la
526 topografía 3-D. In: *El Soplao: una ventana a la ciencia subterránea* (Eds. El
527 Soplao S.L y Conserjería de Cultura, Turismo y Deportes del Gobierno de
528 Cantabria): 42-46.

- 529 Gospodarič R. 1998. Palaeoclimatic record of cave sediments from Postojna
530 karst. *Annales de la Société géologique de Belgique* T 111: 91-95.
- 531 Granger DE, Fabel D, Palmer AN. 2001. Pliocene-Pleistocene incision of the
532 Green River, Kentucky, determined from radiocative decay of cosmogenic
533 ²⁶Al and ¹⁰Be in Mammoth Cave sediments. *GSA Bulletin* 113(7); 825-
534 836.
- 535 Jiménez-Sánchez M, Ballesteros D, Domínguez-Cuesta MJ, Rodríguez-
536 Rodríguez L, Naves B. 2011. Geomorfología de la Cueva de El Soplao. In: El
537 Soplao: una ventana a la ciencia subterránea (Eds. El Soplao S.L y
538 Conserjería de Cultura, Turismo y Deportes del Gobierno de Cantabria): 81-
539 89.
- 540 Hill CA, Forti P, 1997. *Cave minerals of the World 2*. National Speleological
541 Society. Huntsville: 461 pp.
- 542 Hillaire-Marcel C, Gariépy C, Ghaleb B, Goy J., Zazo C, Cuerda J, 1996. U-
543 series measurements in Tyrrhenian deposits from Mallorca – Further
544 evidence for two last-interglacial high sea levels in the Balearic islands.
545 *Quaternary Science Reviews* 15: 53-62.
- 546 Karkanas P, Bar-Yosef O, Goldberg P, Weiner S. 2000 Diagenesis in
547 Prehistoric Caves: the Use of Minerals that Form In Situ to Assess the
548 Completeness of the Archaeological Record. *Journal of Archaeological*
549 *Sciences* 27: 915–929.

550 Kaufman A, Wasserburg GJ, Porcelli D, Bar-Matthews M, Ayalon A, Halicz L.
551 1998. U-Th isotope systematics from the Soreq Cave Israel and climatic
552 correlations. *Earth and Planetary Science Letters* 156: 141–155.

553 Klimchouk A, Andrejchuk V. 2002. Karst breakdown mechanisms from
554 observation in the gypsum caves the western Ukraine: Implications for
555 subsidence hazard assessment. *International Journal of Speleology* 31: 55-
556 88.

557 Lisker S, Porat R., Frumkin A. 2010. Late Neogene rift valley fill sediments
558 preserved in caves of the Dead Sea Fault Escarpment (Israel):
559 palaeogeographic and morphotectonic implications. *Sedimentology*. 57: 429-
560 435.

561 López-Cilla I, Rosales I, Najarro M, Martín-Chivelet J, Velasco F, Tornos F.
562 2009. Etapas de formación de dolomías masivas del entorno de La Florida-El
563 Soplao. Cantabria. *Geogaceta* 47: 65-68.

564 López-Horgue MA, Owen HG, Aranburu A, Fernández-Mendiola PA, Garcia-
565 Mondéjar J. 2009. Early-Late Albian (Cretaceous) of the central region of the
566 Basque-Cantabrian Basin, northern Spain: biostratigraphy based on
567 ammonites and orbitolinids. *Cretaceous Research* 30: 385-400.

568 Ludwig KR. 1999. Isoplot/Ex version 2.00. Berkeley Geochron. Center Spec.
569 Pub. 2. 47.

570 Mahler BJ, Lynch FL, Bennett PC. 1999. Mobile sediment in an urbanizing karst
571 aquifer: Implications for contaminant transport. *Environmental Geology* 39:
572 25–38.

- 573 Mahler BJ, Personne JC, Lods GF, Drogue C. 2000. Transport of free and
574 particulate-associated bacteria in karst. *Journal of Hydrology* 238: 179-193.
- 575 Martini I. 2011. Cave clastic sediments and implications for speleogenesis: new
576 insights from the Mugnano Cave (Montagnola Senese. Northern Apennines.
577 Italy). *Geomorphology* 134: 452-460.
- 578 Meléndez-Arsenio M, Rodríguez-González ML 2011. El agua subterránea,
579 eterna protagonista: el acuífero de La Florida. In: *El Soplao: una ventana a la*
580 *ciencia subterránea* (Eds. El Soplao S.L y Conserjería de Cultura. Turismo y
581 Deportes del Gobierno de Cantabria): 90-93.
- 582 Molokov A. 2001. ESR dating evidence for early man at a Lower Palaeolithic
583 cave-site in the Northern Caucasus as derived from terrestrial mollusc shells.
584 *Quaternary Science Reviews* 20: 1051-1055.
- 585 Murray KF. 1957. The Pleistocene climate and the fauna of Burnet Cave. New
586 Mexico. *Ecology* 38: 129-132.
- 587 Pickering R, Kramers JD, Partridge T, Kodolanyi J, Pettke T. 2010. U-Pb dating
588 of calcite-aragonite layers in speleothems from hominine sites in South Africa
589 by MC-ICP-MS. *Quaternary Geochronology* 5: 544-558.
- 590 Quesada S, Robles S, Rosales I. 2005. Depositional architecture and
591 transgressive-regressive cycles within Liassic backstepping carbonates
592 ramps in the Basque-Cantabrian Basin. N Spain. *Journal of the Geological*
593 *Society of London* 162: 531-548

594 Quinif Y, Meon H, Yans J. 2006. Nature and dating of karstic filling in the
595 Hainaut Province (Belgium). Karstic. geodynamic and paleogeographic
596 implications. *Geodinamica Acta* 19: 73-85.

597 Rossi C, Lozano RP, Isanta N, Hellstrom J. 2010. Manganese stromatolites in
598 caves: El Soplao (Cantabria). *Geology* 38: 1119-1122.

599 Sanna L, De Waele J, Pasini GC, Lauritzen S-E, Pascucci V, Andreucci S.
600 2010. Sea level changes in the Gulf of Orosei based on continental and
601 marine cave deposits. 85° Congresso Nazionale di Geologia, Pisa 6-8
602 settembre 2010, Rendiconti online della Società Geologica Italiana. 11: 48-
603 49.

604 Sasowsky ID, White WB, Schmidt VA. 1995. Determination of stream incision
605 rate in the Appalachian Plateaus by using cave-sediment
606 magnetostratigraphy. *Geology* 23: 415-418.

607 Sasowsky ID. 2007. Clastic Sediments in Caves – Imperfect Recorders of
608 Processes in Karst. *Acta carsologica* 36: 143-149.

609 Sasowsky ID, Clotts RA, Crowell B, Walko SM, LaRock EJ, Hauwert NN. 2007.
610 Paleomagnetic analysis of a long-term sediment trap. Kooken cave.
611 Huntingdon country. Pennsylvania. USA. In: *Studies of cave sediments:
612 Physical and Chemical Records of Paleoclimate* (Eds: ID Sasowsky, J
613 Mylroie. Springer. New York): 71-82.

614 Schmidt VA. 1982. Magnetostratigraphy of sediments in Mammoth Cave.
615 Kentucky. *Science* 217: 827–829.

616 Springer GS, Kite JS. 1997. River-derived slackwater sediments in caves along
617 Cheat River. West Virginia. *Geomorphology*. 18: 91-100.

- 618 Šroubek P, Diehl J, Kadlec J, Valoch K. 2001. A Late Pleistocene paleoclimatic
619 reconstruction based on mineral magnetic properties of the entrance facies
620 sediments of Kulna Cave. Czech Republic. *Geophysical Journal International*
621 147: 247–262.
- 622 Stock GM, Granger DE, Sasowsky ID, Anderson RS, Finkel RC. 2005.
623 Comparison of U–Th, paleomagnetism, and cosmogenic burial methods for
624 dating caves: Implications for landscape evolution studies: *Earth and*
625 *Planetary Science Letters* 236: 388-403.
- 626 Stöll H, Banasiak A, Jiménez-Sánchez M, Moreno A, Forjes FJ, Vadillo I,
627 Domínguez-Cuesta MJ, Pumariaga M. 2008. Registros paleoclimáticos de
628 estalagmitas en Asturias en base a su composición química elemental y la
629 presencia de capas de avenidas. In: *Cuevas turísticas, cuevas vivas*. (Eds.
630 JJ Durán, J López-Martínez. Madrid. Asociación de Cuevas Turísticas
631 Españolas): 53-60
- 632 Suárez F, Ramírez J, Aguilar MJ, Pujalte V. 1972. Mapa Geológico de España
633 1:50.000. hoja nº 57 (Cabezón de la Sal). IGME. Madrid.
- 634 Tornos F, Velasco F. 2011. Un yacimiento mineral muy especial. In: *El Soplao:*
635 *una ventana a la ciencia subterránea* (Eds. El Soplao S.L y Conserjería de
636 Cultura. Turismo y Deportes del Gobierno de Cantabria), 54-68.
- 637 Van Gundy JJ, White WB. 2009. Sediment flushing in Mystic Cave, West
638 Virginia, USA, in response to the 1985 Potomac Valley flood. *International*
639 *Journal of Speleology* 38 (2): 103-109.

640 Van Hengstum PJ, Scott DB, Gröcke DR, Charette MA. 2011. Sea level
641 controls sedimentation and environments in coastal caves and sinkholes.
642 Marine Geology 286: 35-50.

643 Vesper DJ, Loop CM, White W. 2003. Contaminant transport in karst aquifers
644 Speleogenesis and Evolution of Karst Aquifers. Speleogenesis 1: 1-11.

645 Vesper DJ, White WB. 2003. Metal transport to karst springs during storm flow:
646 An example from Fort Campbell. Kentucky/Tennessee. U.S.A. Journal of
647 Hydrology. 276: 20–36.

648 Villa E, Stoll H, Farias P, Adrado L, Edward RL, Cheng H. 2013. Age and
649 significance of the Quaternary cemented deposits of the Duje Valley (Picos
650 de Europa. Northern Spain). Quaternary Research 79: 1-5.

651 White WB. 2007. Cave sediments and paleoclimate. Journal of Cave and Karst
652 Studies 69: 76-93.

653 Zupan Hajna N, Mihevc A, Pruner P, Bosák P. 2010. Palaeomagnetic research
654 on karst sediments in Slovenia. International Journal of Speleology 39: 47-
655 60.

656

Sample ID	Distance from base (mm)	²³⁸ U (ppb)	²³⁴ U/ ²³⁸ U	²³⁰ Th/ ²³² Th	²³⁰ Th/ ²³⁴ U	Age (yrs)	σ + (yrs)	σ - (yrs)
SPL-00	1	47,490 ± 161	1.129 ± 0005	459 ± 6	1.058 ± 0.010	> 500.000*	-	-
SPL-30	30	34,578 ± 206	1.136 ± 0.004	1155 ± 13	0.261 ± 0.002	421.847	69.835	42.886
SPL-60	60	41,315 ± 285	1.111 ± 0.012	4593 ± 47	1.011 ± 0.011	400.315	66.331	41.975
SPL-67	67	18,211 ± 60	1.148 ± 0.010	5188 ± 57	1.027 ± 0.010	32.671	369	367

657

658 **Table 1.** Uranium concentration, measured U and Th activity ratios and ages of
659 subsamples from the flowstone of Pasillo de los Cubos. *The age of sample
660 SPL-00 was beyond the threshold of the U-Th method.

661