

## Chronology of Termination II and the Last Interglacial Period in North Spain based on stable isotope records of stalagmites from Cueva del Cobre (Palencia)

Cronología de la Terminación II y del Último Periodo Interglacial en el norte de España a partir de los registros de isótopos estables de estalagmitas procedentes de la Cueva del Cobre (Palencia)

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Received: 17/08/06 / Accepted: 10/11/06

### Abstract

New insight into the timing and structure of the Last Interglacial Period (Eemian) was obtained through U-Th dating of four speleothems from Northern Spain and an analysis of their stable isotope records. The four stalagmites examined were collected from different levels of Cueva del Cobre, a cold high-mountain cave in the Cantabrian Ranges (N Spain), in which speleothem growth took place essentially during the warmer interstadials. Through 18 TIMS and ICPMS datings and 263 stable isotope analyses, the onset of the Eemian interglacial period was precisely dated at  $150 \pm 2$  ka, an age consistent with a few other palaeoclimatic records but notably younger than the age ascribed by the Milankovitch theory. We also date the Eemian–Weichselian transition ( $\sim 115$  ka) for the first time in the Iberian Peninsula.

U-Th ages revealed a consistent anomaly at  $\sim 105$ -100 ka BP, which could be related to a drastic environmental change during the MIS-5c interstadial. This event would have caused the resetting of the U-Th system at the base of the stalagmites during a short time interval. In addition, we propose a new simple geochemical test to ensure the lack of disturbance of this type of samples for dating purposes.

**Keywords:** Speleothems, Uranium-series, stable isotopes, palaeoclimate, Eemian, Spain.

### Resumen

En este artículo se aportan nuevos datos sobre la cronología y estructura del Último Periodo Interglacial (Eemiense) mediante la datación por U-Th de cuatro espeleotemas procedentes del norte de España y el análisis de sus registros de isótopos estables. Las cuatro estalagmitas estudiadas proceden de distintos niveles de la Cueva del Cobre, una cueva de alta montaña, relativamente fría, situada en la Cordillera Cantábrica, y en la que el crecimiento de espeleotemas tuvo lugar principalmente durante los estadios cálidos. El comienzo del periodo interglacial Eemiense se ha situado de manera precisa en  $\sim 150 \pm 2$  ka mediante 18 edades de TIMS e ICPMS y 263 análisis de isótopos estables de oxígeno de las estalagmitas. Esta edad es coherente con otros registros paleoclimáticos, pero

notablemente más reciente que la edad calculada a partir de los ciclos de Milankovitch. También ha sido posible datar la transición Eemense-Weichseliense (~115 ka) por primera vez en la Península Ibérica.

Por otro lado, las dataciones de U-Th revelaron una anomalía consistente entre ~105-100 ka, que podría estar relacionada con un drástico cambio ambiental durante el interestadio MIS-5c. Este evento podría haber abierto el sistema de U-Th en las bases de las cuatro estalagmitas durante un corto intervalo de tiempo. Además, en este trabajo proponemos por primera vez una sencilla prueba geoquímica para comprobar la ausencia de alteraciones del sistema de U-Th en las muestras elegidas para obtener las dataciones.

*Palabras clave:* Espeleotemas, series de uranio, isótopos estables, paleoclima, Eemense, España.

## 1. Introduction

Knowledge of the climate of past interglacial periods is essential for our understanding of current climate and the forces driving global change. This acknowledgement has generated increasing interest in the Last Interglacial Period (Eemian) (e.g., Landwehr *et al.*, 1997; Broecker, 1998; Cheddadi *et al.*, 1998; Lototskaya and Ganssen, 1999; Sánchez-Goñi *et al.*, 1999; Kukla *et al.*, 2002; Winograd, 2002; Turner, 2002; Gallup *et al.*, 2002; Spötl *et al.*, 2002; Shackleton *et al.*, 2003; van Kolfshoten *et al.*, 2003; Tzedakis *et al.*, 2003; Yuan *et al.*, 2004; Drysdale *et al.*, 2004; Bar-Matthews *et al.*, 2006; Constantin *et al.*, 2006) as the best possible analogue for the Holocene. The notable effort dedicated to this topic has, nevertheless, yielded a large number of contradictory results and uncertainties.

The stable-isotope U-record of Devil's Hole vein calcite (Winograd *et al.*, 1992; Landwehr *et al.*, 1997) has suggested that the onset of the Eemian (i.e., "Termination II") was significantly earlier than previously inferred from the marine stable-isotope record and the Milankovitch theory (Imbrie *et al.*, 1984; Karner and Muller, 2000). In addition to Devil's Hole, other palaeoclimate records indicate that Termination II could have started earlier than the beginning of the Marine Isotope Substage 5e (MIS-5e) (e.g. Lauritzen, 1995; Winograd, 2002; Gallup *et al.*, 2002; Spötl *et al.*, 2002; Shackleton *et al.*, 2003; Yuan *et al.*, 2004). This uncertainty regarding the timing of the penultimate global deglaciation has also reached Europe, where different ages have been proposed for the retreat of the British and Fennoscandian ice sheets (Winograd, 2002). In the framework of this controversial issue, acquiring absolute ages from palaeoclimate proxies to document the ice retreat in Europe and other areas is essential. To this end, speleothems are very useful records, since they are sensitive to climate changes and can be dated precisely by means of U-Th series.

The aim of this study was to analyze four stalagmites that grew during the Eemian in Cueva del Cobre, an extensive cave in the Cantabrian Mountains (N Spain). The area in question occurs at latitudes notably lower than the sites of previously published studies of Eemian records in

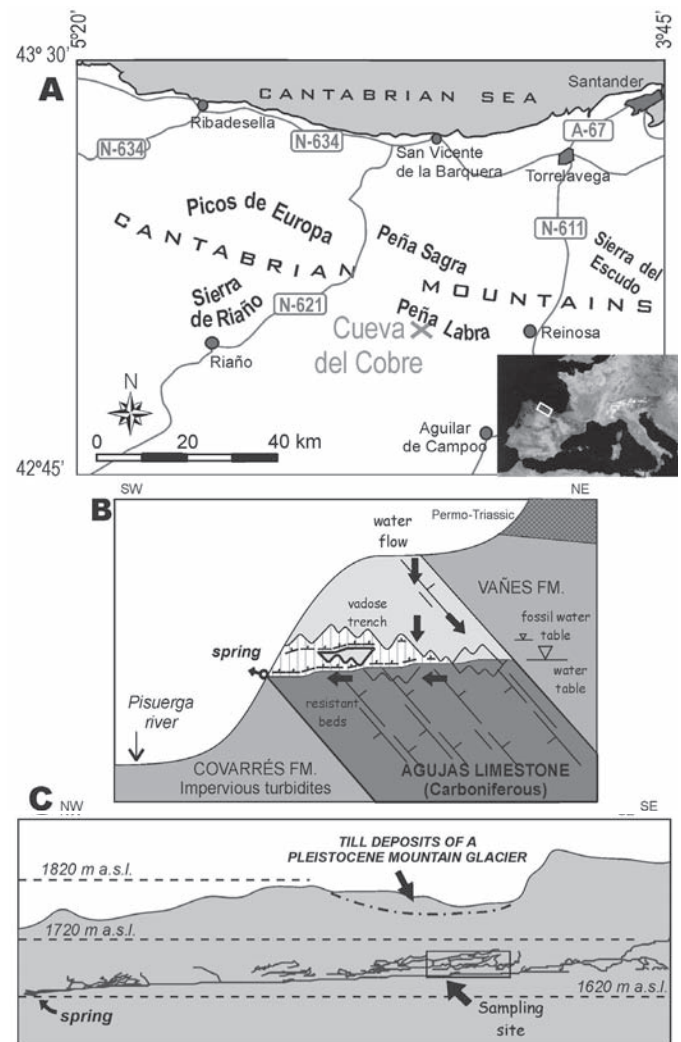


Fig. 1.- (A) Map of Northern Spain showing the location of Cueva del Cobre and the main roads. The cave is sheltered from marine influence by a large mountain range. (B) Schematic profile of Cueva del Cobre in the dip direction, showing the location of the base level and the geometry of the water table (modified from Rossi *et al.*, 1997). (C) Profile of Cueva del Cobre along the strike of the limestone, showing the sampling area (after Rossi *et al.*, 1997).

Fig. 1.- (A) Mapa de localización de la Cueva del Cobre (norte de España) junto con las principales carreteras. La Cordillera Cantábrica aísla la cueva de la influencia marina. (B) Corte esquemático de la Cueva del Cobre según la dirección de buzamiento de las capas de caliza. Se muestra la situación del nivel de base actual y la geometría de la lámina de agua (modificado de Rossi *et al.*, 1997). (C) Perfil de la Cueva del Cobre según la dirección de las capas y zona de muestreo de los espeleotemas (según Rossi *et al.*, 1997).

Europe. Spain was only partly covered by ice during the Pleistocene glacial periods, and deglaciation in response to climate change during the Saalian-Eemian transition is likely to have commenced earlier than at higher latitudes.

Cueva del Cobre is a high mountain cave (~1600-1800 m a.s.l.) located under a prominent Pleistocene mountain glacier during some of the colder intervals of the Pleistocene (Rossi *et al.*, 1997). Previous works have established that the cave is fairly sensitive to climate changes (Muñoz-García *et al.*, 2002; Martín-Chivelet *et al.*, in press) and that speleothem growth took (and takes) place only during warmer climate periods (Muñoz-García *et al.*, 2004a). In this study, we attempt to date the Saalian-Eemian transition by assuming that Termination II provoked the onset of growth of the Eemian stalagmites in the cave.

## 2. Location and geological setting

The Cueva del Cobre in the Sierra de Peñalabra, to the south of the watershed of the Cantabrian Mountains (Northern Spain; Fig. 1A), is a karst cave lying ~1600 to 1800 m a.s.l. in steeply dipping Carboniferous limestones (Fig. 1B). This ideal water-table cave (*sensu* Ford and Ewers, 1978) contains an active low-gradient canyon and several relict low-gradient canyons at higher elevations, amounting to ~10 km of the conduits surveyed (Fig. 1C; Rossi *et al.*, 1997). The only known entrance is the cave resurgence, which appears at ~1600 m a.s.l.

The area has a humid, high-mountain climate with marked seasonality. Mean annual precipitation for the period 1990-2002 exceeded 950 mm in Santa María de Redondo, the closest village 5 km away from the cave, at ~1220 m a.s.l. A significant part of the precipitation in the area above the cave falls as snow between November and April (Martín-Chivelet *et al.*, 2006).

The cave entrance appears at roughly the same height as the timberline. The forests of the Sierra de Peñalabra are mainly comprised of *Fagus sylvatica* and oaks. In the area above the cave, the vegetation consists of grasses and bushes.

## 3. Sampling site

The stalagmites examined were retrieved from relict canyons at heights ~48 to ~63 m above the resurgence. The sampling area is about 1200 m away from the resurgence and more than 100 m below the ground surface (Figs. 1C and 2), and accordingly should not be affected by seasonal fluctuations in the outside air temperature.

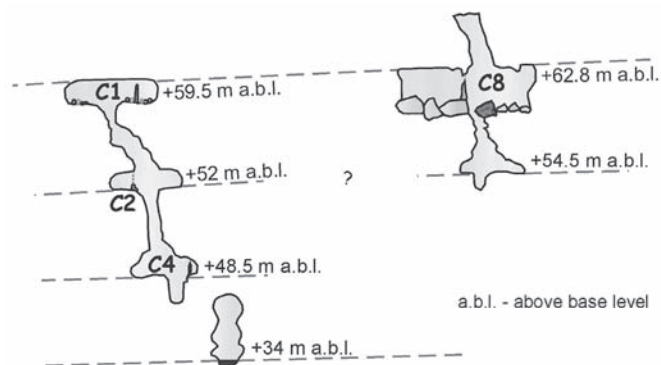


Fig. 2.- Schematic cross-sections of the relict canyons from which the four stalagmites were obtained.

Fig. 2.- Corte esquemático con la situación de los niveles relictos en los que se recogieron las cuatro estalagmitas.

A limited number of temperature measurements suggests that the air temperature at the sampling sites is  $5.5 \pm 0.3^\circ\text{C}$  and remains nearly constant throughout the year. In the relict cave passages where the stalagmites were collected, air currents are not significant and the relative humidity of the air is 98% ( $\pm 2\%$ ).

## 4. Analytical methods

Twenty three  $^{230}\text{Th}/\text{U}$  datings were performed on the 4 stalagmites collected (Fig. 3). Of these datings, 18 corresponded to Termination II, the Eemian period and transition to the Weichselian. Thirteen of these 18 ages were obtained by thermal ionization mass spectrometry (TIMS) at McMaster University (Canada) using a VG 354 instrument. A further 4 stalagmite samples were subjected to induction-coupled mass spectrometry (ICPMS) at the GEOTOP laboratory of the University of Quebec (Montreal, Canada) using a VG ISOLAB instrument. The procedures used for analysis were as described by Li *et al.* (1989). The last sample was examined by alpha spectrometry at the *Polish Academy of Sciences* (Warsaw, Poland). The four ICPMS samples were duplicates of those examined by TIMS obtained by splitting larger samples into two similar, homogeneous subsamples.

Next, 263 samples of the stalagmites for stable isotope analyses were obtained at 10 mm (C8) or 2 mm (C1 and C4) intervals along the central growth axis (Fig. 3) using a 0.8 mm (C8) or a 0.5 mm-diameter drill (C1 and C4). The samples for isotope testing were extracted from thin petrographic sections under the microscope, so that calcite showing any kind of diagenetic overprint could be rejected. For C8, the calcite was dissolved in pure  $\text{H}_3\text{PO}_4$  at  $95^\circ\text{C}$  and the resultant  $\text{CO}_2$  analyzed in a VG-SIRA mass spectrometer fitted with an Autocarb automatic analyzer for carbonates (McMaster University). For C1 and C4,

the calcite was dissolved in pure  $\text{H}_3\text{PO}_4$  at 70°C and the  $\text{CO}_2$  analyzed in a Finnigan MAT 252 with a Carbonate Device III (University of Minnesota). Results are reported as deviations per mil (‰) with respect to the VPDB standard. The precision of the analyses in all cases was  $\pm 0.1$  ‰ for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ .

To establish a reliable palaeoclimatic record based on oxygen isotopes, stalagmites should precipitate at or near the isotope equilibrium (e.g., Schwarcz, 1986). This equilibrium during calcite precipitation was checked for using Hendy's criteria (1971) in stalagmites C1, C4 and C8. Seven individual laminae, were subjected a series of oxygen and carbon isotope analyses. For these tests, samples were obtained along a transverse line from the center of the growth lamina to both its edges, i.e., along the former flow path of the water film. According to Hendy (1971), the oxygen isotope composition of the calcite in each layer should be largely independent of the distance from the apex, when no kinetic fractionation occurs and calcite precipitates in isotopic equilibrium. Besides, no covariation between carbon and oxygen isotopes should be observed in each growth layer.

Petrographic examination was performed using a Nikon Eclipse E400 POL microscope on 40 double-polished, uncovered thin sections, about  $\sim 500$   $\mu\text{m}$  thick. In addition, a polished slab about 5 mm thick was prepared for each of the stalagmites (Fig. 3) and mapped to keep as reference.

## 5. Description of the samples

In polished slabs and thin sections, the stalagmites showed no obvious signs of alteration and/or recrystallization. All the stalagmites were made up of columnar calcite which, according to Frisia *et al.* (2000), typically precipitates by slow degassing of  $\text{CO}_2$  at or very close to conditions of isotopic equilibrium. The four stalagmites varied in size and colour (Fig. 3). C1 is a cylindrical stalagmite, 73 cm long and 7 cm wide, collected  $\sim 59.5$  m above the base level. In polished slabs, C1 appears transparent and yellowish. At  $\sim 67$  cm from the base, a dark band corresponding to a series of hiatuses marks the end of apparent continuous growth. C2 is a conical stalagmite, 13 cm long and 10 cm wide at the base, obtained  $\sim 52$  m above the base level under an active drip. In polished slabs, C2 appears very dark and its growth pattern seems complex, indicating alternate periods of precipitation and detrital deposition. C4 is a cylindrical stalagmite, 52 cm long and 7 cm wide, obtained  $\sim 48.5$  m above the base level. In polished slabs, C4 shows a milky appearance and two surfaces that correspond to interruptions of growth. In this report, we will only discuss the portion of stalag-

mite below the lowest hiatus found  $\sim 26$  cm from the base. C8, collected  $\sim 62.8$  m above the base level from under an active drip, is roughly conical in shape. Due to its relatively large size, C8 could not be entirely removed from the cave. The portion recovered was 68 cm long and 15 cm wide at the base. C8 shows a marked growth banding formed by alternating thick light- and dark brown bands; under the microscope, growth appears to be continuous.

## 6. Results

### 6.1. U-Th dating

The absolute ages obtained for 18 the samples ranged from 140 to 90 ka BP (late Pleistocene). Table 1 provides a summary of the dating results. The  $^{238}\text{U}/^{234}\text{U}$  activity ratios for all the datings were in –or close to– the range 1-1.5, the normal range for meteoric waters. Only stalagmite sample C2b showed initial thorium contamination ( $^{230}\text{Th}/^{232}\text{Th} = 6.78$ ; Ivanovich and Harmon, 1992). However, when the absolute ages obtained were correlated with stratigraphy, some of the datings appeared to be out of chronostratigraphic order. Unfortunately, this is a common problem when trying to date speleothems (e.g., Frumkin *et al.*, 1999; Quinif and Maire, 2004; Muñoz-García *et al.*, 2004b), since usually they show no clear physical or petrographic pattern *a priori* that would prompt their rejection.

We followed a simple procedure to discriminate between “good” and “anomalous” age-datings. This test proved useful, and we would recommend its use in future studies. It consists of the following steps:

1) *Identify all the age-datings that could be anomalous on the basis of their stratigraphic position.*

For stalagmite C1, the age of the base (C1b;  $105.2 \pm 1.2$  ka BP) is notably younger than the date obtained for sample C1-6-B immediately above the base ( $136.6 \pm 3.0$  ka BP) and probably too young to stratigraphically match the middle sample C1m ( $103.1 \pm 1.7$  ka BP) corresponding to 40 cm above the base. The uppermost samples C1-22-D and C1x3, which are virtually of the same age ( $90.2 \pm 1.3$  and  $91.3 \pm 1.7$  ka BP, respectively), are in line with the coherent chronostratigraphic succession of the two previous dates. The U-Th datings for stalagmite C4 follow the stratigraphic order (Table 1) except the two samples from the base (C4b-TIMS and C4b-ICPMS). Finally, for stalagmite C8, seven valid U-Th dates were obtained (Table 1), all of which showed accurate ratios and acceptable error ranges, although many were out of stratigraphic order.

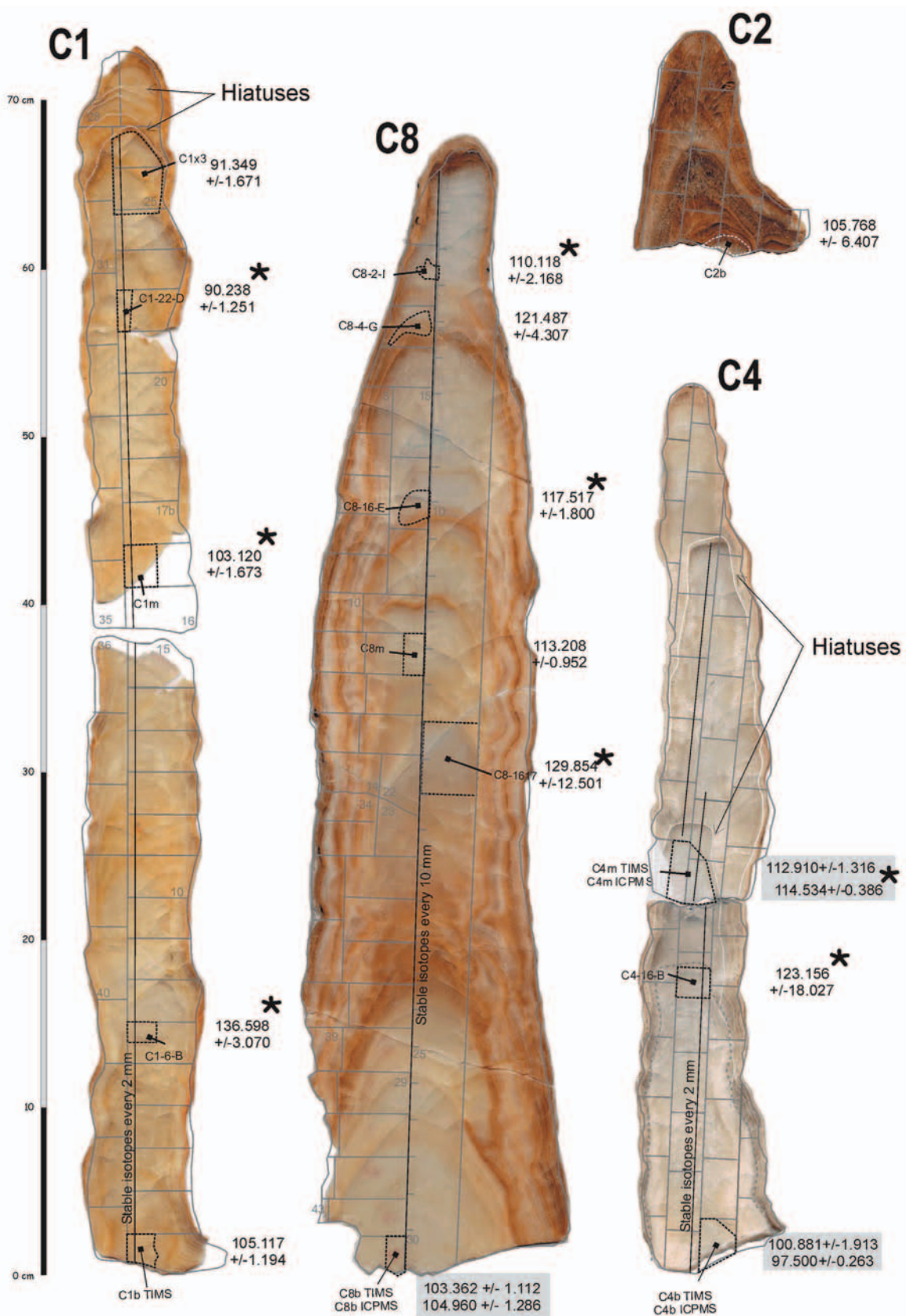


Fig. 3.-  $^{230}\text{Th}/\text{U}$  dating results (ka BP) and positions of the samples used for the stable isotope analyses. Ages indicated in the grey rectangles are duplicates yielded by TIMS and ICP-MS and should therefore be the same. Stars indicate the results used to set the chronology for this study. Fig. 3.- Resultados de las dataciones de  $^{230}\text{Th}/\text{U}$  (ka BP) y posición de las muestras utilizadas para los análisis de isótopos estables. Las edades situadas dentro de un rectángulo gris corresponden a muestras duplicadas obtenidas por medio de TIMS e ICPMS, y por lo tanto deberían ser iguales. Los asteriscos señalan los resultados utilizados para obtener la cronología de este estudio.

Stalagmite	Sample	m-s [U] (ppm)	$^{230}\text{Th}/^{232}\text{Th}$	$^{230}\text{Th}/^{234}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	Age (ka)	Counting technique
C1	C1x3	0.12	1576 +/- 20	0.591 +/- 0.007	1.485 +/- 0.003	91.3 +/- 1.7	TIMS
	C1-22-D	0.16	802 +/- 8	0.586 +/- 0.005	1.473 +/- 0.002	90.2 +/- 1.3	TIMS
	C1m	0.15	2954 +/- 33	0.639 +/- 0.007	1.478 +/- 0.001	103.1 +/- 1.7	TIMS
	C1-6-B	0.14	1303 +/- 16	0.754 +/- 0.009	1.460 +/- 0.002	136.6 +/- 3.0	TIMS
	C1b	0.13	863 +/- 7	0.644 +/- 0.004	1.406 +/- 0.002	105.2 +/- 1.2	TIMS
C2	C2b	0.09	6.8 +/- 0.2	0.69 +/- 0.02	1.142 +/- 0.002	105.8 +/- 6.4	TIMS
C4	C4m ICP	0.42	7484 +/- 23	0.651 +/- 0.001	0.999 +/- 0.001	114.53 +/- 0.39	ICPMS
	C4m TIMS	0.47	5297 +/- 41	0.648 +/- 0.004	1.019 +/- 0.001	112.9 +/- 1.3	TIMS
	C4-16-B	0.56	7336 +/- 532	0.68 +/- 0.05	1.006 +/- 0.002	123 +/- 18	TIMS
	C4b ICP	0.72	3464.3 +/- 7.9	0.5904 +/- 0.0009	0.979 +/- 0.001	97.50 +/- 0.26	ICPMS
	C4b TIMS	0.70	2082 +/- 80	0.604 +/- 0.007	0.988 +/- 0.002	100.9 +/- 1.9	TIMS
C8	C8-2-I	0.12	667.3 +/- 7.8	0.649 +/- 0.007	1.144 +/- 0.003	110.1 +/- 2.2	TIMS
	C8-4-G	0.10	255.3 +/- 4.9	0.68 +/- 0.01	1.063 +/- 0.002	121.5 +/- 4.3	TIMS
	C8-16-E	0.14	1542 +/- 14	0.671 +/- 0.006	1.116 +/- 0.002	117.5 +/- 1.8	TIMS
	C8m ICP	0.11	1173.0 +/- 6.1	0.651 +/- 0.003	1.049 +/- 0.001	113.21 +/- 0.95	ICPMS
	C8-1617	0.15	214 +/- 164	0.70 +/- 0.03	1.11 +/- 0.05	130 +/- 12.5	ALPHA
	C8b TIMS	0.09	482.4 +/- 3.4	0.621 +/- 0.004	1.082 +/- 0.001	103.6 +/- 1.1	TIMS
	C8b ICP	0.10	720.4 +/- 5.1	0.625 +/- 0.004	1.079 +/- 0.003	105.0 +/- 1.3	ICPMS

Table 1.- Analytical results of the  $^{230}\text{Th}/\text{U}$  datings for the four stalagmites from Cueva del Cobre. Uncertainties correspond to  $2\sigma$  for mass spectrometry samples and  $1\sigma$  for alpha spectrometry.

Tabla 1.- Resultados analíticos de las dataciones de  $^{230}\text{Th}/\text{U}$  de las cuatro estalagmitas procedentes de la Cueva del Cobre. Las incertidumbres corresponden a  $2\sigma$  para las muestras analizadas por espectrometría de masas y a  $1\sigma$  para las de espectrometría alfa.

## 2) Repeat the analyses yielding anomalous ages to decide between natural or artificial causes for these anomalous data.

All our replicate samples, including two of the three yielding anomalous ages for the bases (C4 and C8) provided similar results (Fig. 3) in the tests performed at different laboratories using different methods (McMaster University – TIMS and GEOTOP – ICPMS) suggesting the anomalous ages are a result of the natural U/Th ratio in calcite and not due to an artefact. Duplicate samples from the base of C8 yielded similar ages ( $103.6 \pm 1.1$  and  $105.0 \pm 1.3$  ka BP). The duplicate samples C4m-TIMS and C4m-ICPMS were also within the error range ( $112.9 \pm 1.3$  and  $114.53 \pm 0.39$  ka BP). The ages obtained for the base of C4 (C4b-TIMS and C4b-ICPMS) were similar despite the different counting methods used ( $100.9 \pm 1.9$  and  $97.50 \pm 0.26$  ka BP). These two techniques (TIMS and ICPMS) yielded uranium contents (0.70, 0.72 ppm, respectively) for C4b at least 0.2 ppm higher than for the remaining samples from the same stalagmite, suggesting natural uranium contamination.

## 3) Search for U-Th system alterations: uranium plots.

For replicate samples yielding similar anomalous ages, we can assume the anomaly is caused by a natural change in the U-Th system. To establish such an alteration, a graph of departures from the mean uranium values

of each selected interval of the stalagmite is prepared by plotting total uranium contents (x axis) against  $^{234}\text{U}/^{238}\text{U}$  activity ratios (y axis). The accuracy of this method seems to increase when dealing with relatively short time intervals such as here.

The uranium total content in the calcite of the speleothems depends on many factors: climate, the routing of ground water, vegetation above the cave, dust, etc. (Ayalon *et al.*, 1999). Then, if the environmental conditions were similar during calcite deposition for each speleothem, then both total uranium contents and  $^{234}\text{U}/^{238}\text{U}$  ratios would be similar for all the samples of a single speleothem. Hence, different samples would yield relatively homogeneous data and these would appear as a cluster in the graph. Similarly, any alterations caused during periods of time under different environmental conditions, will lead to different uranium values and the data for the particular sample will appear separate from the cluster.

Figures 4A, 5A and 6A show the uranium plots for stalagmites C1, C4 and C8. It may be seen that 3 of the C1 samples, the ones in correct stratigraphic order, show fairly consistent deviations from mean uranium contents and  $^{234}\text{U}/^{238}\text{U}$  ratios, while the anomalous C1 samples shows markedly different deviations. These deviations are not necessary larger, but still they locate the samples away from the homogeneous group in the graph. In the case of C4 (Fig. 5A), the uranium test results also show how the three samples whose ages are in stratigraphic or-

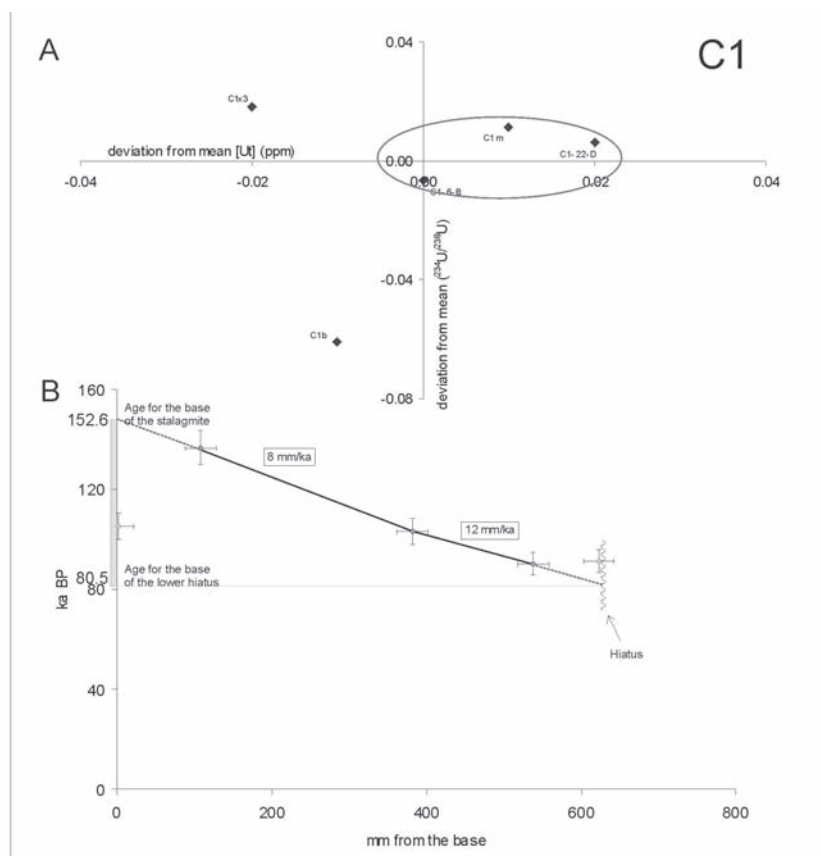
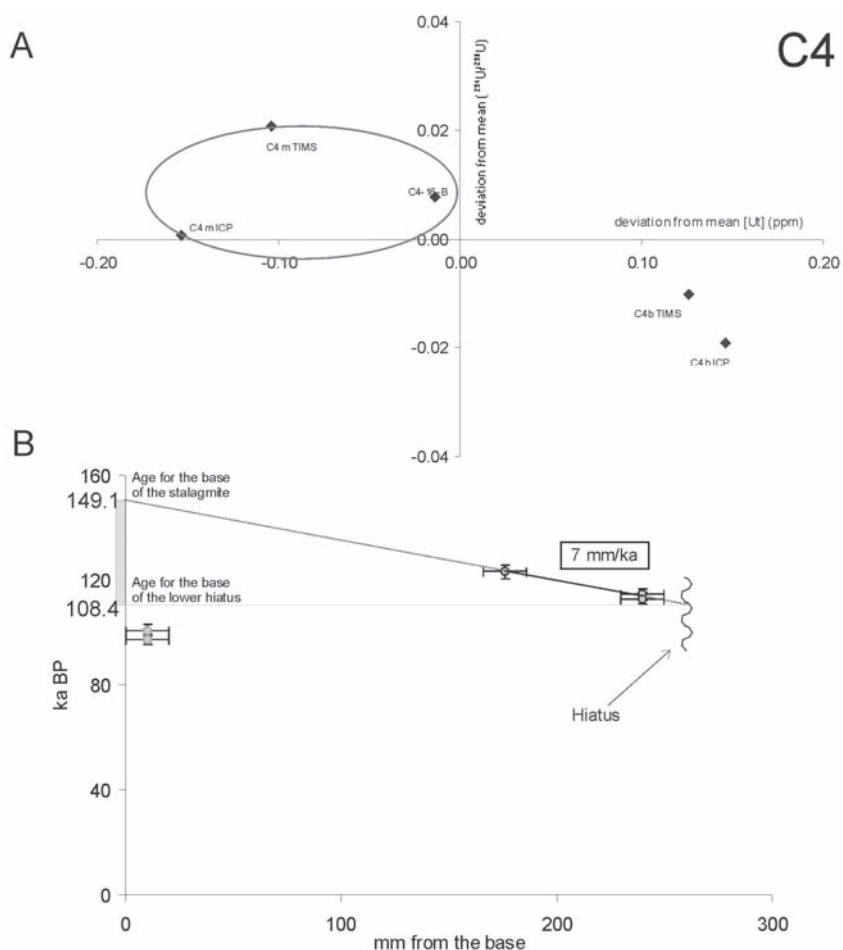


Fig. 4.- A) “Uranium test” for the <sup>230</sup>Th/U results for C1. The X axis corresponds to deviations from the mean total uranium content (ppm) calculated using all the results of similar age. The Y-axis presents the deviation from mean <sup>234</sup>U/<sup>238</sup>U activities. The ellipse shows the ages with homogeneous values. B) Graphic correlation for stalagmite C1 showing the calculated age for its base and the base of the hiatus. Anomalous ages (grey colour) are included as a reference.

Fig. 4.- A) “Test de uranio” aplicado a los resultados de las dataciones de <sup>230</sup>Th/U de C1. El eje X corresponde a las desviaciones de la media del contenido total de uranio (ppm) calculado utilizando todos los resultados de edad similar. El eje Y presenta la desviación de la media de las actividades <sup>234</sup>U/<sup>238</sup>U. La elipse muestra las edades con valores homogéneos. B) Correlación gráfica para la estalagmita C1 en la que se indica las edades calculadas para la base de la estalagmita y el comienzo del hiato. Las edades anómalas (color gris) se incluyen como referencia.

Fig. 5.- A) “Uranium test” for the <sup>230</sup>Th/U results for C4. The X axis corresponds to deviations from the mean total uranium content (ppm) calculated using all the results of similar age. The Y-axis presents the deviation from mean <sup>234</sup>U/<sup>238</sup>U activities. The ellipse shows the ages with homogeneous values. B) Graphic correlation for stalagmite C4 showing the calculated age for its base and the base of the lowest hiatus. Anomalous ages (grey colour) are included as a reference.

Fig. 5.- A) “Test de uranio” aplicado a los resultados de las dataciones de <sup>230</sup>Th/U de C4. El eje X corresponde a las desviaciones de la media del contenido total de uranio (ppm) calculado utilizando todos los resultados de edad similar. El eje Y presenta la desviación de la media de las actividades <sup>234</sup>U/<sup>238</sup>U. La elipse muestra las edades con valores homogéneos. B) Correlación gráfica para la estalagmita C4 en la que se indica las edades calculadas para la base de la estalagmita y el comienzo del hiato inferior. Las edades anómalas (color gris) se incluyen como referencia.



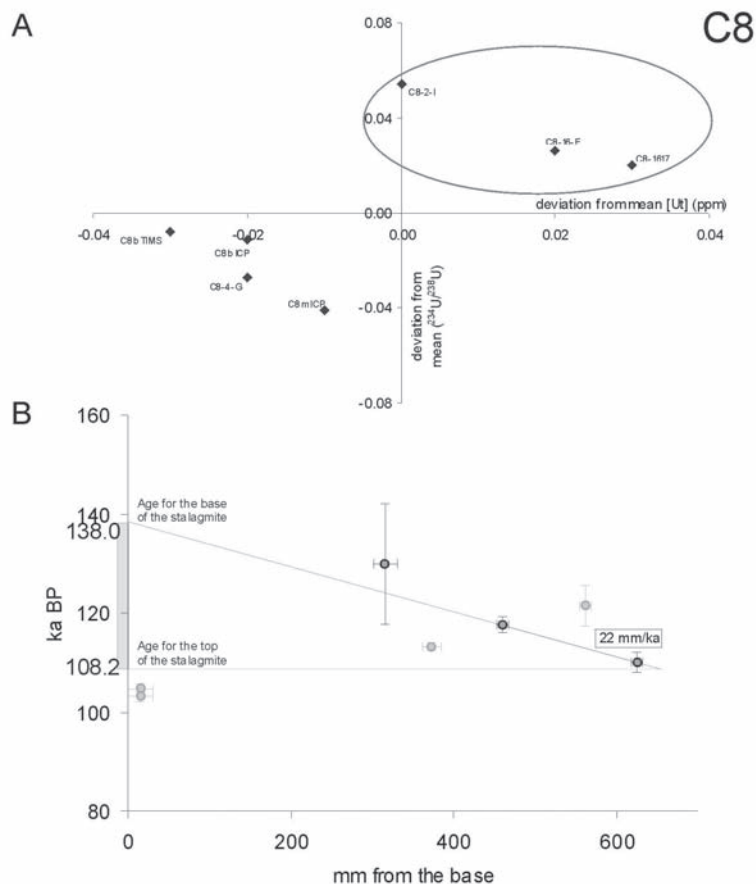


Fig. 6.- A) “Uranium test” for the  $^{230}\text{Th}/\text{U}$  results for C8. The X axis corresponds to deviations from the mean total uranium content (ppm) calculated using all the results of similar age. The Y-axis presents the deviation from mean  $^{234}\text{U}/^{238}\text{U}$  activities. The ellipse shows the ages with homogeneous values. B) Graphic correlation for stalagmite C8 showing the calculated age for its base and tip. Anomalous ages (grey colour) are included as a reference.

Fig. 6.- A) “Test de uranio” aplicado a los resultados de las dataciones de  $^{230}\text{Th}/\text{U}$  de C8. El eje X corresponde a las desviaciones de la media del contenido total de uranio (ppm) calculado utilizando todos los resultados de edad similar. El eje Y presenta la desviación de la media de las actividades  $^{234}\text{U}/^{238}\text{U}$ . La elipse muestra las edades con valores homogéneos. B) Correlación gráfica para la estalagmita C8 en la que se indica las edades calculadas para la base y el ápice de la estalagmita. Las edades anómalas (color gris) se incluyen como referencia.

der, show quite homogeneous deviations, while those for the base of the stalagmite appear separate from these. For stalagmite C8, the results cluster as two groups (Fig. 6A). In this figure, the ages with positive uranium deviations (marked in the figure) are in coherent stratigraphic order.

#### 4) Graphic correlation.

The validity of the previous test in each case can be checked by constructing a graphic correlation diagram (diagrams in which the ages are plotted against their stratigraphical position). If the results are valid, the age-datings of the homogeneous group should show a coherent chronostratigraphic sequence, i.e., give consistent growth rates for the speleothem, whereas anomalous ages will appear apart from the particular growth pattern. Graphic correlation plots are also useful for interpolating and extrapolating absolute ages through the stalagmite axis.

Figures 4B, 5B and 6B show graphic correlation diagrams for stalagmites C1, C4 and C8, respectively. In all cases, ages scattered in the main cluster are in correct stratigraphic order. Moreover, in the case of C8, the rest of the ages showing negative deviations are in reverse order and, if used to calculate the chronology, they would indicate impossible (negative) growth rates (Fig. 6B).

The fact that all the anomalous ages grouped together, could suggest the same origin for all the anomalies in this speleothem.

#### 5) Search for the origin of U-Th system alterations

Although anomalous ages should not be used in the chronostratigraphic analyses, their origin should be understood so that we can improve the sample selection process in future datings. Besides, these may provide interesting information on alteration processes occurring in the stalagmites, which could also have palaeoenvironmental implications. For this purpose, a detailed petrographic study should be performed on samples yielding inhomogeneous values as an effort to find a possible origin for the U-Th system alteration.

In our case, the convergence of the four dates at the bases of the four stalagmites is quite remarkable. So far, we have shown that three of these anomalous ages are attributable to some alteration of the original calcite. The last date corresponding to the base of stalagmite C2, is very similar to the other three, but so far it is impossible to know if C2b has also been altered, since only one valid U-Th date was obtained (Table 1) for this small, detrital-rich speleothem. In any case, the reason for the base ages



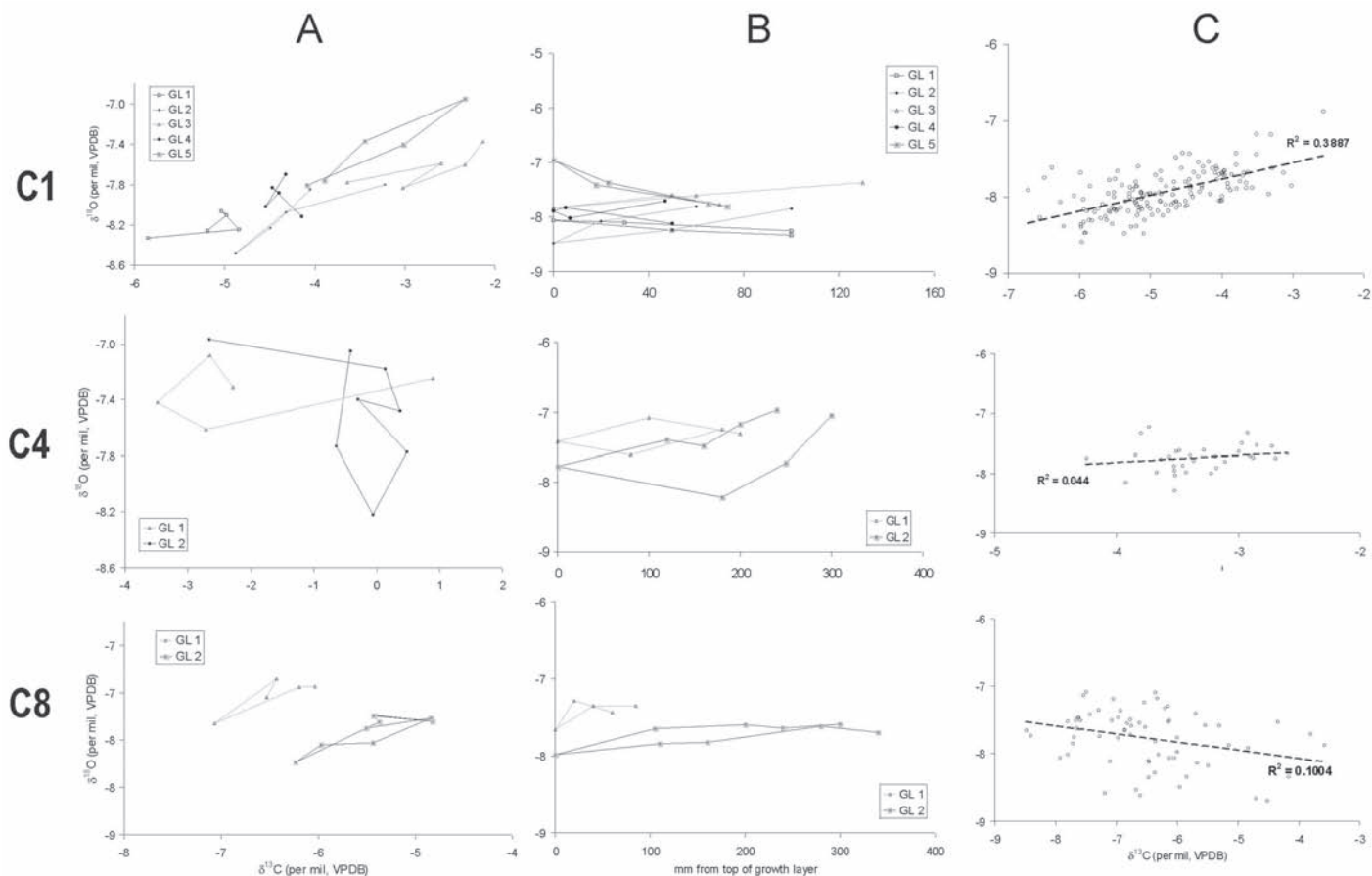


Fig. 7.- Isotopic equilibrium tests for stalagmites C1, C4 and C8, following the criteria of Hendy (1971). A) Plots of  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  for individual growth layers (GL). B)  $\delta^{18}\text{O}$  variation in individual growth layers. C) Plots of  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  along growth axes. Note that both parameters show no significant correlation:  $R^2$  was in the range 0.04 to 0.39.

Fig. 7.- Pruebas de equilibrio isotópico para las estalagmitas C1, C4 y C8, según los criterios de Hendy (1971). A) Covariación de  $\delta^{18}\text{O}$  y  $\delta^{13}\text{C}$  a lo largo de una única lámina de crecimiento (GL). B) Variación de  $\delta^{18}\text{O}$  a lo largo de una única lámina de crecimiento. C) Covariación de  $\delta^{18}\text{O}$  y  $\delta^{13}\text{C}$  a lo largo del eje de crecimiento. Nótese que no se encuentra ninguna correlación estadísticamente significativa:  $R^2$  varía entre 0.04 y 0.39.

coinciding is unclear. To reset the ages to zero at a time around 105-100 ka BP, it would have been necessary to remove the  $^{230}\text{Th}$  generated there previously. However, thorium is very insoluble in meteoric and dripping waters. Hence, the most likely way of altering an age would be by varying the U/Th ratio, introducing more uranium.

The easiest mechanism whereby this could be achieved would be to precipitate new calcite in pores at the base and/or middle of the stalagmites. This calcite could have been formed by very abundant drips that precipitated more to the base than to the top of the stalagmites. This is suggested by the almost perfect trend of the samples belonging to the inhomogeneous group comprising C8 (Fig. 6B), which matches that shown by the lower samples in the stalagmite containing younger calcite. Since the stalagmites were collected at different levels, an abundant drip would need to be caused by very wet conditions outside the cave, and would correspond to the warm period

equivalent to MIS 5c. However, unless totally destructive, this mechanism of “resetting” would give each stalagmite a different resultant date, younger than the true one but not the same in each, except by coincidence. It was impossible to find traces of the new calcite in the axial part of the stalagmites, but millimetric and sub-millimetric pores were found only in the basal parts of all the stalagmites.

## 6.2. Stable isotopes

The stalagmite samples yielded positive results in the Hendy test (Fig. 7), suggesting that calcite precipitation occurred under conditions of (or near to) the isotopic equilibrium.  $\delta^{18}\text{O}$  values remained almost constant in each growth layer (Fig. 7B), showing only minor changes (under 0.5 ‰ in all cases). These changes reflected no clear trend and could be related to the difficulty in

precisely tracking individual growth layers (up to 30 cm long in some cases) in these poorly laminated samples, or in extracting comparable samples from layers that show notable lateral thickness changes.

Figure 7C summarizes the carbon and oxygen stable isotope records obtained along the growth axes of stalagmites C1, C4 and C8. These plots depict no significant correlation between carbon and oxygen values, a finding that also supports isotopic equilibrium during precipitation.

## 7. Stable isotope records and implications for the Eemian chronology

In a previous study, we demonstrated that speleothem growth in the Cueva del Cobre was essentially limited to the warmer time intervals such as the Eemian and Holocene. Intense speleothem growth in the Cueva del Cobre has been dated as 155 to 80 ka BP (which broadly corresponds to MIS-5), disperse growth as 55 to 25 ka BP (around MIS-3) and active speleothem formation from 10 ka BP to the present (Muñoz-García *et al.*, 2004a). To date, no speleothem corresponding to cold periods equivalent to MIS-4 and 2 has been retrieved from the Cueva del Cobre.

The high mountain climate, the cold temperature of the cave (today  $5.5 \pm 0.3^\circ\text{C}$ ), and its location below a former mountain glacier would explain the practical absence of speleothem growth during colder intervals, when ice accumulated over the cave, and the temperature inside the cave could be close to  $0^\circ\text{C}$ . Accordingly, active periods of stalagmite growth would occur when the glacier had retreated and the soil recovered some biological activity, i.e., during periods of deglaciation such as those during rapid global warming associated with glacial terminations.

Thus if we could date the onset of intense speleothem growth in the Eemian, we could assign a minimum age estimate for Termination II in Spain and then characterize this stage by means of stable isotopes.

Figures 4B, 5B and 6B show graphic correlation plots constructed to obtain age estimates by interpolation and extrapolation. In this analysis, stalagmite C1 yielded extrapolated ages between 151.1 and 80.5 ka BP (Fig. 4B) and the section of stalagmite C4 examined indicated its growth between 149.1 and 108.4 ka BP (Fig. 5B). The growth of stalagmite C8 was aged between 138.0 and 108.2 ka BP. In this last case, chronostratigraphic extrapolation was based on TIMS samples C8-16-E and C8-C-1, and is supported by sample C8-1617 (Fig. 6B).

This later age, obtained by alpha-spectrometry counting, shows a large range of error, so should be considered with caution. In effect, if we used this age for extrapolation and gave it the same weight as the other two samples, an improbable age would be assigned for the base of this stalagmite.

The chronology for this study was finally set and the ages of stable isotope samples were linearly interpolated between the dated horizons. Figure 8 provides the isotope results for all the stalagmites. At first glance, the records of the three stalagmites, though still incomplete, show similar  $\delta^{18}\text{O}$  values and variations (for example see C1 and C8 between 120 and 110 ka BP).

To calibrate these oxygen records from Cueva del Cobre, we compared them to three different proxies: stable isotopes in ice, vein calcite and marine cores. Oxygen isotope records were plotted (Fig. 8) together with those obtained from SPECMAP (Imbrie *et al.*, 1984 and 1990), the Vostok Ice Core (Petit *et al.*, 1999), and the Devil's Hole vein (Landwehr *et al.*, 1997), although this last proxy was recently challenged as a regional record (Herbert *et al.*, 2001).

Maximum and minimum oxygen isotope values for C8 showed good correlation with Marine Isotope Substages 5e and 5d in SPECMAP and with the corresponding maximum and minimum temperatures deduced from the Devil's Hole and Vostok records (Eemian and beginning of the Weichselian and Wisconsin Glacial periods). In addition, the upper part of C1 preserves a record, which can be quite easily correlated with the Vostok  $\delta\text{D}$  series (arrows in figure 8). This correlation confirms that the higher  $\delta^{18}\text{O}$  values of the calcite correspond to relatively warm periods and vice versa, and consequently that the oxygen isotope composition of the calcite is dominated by the isotope composition of atmospheric palaeoprecipitation (Schwarcz, 1986; Gascoyne, 1992). A similar relationship was inferred for other speleothems of Holocene age from the same cave (Muñoz-García *et al.*, 2002; Martín-Chivelet *et al.*, 2006).

Two of the stalagmites (C1 and C4) started to grow at 151.1 and 149.1 ka BP respectively. Stalagmite C8 may also have commenced growth at this age, although since a basal portion of this speleothem is still in place inside the cave, we can only be sure that the base of C8 is older than 138.0 ka BP. Besides, the growth of two of the stalagmites (C4 and C8) stopped at the same time (108.4-108.2 ka BP), just after the beginning of the Weichselian period for this area deduced from the isotopic record of C1 (~115 ka BP), which is coherent with the age proposed by Drysdale *et al.* (2006) for this shift in Italy (~112 ka). One of the stalagmites (C1) preserves a complete record

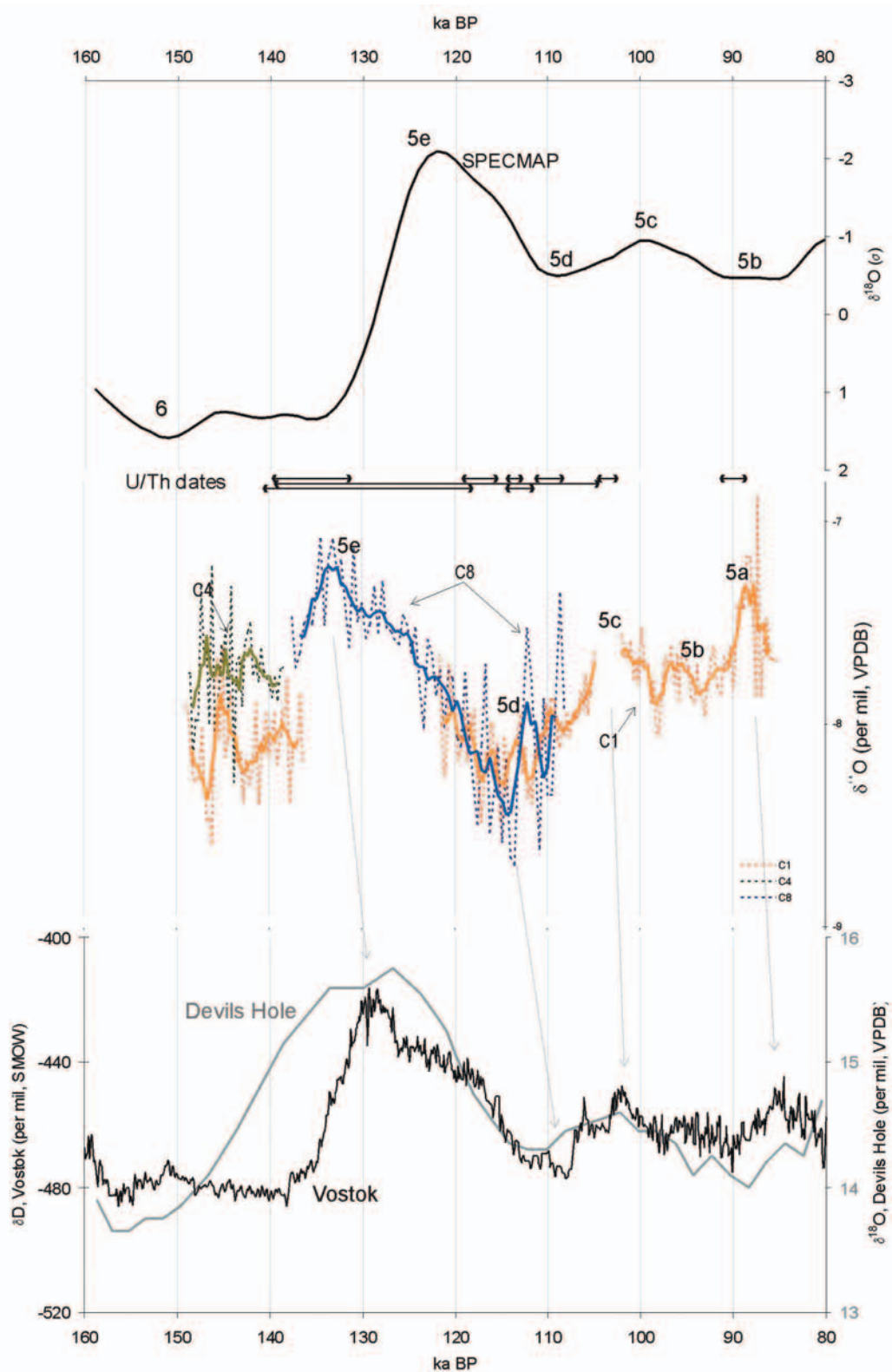


Fig. 8.- Oxygen isotope records obtained in the speleothems from Cueva del Cobre compared to the SPECMAP (top), Devil's Hole and Vostok records (bottom). Raw data from the Cueva del Cobre are shown as dashed lines, and running means (5 values) are shown as thicker solid lines. The numbers of MIS and arrows show a possible correlation between the oxygen stable isotope records from the Cueva del Cobre and the curves of independent records.

Fig. 8.- Comparación de los registros de isótopos estables de oxígeno de los espeleotemas de la Cueva del Cobre con los de SPECMAP (arriba), Devils Hole y Vostok (abajo). Los datos sin tratar de la Cueva del Cobre se representan como líneas punteadas y la media móvil (5 valores) como líneas continuas más gruesas. Los números de los Estadios Isotópicos Marinos y las flechas muestran una posible correlación entre el registro de isótopos estables de oxígeno de la Cueva del Cobre y las curvas de los otros indicadores.

of MIS 5 until ~80 ka BP and its growth ceases at the onset of MIS 4.

The chronology inferred from this study is consistent with the ages proposed by other authors for the bases of European Eemian speleothems (Gascoyne *et al.*, 1981; Baker *et al.*, 1993 and 1995; Lauritzen, 1995; Berstad *et al.*, 1997; Spötl *et al.*, 2002; Drysdale *et al.*, 2004; Bar-Matthews *et al.*, 2006; Constantin *et al.*, 2006). Collectively, these datings suggest that by ~133 ka BP to possibly ~145 ka BP, the ice sheets had retreated and that biologically active soils developed in the Alps, the British Islands and northern Europe (Winograd, 2002). It is therefore easy to envisage that favorable conditions for speleothem growth may have been met a few thousand years earlier in high mountains of Spain (~149-151 ka BP), because of its lower latitudes and warm influence from Africa and the Mediterranean.

The records from Cueva del Cobre correlate well with other proxies, especially Devil's Hole (Winograd *et al.*, 1992) and the Vostok ice core (Petit *et al.*, 1999). Good agreement between the ages of C8 and the Devil's Hole calcite record suggests that the latter could represent global changes (at least for continental mid-latitude climates) as generally accepted, and not only regional palaeotemperatures, as suggested by Herbert *et al.* (2001).

## 8. Conclusions

Our findings point to the growth during the Eemian of some of the stalagmites of the Cueva del Cobre in northern Spain. Interestingly, in the three stalagmites for which we obtained more than one age, some of these ages were out of stratigraphic order, although in most cases there was no initial thorium contamination and all U/Th and U/U ratios and errors were acceptable. The ages of the bases of the four stalagmites fall within a narrow range between 97 and 105 ka BP. When anomalous datings were repeated in different laboratories, it was found that the ages yielded corresponded to the real U/Th ratio in the calcite and not to an artefact. Two of the four stalagmites were found under active drips, but we detected no physical or petrographic signs that could explain the erroneous ages. We propose a simple geochemical test based on mass-spectrometer uranium data to separate disturbed from undisturbed samples. According to the chosen samples selected by this method, extrapolated ages for the bases of two of the stalagmites (151.1 and 149.1 ka BP) and a minimum age obtained for another of the stalagmites (~138.0 ka BP) allowed the comparison of the oxygen isotope records of these synchronous stalagmites from the Cueva del Cobre, indicating good correlation among them and with other proxies. The start of the

growth of these speleothems could be related to the onset of the Eemian. According to our samples, Termination II would be earlier than previous estimates, closer in time to that ascribed by the Devil's Hole or Vostok records than to the warming period previous to MIS 5e defined by the SPECMAP curve. This early warming would be correlative to that recorded by speleothems from other European high mountain or high latitude caves. The end of their growth (108.2-108.4 ka BP) could also be correlative to the onset of the Weichselian period or the MIS 4 (80.5 ka BP), depending on the sample.

A possible "U/Th-system alteration event" could have taken place during relatively warm and wet conditions around 105-100 ka BP, almost coincident with the peak of MIS 5c and continental equivalents.

In conclusion, the samples examined here provide the following insights: (1) the absolute ages and stable isotope records of the Cueva del Cobre speleothems locate the onset of the Eemian interglacial as early as ~151-149 ka BP, an age comparable to those provided by other palaeoclimate records from Northern Europe and North America, but notably younger than the age calculated by the Milankovitch theory; (2) our U-Th datings for these speleothems also give a precise age for the first time in Spain for the end of the Eemian interglacial (isotopic shift at ~115 ka; stop of speleothemic growth at ~108 ka); and (3) these U-Th ages reveal a consistent anomaly at ~105-100 ka BP, which could be related to a drastic climate change during the interstadial MIS-5c. This event reset the U-Th system at the base of the stalagmites during a short time interval. Future work will provide further insight into the conditions and mechanisms under which the U-Th system may have been disturbed.

## Acknowledgements

This study is a contribution to Projects REN2001-1409/CLI and CGL2004-01866 of the Spanish Ministry of Education and Science. The authors thank the authorities of the Fuentes Carrionas-Fuente Cobre Natural Park (Junta de Castilla-León) for providing the facilities and permissions required for our work. We also thank Drs. Helena Hercman (Polish Academy of Science, Poland) and M<sup>a</sup> Teresa Crespo (CIEMAT, Spain) for their help with the alpha spectrometry datings. We are also indebted to Adriano Cortel, Carmen Pino, Araceli Saria and José Matas for help with the fieldwork and collection of rock samples, and to Gilberto Herrero, Beatriz Moral and María Isabel Sevillano for help with preparing the samples and laboratory assistance. The manuscript benefited of comments and suggestions from two anonymous referees. The English was edited by A. Burton.

## References

- Ayalon, A., Bar-Matthews, M., Kaufman, A. (1999): Petrography, strontium, barium and uranium concentrations, and strontium and uranium isotope ratios in speleothems as palaeoclimatic proxies: Soreq Cave, Israel. *The Holocene*, 9(6): 715-722.
- Baker, A., Smart, P.L., Ford, D.C. (1993): Northwest European paleoclimate as indicated by growth frequency variations of secondary calcite deposits. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 100: 291-301.
- Baker, A., Smart, P.L., Edwards, R.L. (1995): Paleoclimate implications of mass spectrometric dating of a British flowstone. *Geology*, 23: 309-312.
- Bar-Matthews, M., Ayalon, A., Vaks, A., Frumkin, A., Schilman, B., Almogi-Labin, A., Matthews, A. (2006): Speleothems, what do they tell us about climate, the timing of climate change, and the migration of desert borders. In: Onac, Tamas, Constatin, Persoiu (Eds.). *Archives of climate change in karst*. Karst Waters Institute, Special Publication 10, Romania: 1-2.
- Berstad, I.M., Einevoll, S., Lauritzen, S.-E. (1997): U-series dating and stable isotope analysis of some last interglacial speleothems from north Norway. *Proceedings of the 12<sup>th</sup> International Congress of Speleology*, Switzerland: p. 53-54.
- Broecker, W.S. (1998). The end of the present interglacial: how and when? *Quaternary Science Reviews*, 17: 689-694.
- Cheddadi, R., Mamakowa, K., Guiot, J., de Beaulieu, J.-L., Reille, M., Andrieu, V., Granoszewski, W., Peyron, O. (1998): Was the climate of the Eemian stable? A quantitative climate reconstruction from seven European pollen records. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 143: 73-85.
- Constantin, S., Lauritzen, S.-E., Lundberg, J. (2006): New data on the chronology of the Termination II and paleoclimate during MIS-5, based on the study of a stalagmite from Closani Cave (SW Romania). In: Onac, Tamas, Constatin, Persoiu (Eds.). *Archives of climate change in karst*. Karst Waters Institute, Special Publication 10, Romania: 98-100.
- Drysdale, R.N., Zanchetta, G., Hellstrom, J.C., Fallick, A.E., Zhao, J.-X., Isola, I., Bruschi, G. (2004): Paleoclimatic implications of the growth history and stable isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) geochemistry of a Middle to Late Pleistocene stalagmite from central-western Italy. *Earth and Planetary Science Letters*, 227:215-229.
- Drysdale, R., Zanchetta, G., Hellstrom, J., Fallick, T. (2006): New age constraints for the Last Interglacial from Italian speleothems. In: Onac, Tamas, Constatin, Persoiu (Eds.). *Archives of climate change in karst*. Karst Waters Institute, Special Publication 10, Romania: 109-112.
- Ford, D.C., Ewers, R.O. (1978): The development of limestone cave systems in the dimensions of length and depth. *Canadian Journal of Earth Sciences*, 15: 1783-1798.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F. (2000): Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and Southwestern Ireland. *Journal of Sedimentary Research*, 70: 1183-1196.
- Frumkin, A., Ford, D.C., Schwarcz, H.P. (1999): Continental oxygen isotopic record of the last 170,000 years in Jerusalem. *Quaternary Research*, 51: 317-327.
- Gallup, C.D., Cheng, H., Taylor, F.W., Edwards, R.L. (2002): Direct determination of the timing of sea level change during Termination II. *Science*, 295: 310-313.
- Gascoyne, M. (1992): Palaeoclimate determination from cave calcite deposits. *Quaternary Science Reviews*, 11: 609-632.
- Gascoyne, M., Curren, A.P., Lord, T.C. (1981): Ipswichian fauna of Victoria Cave and the marine paleoclimate record. *Nature*, 294: 652-654.
- Hendy, C.H. (1971): The isotopic geochemistry of speleothems-I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta*, 35: 801-824.
- Herbert, T.D., Chuffert, J.D., Andreasen, D., Heusser, L., Lyle, M., Mix, A., Ravelo, A.C., Stott, L.D., Herguera, J.C. (2001): Collapse of the California Current during glacial maxima linked to climate change on land. *Science*, 293: 71-76.
- Imbrie et al. (1984): The orbital theory of Pleistocene climate: support from a revised chronology of the marine  $\delta^{18}\text{O}$  record. In: Berger et al. (Eds.). *Milankovitch and Climate, part 1*. Plenum Reidel, Dordrecht: 269-305.
- Imbrie, J. et al. (1990): SPECMAP Archives. IGBP PAGES/World Data Center-A for Paleoclimatology Data Contribution Series # 90-001. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA.
- Ivanovich, M., Harmon, R.S. (1992): *Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*. Clarendon Press, Oxford: 910 p.
- Karner, D.B., Muller, R.A. (2000): A causality problem for Milankovitch. *Science*, 288: 2143-2144.
- Kukla, G.J., Bender, M.L., de Beaulieu, J.-L., Bond, G., Broecker, W.S., Cleveringa, P., Gavin, J.E., Herbert, T.D., Imbrie, J., Jozel, J., Keigwin, L.D., Knudsen, K.-L., McManus, J.F., Merkt, J., Muhs, D.R., Müller, H., Poore, R.Z., Porter, S.C., Seret, G., Shackleton, N.J., Turner, C., Tzedakis, P.C., Winograd, I.J. (2002): Last interglacial climates. *Quaternary Research*, 58: 2-13.
- Landwehr, J.M., Coplen, T.B., Ludwig, K.R., Winograd, I.J., Riggs, A.C. (1997): Data for Devils Hole core DH-11. *U.S. Geological Survey Open-File Report 97-792*.
- Lauritzen, S.-E. (1995): High-resolution paleotemperature proxy record for the last interglaciation based on Norwegian speleothems. *Quaternary Research*, 43: 133-146.
- Li, W.-X., Lundberg, J., Dickin, A.P., Ford, D.C., Schwarcz, H.P. (1989): High-precision mass-spectrometric uranium-series dating of cave deposits and implications for palaeoclimate studies. *Nature*, 339: 534-536.
- Lototskaya, A., Ganssen, G.M. (1999): The structure of Termination II (penultimate deglaciation and Eemian) in the North Atlantic. *Quaternary Science Reviews*, 18: 1641-1654.
- Martin-Chivelet, J., Muñoz-García, M.B., Domínguez-Villar, D., Turro, M.J. and Ortega, A.I. (2006): Comparative analysis of stalagmites from two caves of northern Spain. Implications for Holocene paleoclimate studies. *Geologica Belgica*, 9/3-4: 323-335.

- Muñoz-García, M. B., Rossi, C., Martín-Chivelet, J., Ford, D. C., and Schwarcz, H. P. (2002): Isotopic record of a Holocene stalagmite from Cueva del Cobre (Cantabrian Mountains, N Spain): paleoclimatic implications. *Cave climate and paleoclimate - The best record of the Global Change. International Workshop*.
- Muñoz-García, M.B., Martín-Chivelet, J., Rossi, C. (2004a): Implicaciones paleoclimáticas de la distribución geocronológica de espeleotemas en la Cueva del Cobre (Palencia). *Geogaceta*, 35: 179-182.
- Muñoz-García, M. B., Martín-Chivelet, J., Rossi, C., Schwarcz, H. P., and Ford, D. C. (2004b): Dating late Pleistocene stalagmites in Cueva del Cobre (N Spain): problems for characterizing the Eemian. *Les séries sédimentaires endokarstiques. Mémoires de l'environnement. Colloque international, Han-sur-Lesse (Belgique)*. p. 24.
- Petit J.R., Jouzel J., Raynaud D., Barkov N.I., Barnola J.M., Basile I., Bender M., Chappellaz J., Davis J., Delaygue G., Delmotte M., Kotlyakov V.M., Legrand M., Lipenkov V., Lorius C., Pépin L., Ritz C., Saltzman E., Stievenard M. (1999): Climate and Atmospheric History of the Past 420,000 years from the Vostok Ice Core, Antarctica. *Nature*, 399: 429-436.
- Quinif, Y. and Maire, R. (2004): Calcite and aragonite in speleothems - Consequences on radioisotopes geochemistry. *Les séries sédimentaires endokarstiques. Mémoires de l'environnement. Colloque international, Han-sur-Lesse (Belgique)*, p. 15.
- Rossi, C., Muñoz, A., Cortel, A. (1997): Cave development along the water table in Cobre System (Sierra de Peñalabra, Cantabrian Mountains, N Spain). *Proceedings of the 12th International Congress of Speleology*, Switzerland: 179-182.
- Sánchez-Goñi, M.F., Eynaud, F., Turon, J.L., Shackleton, N.J. (1999): High resolution palynological record off the Iberian margin: Direct land-sea correlation for the Last Interglacial complex. *Earth and Planetary Science Letters*, 171: 123-137.
- Schwarcz, H.P. (1986): Geochronology and isotopic geochemistry of speleothems. In: Fritz, P. and J.Ch. Fontes (eds.), *Handbook of Environmental Isotope Geochemistry*. Elsevier, Amsterdam: 271-303.
- Shackleton, N.J., Sánchez-Goñi, M.F., Pailler, D., Lancelot, Y. (2003): Marine Isotope Substage 5e and the Eemian Interglacial. *Global and Planetary Change*, 36: 151-155.
- Spötl, C., Mangini, A., Frank, N., Eichstädter, R., Burns, S.J. (2002): Start of the last interglacial period at 135 ka: Evidence from a high Alpine speleothem. *Geology*, 30(9): 815-818.
- Turner, C. (2002): Forma status and vegetational development of the Eemian Interglacial in northwestern and southern Europe. *Quaternary Research*, 58: 41-44.
- Tzedakis, P.C., Frogley, M.R., Heaton, T.H.E. (2003): Last Interglacial conditions in southern Europe: evidence from Ioannina, northwest Greece. *Global and Planetary Change*, 36: 157-170.
- van Kolfshoten, Th., Gibbard, P.L., Knudsen, K.L. (2003): The Eemian Interglacial: a Global Perspective. Introduction. *Global and Planetary Change*, 36: 147-149.
- Winograd, I.J. (2002): Evidence from uranium-series-dated speleothems for the timing of the penultimate deglaciation of northwestern Europe. *Quaternary Research*, 58: 60-61.
- Winograd, I.J., Coplen T.B., Landwehr, J.M., Riggs, A.C., Ludwig, K.R., Szabo, B.J., Kolesar, P.T., Revesz, K.M. (1992): Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. *Science*, 258: 255-260.
- Yuan, D., Cheng, H., Edwards, R.L., Dykoski, C.A., Kelly, M.J., Zhang, M., Qing, J., Lin, Y., Wang, Y., Wu, J., Dorale, J.A., An, Z., Cai, Y. (2004): Timing, duration, and transitions of the Last Interglacial Asian monsoon. *Science*, 304: 575-578.