Palaeoenvironmental reconstruction based on a detailed stable isotope analysis and dating of a Holocene speleothem from Valporquero Cave, Northern Spain

Reconstrucción paleoambiental a partir del estudio detallado de los isótopos estables y la datación de un espeleotema holoceno de la Cueva de Valporquero, norte de España

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ABSTRACT

Ages of ca. 8170 and 7180 BP have been established through a Th/U dating for the base and the top, respectively, of a speleothem collected inside Valporquero Cave (Cantabrian Zone, northern Iberian Peninsula). Three series of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) stable isotope analyses have been carried out parallelly to the stalagmite axis, sampling being done in each growth layer, for a total amount of 66 analyses. The high degree of correspondence between the results of the analyses in the three series is highly significant, showing each similar general tendencies. The isotopic sequence can thus be considered as representative for the regional environmental conditions along the mid-Holocene period which is being studied. In the oxygen and carbon isotopical variation graphics, five sections with different characteristics can be distinguished, which correspond to four isotopically different periods: The first and third ones show more negative values than the mean general value; the second one offers less negative values, and the fourth one includes variations close to the mean. Differences bigger than 1‰ between maximum and minimum values are appreciated in the oxygen isotopic curve, which could probably correspond to environmental temperature oscillations wider than 4°C during the studied period.

RESUMEN

Las dataciones absolutas (Th/U) realizadas en el techo y en la base de un espeleotema de la Cueva de Valporquero (Zona Cantábrica, norte de la Península Ibérica) arrojan edades en torno a 7180 y 8170 BP, respectivamente. Se han realizado tres series de análisis de isótopos estables del carbono ($\delta^{13}C$) y del oxígeno ($\delta^{18}O$), paralelas al eje de la estalagmita, muestreando todas las capas de crecimiento del espeleotema, con un total de 66 determinaciones realizadas. La correspondencia entre las tres series de análisis es altamente significativa, con tendencias generales similares, por lo que la secuencia isotópica se considera representativa de las condiciones ambientales regionales para la etapa estudiada del Holoceno medio. En las gráficas de las variaciones isotópicas del oxígeno y del carbono se pueden diferenciar cinco tramos con tendencias diferentes, que delimitan cuatro periodos isotópicamente distintos: el primero y el tercero presentan valores más negativos que el valor medio general; el segundo presenta valores menos negativos, y el cuarto muestra oscilaciones cercanas a la media. Entre los máximos y mínimos de la curva del oxígeno existen diferencias superiores a 10 ‰, lo que refleja posiblemente oscilaciones de la temperatura ambiental mayores de 4°C, para el periodo considerado.

Key words: *stable isotopes, speleothems, palaeoclimate, Iberian Peninsula, Holocene.*

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Introduction and geological setting

The Holocene (Isotopic Stage 1) has been classified, from an isotopical point of view, as a relatively warm period (*eg.* Shackleton and Opdyke, 1973; Williams *et al.*, 1988). Such conditions meant a favourable period for speleothem growth in endokarstic environments on a global scale (eg. Henning *et al.*, 1983) and such considerations have also been proved valid for the Iberian Peninsula (*eg.* Durán *et al.*, 1988; Durán, 1989). However, not all the Holocene went off under homogeneous palaeoenvironmental conditions and, consequently, continental carbonated deposits of such age are not continous in all the karstic regions.

The objective of this work is to analyse and to obtain a palaeoclimatic interpretation of a Holocene stalagmite

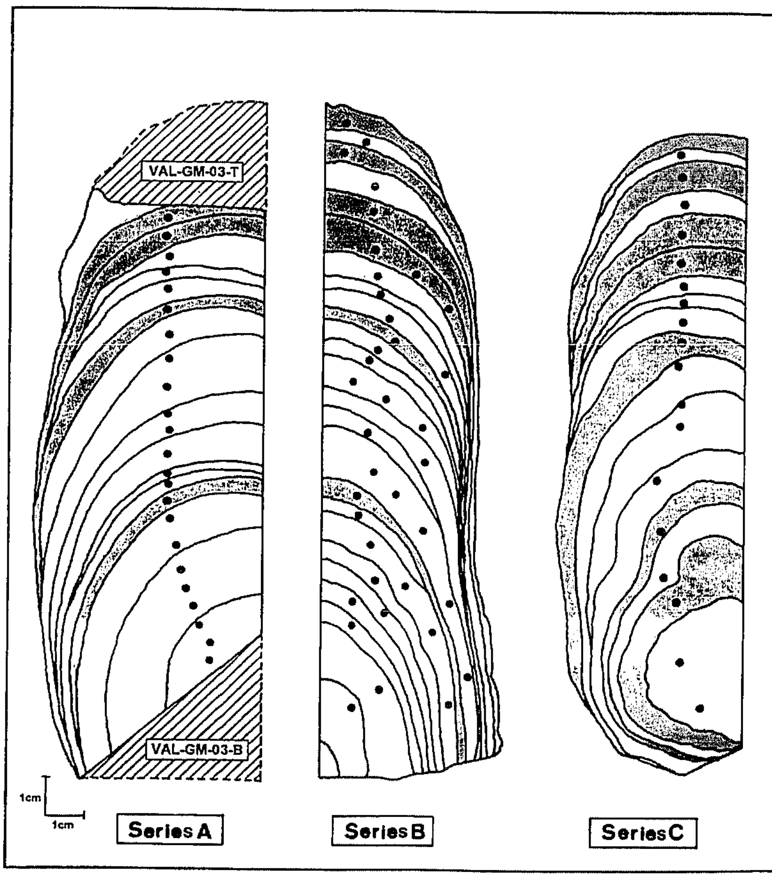

Figura 1. Location of the analysed samples in the studied speleothem.

Figure 1. Situación de las muestras analizadas en el espeleotema estudiado.

from Valporquero Cave, located at an altitude of around 1400 m, in the southern area of the Cantabrian region, province of León, northern Iberian Peninsula. The stalagmite under study was formed coincidentally with a positive pulse in the recharge of the carbonated aquifer and it belongs to the last generation of speleothems existing in the cave, being clearly individualised from a morphological point of view. The Holocene event represented in this speleothem happened as a consequence of suitable palaeoenvironmental conditions for an increase in water infiltration and for the settling of carbonate deposits in the endokarst.

Valporquero Cave developed in Palaeozoic limestones (Valdeteja and Barcaliente formations) belonging to the Correcillas Unit (Pérez Estaún *et al.*, 1988), in the Cantabrian Zone of the Hesperic Massif. The cave is a 3500 m long underground karstic system, hydrogeologically active, with an underground river and several palaeolevels of different altitude and age (Durán and Heredia, 1997; López-Martínez *et al.*, 1998). There is a vertical difference of 221 m between the upper entry to the karstic system, Sil de las Perlas, and the place where the river exits, La Covona, being the estimated volume of the cave around 500 000 m^3. The area where the cave is located has a present mean annual temperature below 9°C and a precipitation regime of about 1400 mm/year, being snow common between January and May. Several speleothem generations are present inside the cave, some of them having been dated. The older group of speleothems is more than 300 Ka; the second belongs to isotopic stage 5 (140-125 Ka); and the third one is Holocene (isotopic stage 1) (Durán and Heredia, 1997; Barea *et al.*, 1998).

Studied materials

The studied stalagmite belongs to the Holocene generation of speleothems, the most recent one. The sample has been taken from the underground hall named Grandes Maravillas (*Big Wonders*), located in the upper level of the cavity, the oldest one of all the existing. It is a subaerean stalagmite, deposited lying on a group of epiaquatic chemical deposits formed during a period of high waters in isotopic stage 5 (*ca.* 130 000 BP). The stalagmite sample (reference VAL-GM-03) is 165 mm long and has a diameter of 80 mm. It has a uniform composition of aragonite, including 26 main layers that can be visually differentiated. Considering the thickness of the sample, 78 % of the layers are white and the others (7 layers) range from light-grey to black. A series of samples were taken from the stalagmite for dating and for oxygen (^{18}O) and carbon (^{13}C) stable isotope analyses. The samples for absolute dating were collected from the base (VAL-GM-03-B) and from the top end (VAL-GM-03-T) of the speleothem (Fig.1). The pieces were scabbled to avoid contamination from external layers and from contact with the previous epiaquatic speleothem generation. The samples for the stable isotope analyses were divided into three series, alongside three different planes parallel to the stalagmite growth axis. 23 samples were obtained from the A series, 25 from the B series and 18 from the C series (Fig. 1). The last one, the most external of the three, corresponds to a plane located at 1 cm from the stalagmite surface. The other two series come from more central positions, being located in two planes one perpendicular to the other.

Analitical methods

The cited samples have been object of geochronological (Uranium series, Th/U) and stable isotopes (oxygen and carbon) analyses. The dating of the samples has been done in the Instituto Jaume Almera, CSIC, Barcelona. The stable isotopes analyses have been done in two different laboratories (Estación Experimental del Zaidín, CSIC, Granada, and Geochemistry Laboratory of the University of Lausanne, Switzerland) in order to check the validity of the results.

Samples were measured for their carbonate $\delta^{13}C$ and $\delta^{18}O$ content following the general methods outlined by McCrea (1950). A fractionation factor of 1.00931 between $CaCO_3$ and H_3PO_4 was applied (Swart *et al.*, 1991). Carbonate $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios were measured on a Finningan MAT 251 multi collector Mass Spectrometer and on a Finningan Mat Delta-S Mass Spectrometer, and converted to $\delta^{13}C$ and $\delta^{18}O$ values by the standard equations:

$$\delta^{13}C_{sample} = \left(\frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1 \right) *1000$$

$$\delta^{18}O_{sample} = \left(\frac{^{18}O/^{16}O_{sample}}{^{18}O/^{16}O_{standard}} - 1 \right) *1000$$

All the $\delta^{13}C$ and $\delta^{18}O$ values are expressed in the usual «δ» notation and are reported relative to PDB in parts per thousand. The working standard in both laboratories is calibrated relative to NBS-19. For NBS-19, the values for $\delta^{13}C$ and $\delta^{18}O$ are 1.95‰ and -2.20 ‰, respectively (Coplen *et al.*, 1993). In both mass spectrometers the standard deviation of the analyses was ± 0.1 ‰ for $\delta^{18}O$ and ±0.05 ‰ for $\delta^{13}C$.

The dates of two samples were determined by the uranium series disequilibrium method (Ivanovich and Harmon, 1992). This method is based on the uranium solubility in natural waters while the thorium content in these natural waters is negligible. During the speleothem formation, $CaCO_3$ traps the uranium present in the water and the uranium series clock is reset. The age of the speleothem is determined by the growth of ^{230}Th, the daughter of ^{234}U.

The radiochemical procedure for U and Th isolation follows the method described by Bischoff and Fitzpatric (1991). The radioisotope activities were determinated by alpha spectrometry and the age calculation according to Rosenbauer (1991).

The two analyzed speleothem samples are very pure in $CaCO_3$ content and the ^{232}Th is not detected. Thus, the nominal dates are calculated directly from the daughter/parent ratio assuming that all the measured ^{230}Th was formed by *in situ* decay from contained ^{234}U. The high uranium content (2.04 and 0.26 ppm in ^{238}U) and also the relatively high $^{234}U/^{238}U$ ratios supports the consistency of the obtained dates.

Results

The results yielded from the analyzing of the studied samples (Fig. 1) are included in table 1 (dating of the base and the top of the stalagmite) and in figures 2 and 3 ($\delta^{18}O$ and $\delta^{13}C$ values in the three studied series).

The speleothem can be dated between *ca.* 8100 BP and *ca.* 7180 BP. If a uniform stalagmite growth rate is considered, it will mean an accretion speed of about 156 mm/1000 years, or in other words, 1 cm of growth every 63.8 years. This is a relatively high rate, since values below 70 mm/1000 years have been pointed out, for similar periods, in other European regions (*eg.* McDermott *et al.*, 1999).

The three analysed isotopic series (Fig. 1) show similar tendencies in ^{18}O and ^{13}C contents (Figs. 2 and 3), with very similar mean values (-5.17, -5.07 and -5.2 for $\delta^{18}O$, and -2.0, -1.7 and -1.7 for $\delta^{13}C$). In general, the most complete curves (series A and B) show five well differentiated sectors:

1. the closer to the base of the stalagmite (left side of the graphics) ; data move to more negative values, below the mean value,
2. the following sector (the first one present in C series) shows a general tendency to less negative values, with some variations, reaching in all cases to the less negative values of the sequence,
3. the third sector suffers a strong decrease to the most negative values, in ^{18}O and ^{13}C, reaching all the curves the absolute minimum,
4. in the fourth sector values are again less negative, getting close to the mean, and
5. the fifth sector shows a succession of changes in their tendency; positions keep more or less stable around the mean values in the case of ^{18}O and with a slight increasing tendency to less negative values in ^{13}C.

Four periods of similar isotopic characteristics can be distinguished if the sequences are compared to their respective mean values:

a. the first period consists of values below the mean (curve going downwards, sector 1 formerly described; curve going upwards, a part of previous sector 2),

b. the second period is, with few exceptions, over mean values, including the absolute maximum in all of the curves (that is, the inflexion between sectors 2 and 3).

c. the third period has values below the mean, and

d. the fourth period corresponds to sector 5 formerly described.

The small correlation (values of the correlation coefficient below 0.7 in all the analised layers, except one) between the isotopic contents of oxygen and carbon measured separately in different layers point out that precipitation happened, in general, under isotopic equilibrium conditions, validating these results the use of the data for palaeoenvironmental reconstruction.

Discussion and conclussions

The results point out the existence of a humid and more or less warm period inside the Holocene, between *ca.* 8100 and 7200 BP, which corresponds to when the speleothem under study was formed. This took place in a region that nowadays has a relatively cold climate, because of the altitude and the continental influence, and where a cold morphogenesis during the Pleistocene glacial phases has been evidenced and where subsequent periglacial effects took place.

Four periods can be deduced from the vertical variations in the ^{18}O content,

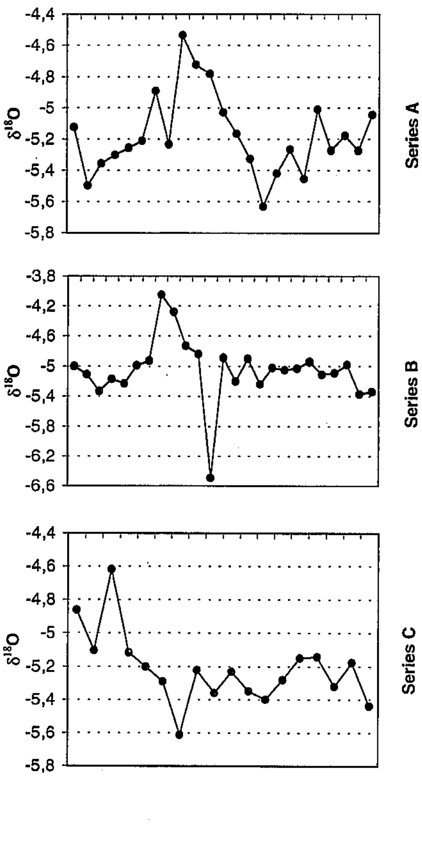

Figure 2. Distribution of $\delta^{18}O$ values along the different layers of the speleothem in the three analysed series. The left side of the graphics corresponds to the start of the series, close to the base of the stalagmite. The values are reported relative to PDB in parts per thousand.

Figura 2. Distribución de los valores de $\delta^{18}O$ de las diferentes bandas del espeleotema en las tres series analizadas. El extremo izquierdo de las gráficas corresponde al inicio de las series analizadas, próximo a la base de la estalagmita. Los valores son con respecto al patrón PDB y están expresados en tantos por mil.

Sample	U(ppm)	^{232}Th (ppm)	$^{234}U/^{238}U$	$^{234}Th/^{234}U$	Age (years BP)
VAL-GM-03B	2.04	-	2.53± 0.03	0.07± 0.00	8116± 335
VAL-GM-03T	0.26	-	1.84± 0.04	0.06± 0.00	7178± 405

Table 1: Results of Th/U dating of the speleothem.

Tabla 1: Resultados de las dataciones absolutas (Th/U) del espeleotema.

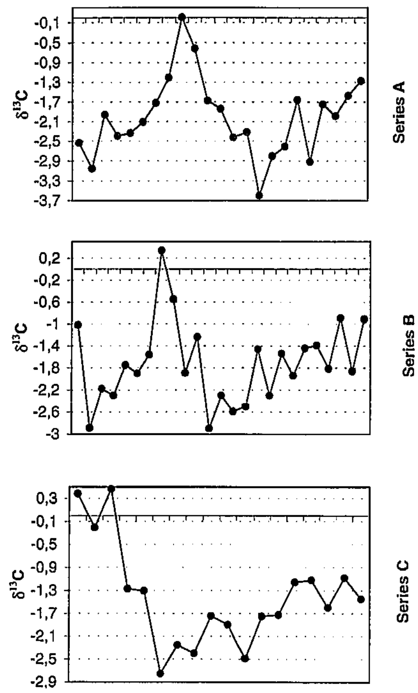

Figure 3. Distribution of $\delta^{13}C$ values along the different layers of the speleothem in the three analysed series. The left side of the graphics corresponds to the start of the series, close to the base of the stalagmite. The values are reported relative to PDB in parts per thousand.

Figura 3. Distribución de los valores de $\delta^{13}C$ de las diferentes bandas del espeleotema en las tres series analizadas. El extremo izquierdo de las gráficas corresponde al inicio de las series analizadas, próximo a la base de la estalagmita. Los valores son con respecto al patrón PDB y están expresados en tantos por mil.

alongside the growth axis of the studied stalagmite: less warm, warm, less warm and warm, respectively. Climatic tendencies consistent with these have also been confirmed by the ^{13}C analysis.

The isotopic equilibrium was confirmed by the mentioned general small correlation between the values in the same layer, as well as for the cause that being the oxigen more or less constant, the carbon suffered changes.

The relatively high differences in ^{18}O values along the stalagmite axis (up to 1‰ in the series with less variability) indicate palaeotemperature variations of about 4°C during the studied part of the Holocene.

The palaeoclimatic variations deduced from the results of this study are consistent with existing data from other terrestrial and marine sequences. In this way, similar isotopic and palaeoclimatic tendencies to those obtained in the study of the Valporquero Cave have been pointed out by McDermott *et al.* (1999) after the study of a speleothem from the Grotta di Ernesto, NW Italy. Also aragonite speleothems of a similar age exist in Nerja Cave, southern Iberian Peninsula (Durán, 1996). The same author points out a relative maximum in the speleothems and travertines frequential distribution in southern Spain. This could be in connection with palaeoclimatic variations in the western Mediterranean and northern Africa region between 8000 and 5000 BP. It is also interesting to mention that the mean isotopic composition of the travertines studied by this author ($\delta^{18}O$ = -5.025 ‰) is very similar to the value of this mean in the speleothem studied in the present work ($\delta^{18}O$ = -5.07 ‰). During the period taken into consideration, humid conditions have also been pointed out in northern Africa, as a result of the study of lacustrine sediments (Rognon, 1976; Fontes *et al.*, 1985). These authors signalate a pluvial optimum *ca.* 8-7 Ka. The termal maximum detected in the speleothem of Valporquero Cave is about 7540 BP. Finally, after the study of marine sequences, related with more global warm conditions, Lario *et al.* (1993) deduced high sea levels in the Spanish Mediterranean coast *ca.* 6000 BP.

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