Late Pleistocene Paleoclimates and sea-level change in the Mediterranean as inferred from stable isotope and U-series studies of overgrowths on speleothems, Mallorca, Spain

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Abstract

Phreatic overgrowths on speleothems form at the surface of brackish pools which are present in many coastal caves of Mallorca (Spain). Unlike common vadose speleothems formed in subaerial environments, their occurrence directly identifies the height of the sea level at the time of the carbonate deposition, because such pools are physically connected with the sea. These deposits from the Late Pleistocene have recorded the same global variations in oxygen isotopes as planktonic and benthonic foraminifera, corals and cave deposits. A number of phreatic overgrowths on speleothems have been dated using the Th/U method in order to determine the position of the sea level during Late Quaternary. The same samples, as well as some subaerial speleothems, have been analysed for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios. The former samples allow the analysis of variations in sea water component in the brackish pools associated with glacio-eustatic Mediterranean fluctuations, and the latter permit inferences concerning past continental climate changes. Some high sea-stands have been recognized in correspondence with Oxygen Isotope Stages (OIS): 9 or older, 7, 5e, 5c and 5a. Phreatic overgrowths on speleothems have also been formed during a colder phase (OIS 4), demonstrating that also in that period there were environmental conditions favourable for this kind of carbonate precipitation. Vadose crystallizations have recorded a cold period at 36 ka, corresponding with the end of OIS 3. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the most outstanding aspects of the littoral endokarst (subsurface karst) in Mallorca is the presence of sea level controlled phreatic overgrowths on speleothems. These kind of deposits are frequently found in the subterranean pools of Mallorcan caves, in correspondence with the current sea level (Pomar et al., 1979). The main interest in these carbonate precipitates is that they record ancient positive fluctuations of the sea level, corresponding to interglacial periods, as indicated by means of strictly horizontal alignment of the phreatic overgrowths inside coastal caves. The formation of these kinds of crystalline deposits is related to paleolevels attained by the ground water-table, as a result of glacio-

eustatic sea-level oscillations (Ginés et al. 1981a; Pomar et al., 1987).

The phreatic overgrowths on speleothems of the Mallorcan caves are morphologically, texturally and mineralogically variable (Ginés et al. 1981b; Pomar et al. 1976). These authors pointed out the paleoclimatic significance of speleothem mineralogy, by relating the presence of aragonite to warmer events which, in beach sediments, results in the appearance of malacological thermophile fauna typical of the Eutyrrhenian (OIS 5).

In the case of Mallorca, a great number of phreatic crystallization paleolevels have been observed between the current sea level and +40 m. Ginés and Ginés (1974) have considered the possibility of correlating these deposits altimetrically with Middle and Upper Pleistocene shorelines, identified by means of the stratigraphic and paleontological study of the Pleistocene beach deposits (Butzer, 1975; Cuerda, 1975, 1989). Ginés and Ginés (1974) suggested that the phreatic overgrowth

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crystallizations situated 30 metres above the present sea level should date back at least to OIS 7.

In 1981 a preliminary isotopic dating program of Mallorcan phreatic overgrowths on speleothems was started. The analysis carried out using the uranium-series method confirmed the previously established chronological model, with regard to altimetric correlations between overgrowths on speleothems and Pleistocene beach deposits. This dating program shows ages that range from 3.9 ka (clearly Holocene) to greater than 350 ka, the limit of this method (Hennig et al., 1981; Ginés and Ginés, 1989, 1993). The overgrowths with ages less than 250 ka are well-correlated with the climatic events that involve a sea level similar to, or higher than that of the present day (OIS 1, 5, and 7, which correspond to warm periods). The samples with ages above 300 ka (paleolevels higher than 30 m a.s.l.) have to be assigned tentatively at least to OIS 9 or 11 (Shackleton and Opdyke, 1973).

In 1994 the study of speleothems was extended to new caves and samples that were also analyzed for O and C isotopic composition in order to collect information about past climate changes. The content of such research, whose first results have been advanced in Vesica, Tuccimei et al. (1996) and Tuccimei et al. (1997), are presented in this paper.

2. Geological and karstic setting

From the geomorphological point of view, the island of Mallorca (Fig. 1) features a wide range of endo- and exokarst (surface karst). These lithologies are of Mesozoic and Cenozoic age and have been framed within the context of plate tectonics of the western Mediterranean, between the European and the African plates.

The present morphology of the island is a horst and graben system (Gelabert, 1997), with the horsts corresponding to the mountain ranges and the graben corresponding to the basins and lowland plateaus.

The numerous endokarstic forms along the eastern coast of Mallorca, including the Serres de Llevant and Migjorn areas of the island, (Ginés, 1995) have been the
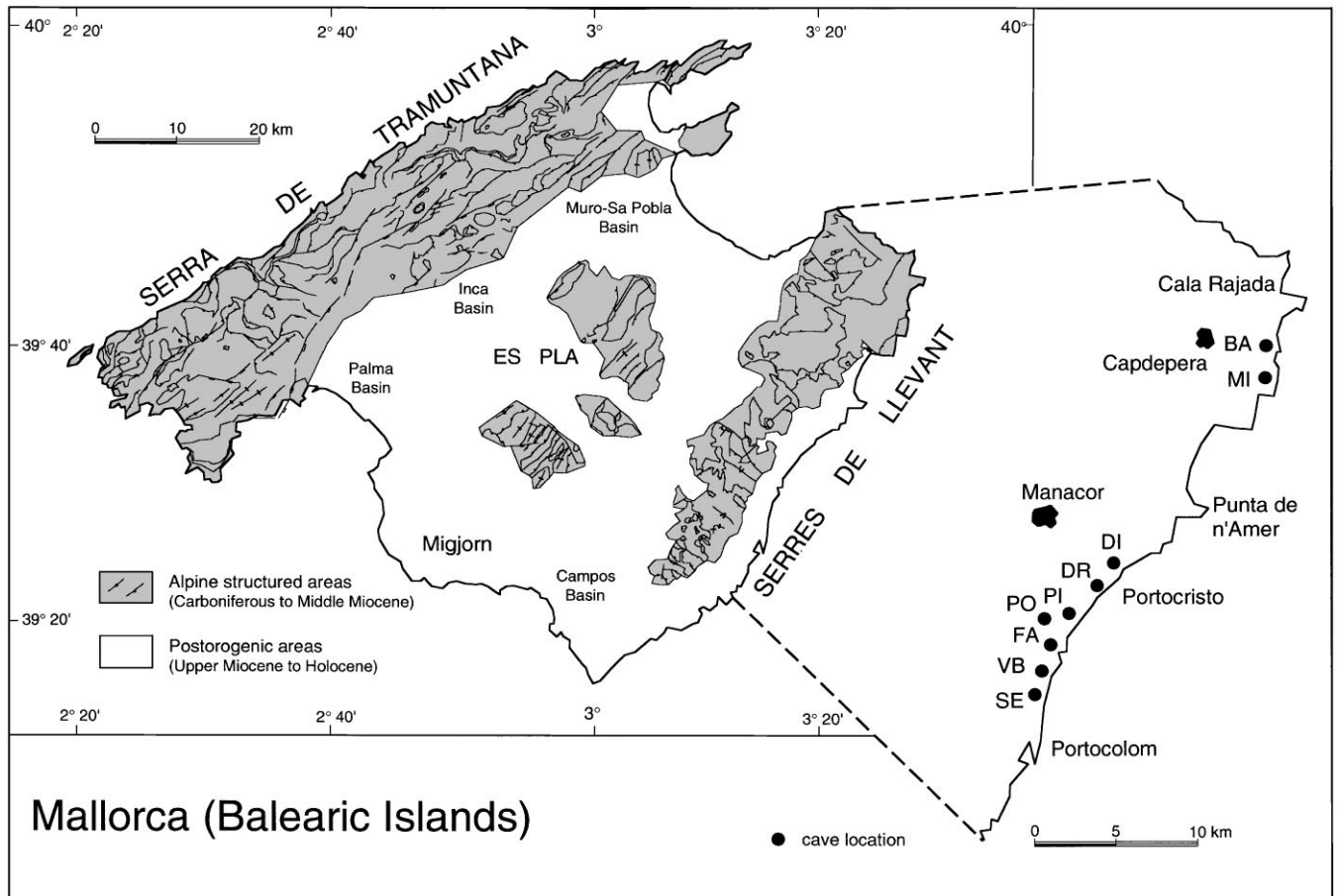

Fig. 1. Mallorca, with location of investigated caves. BA: Cova de na Barxa, MI: Cova de na Mitjana (Capdepera municipality). DI: Cova del Dimoni, DR: Coves del Drac, PI: Coves del Pirata, PO: Cova del Pont, FA: Cova de Cala Falcó, VB: Cova de Cala Varques B, SE: Cova des Serral (Manacor municipality).

object of considerable attention from the end of the last century. The caves are initiated as a network of solutional voids generated in the littoral phreatic zone by means of mixing processes between fresh continental water and saline sea water (Back, et al. 1984).

During the Pleistocene existing cavities have undergone successive wall and ceiling collapses, which have alternated and co-existed with phases of intense stalagmite formation. The breakdown processes are important because they largely determine the present form of this kind of cave and the size of the opening. These caves have been affected by the glacio-eustatic oscillations controlling the deposition of speleothem overgrowths on speleothems and paleontological breccias with speleochronological and paleoclimatic value (Ginés and Ginés, 1986, 1995).

The current sea level determines the presence and level of underground brackish pools, the surfaces of which respond to minor fluctuations, such as tides. The phreatic pools are the result of submergence of the lower chambers of the littoral caves as a consequence of rising sea levels. This process of phreatic carbonate accretion occurs actively today. Spectacular overgrowths on speleothems are also present that illustrate ancient Mediterranean interglacial high sea levels.

3. Coastal phreatic overgrowths on speleothems

The littoral karstic areas of Mallorca, mainly the south-eastern coast (Migjorn), have many caves partially submerged by brackish waters (Fig. 2) and abundant subaqueous speleothems associated with this particular geochemical environment. Calcite rafts often forms on the surface of these cave pools, along with characteristic bulky overgrowths (Fig. 3a) developed around those stalagmites or stalactites situated with the range of the current water-table (Pomar et al., 1979). Phreatic overgrowths of calcite and aragonite from few metres up to + 30 m above the level of present day brackish ponds are also common (Pomar et al., 1976; Ginés et al., 1981b). The bands of speleothems marked by these overgrowths
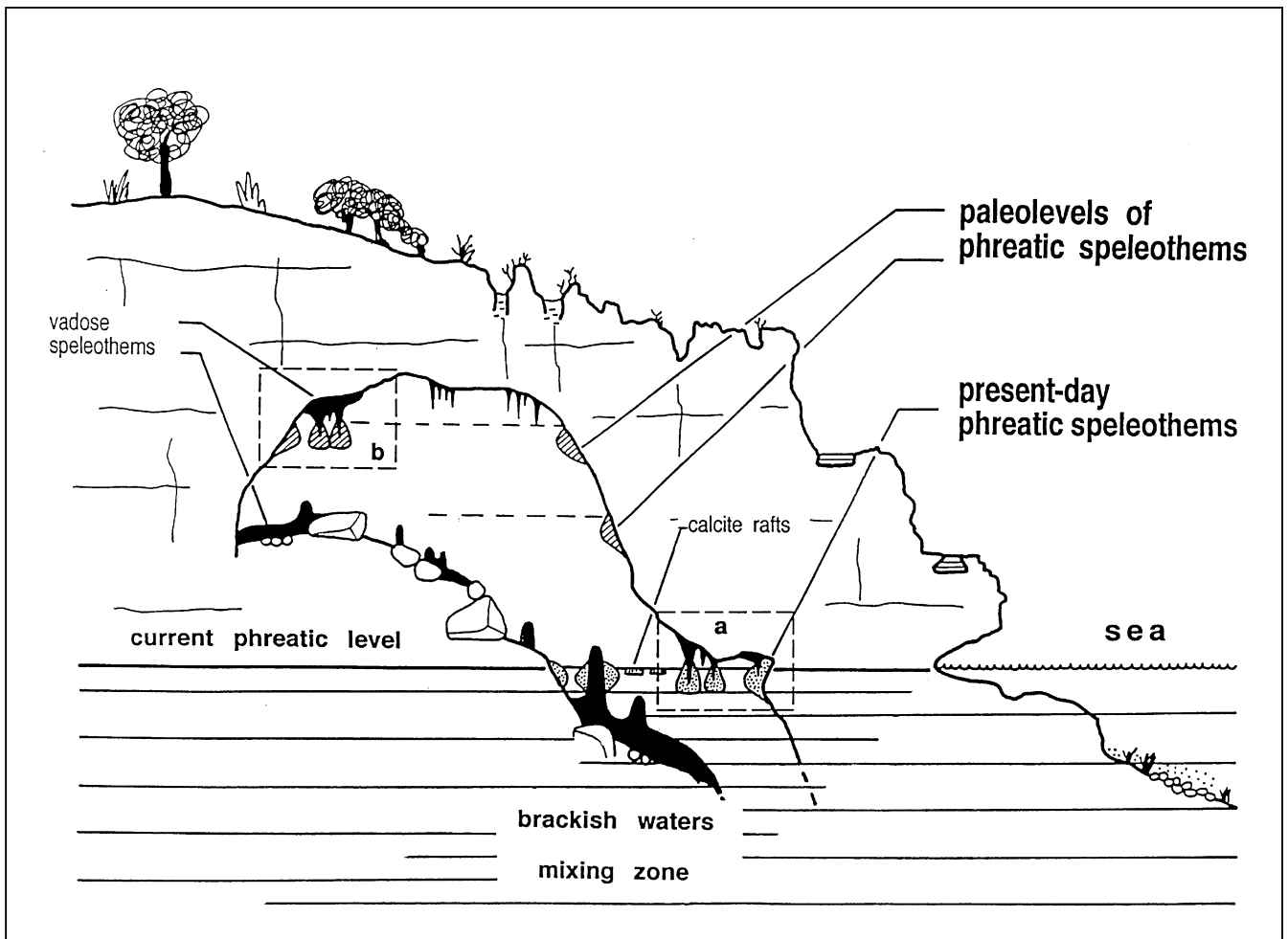

Fig. 2. Schematic representation of littoral karst in Mallorca outlined in an ideal cross-section. Note the presence of phreatic overgrowths on speleothems related with past- and present sea levels. Dashed squares, a and b, are photographs shown in Fig. 3.
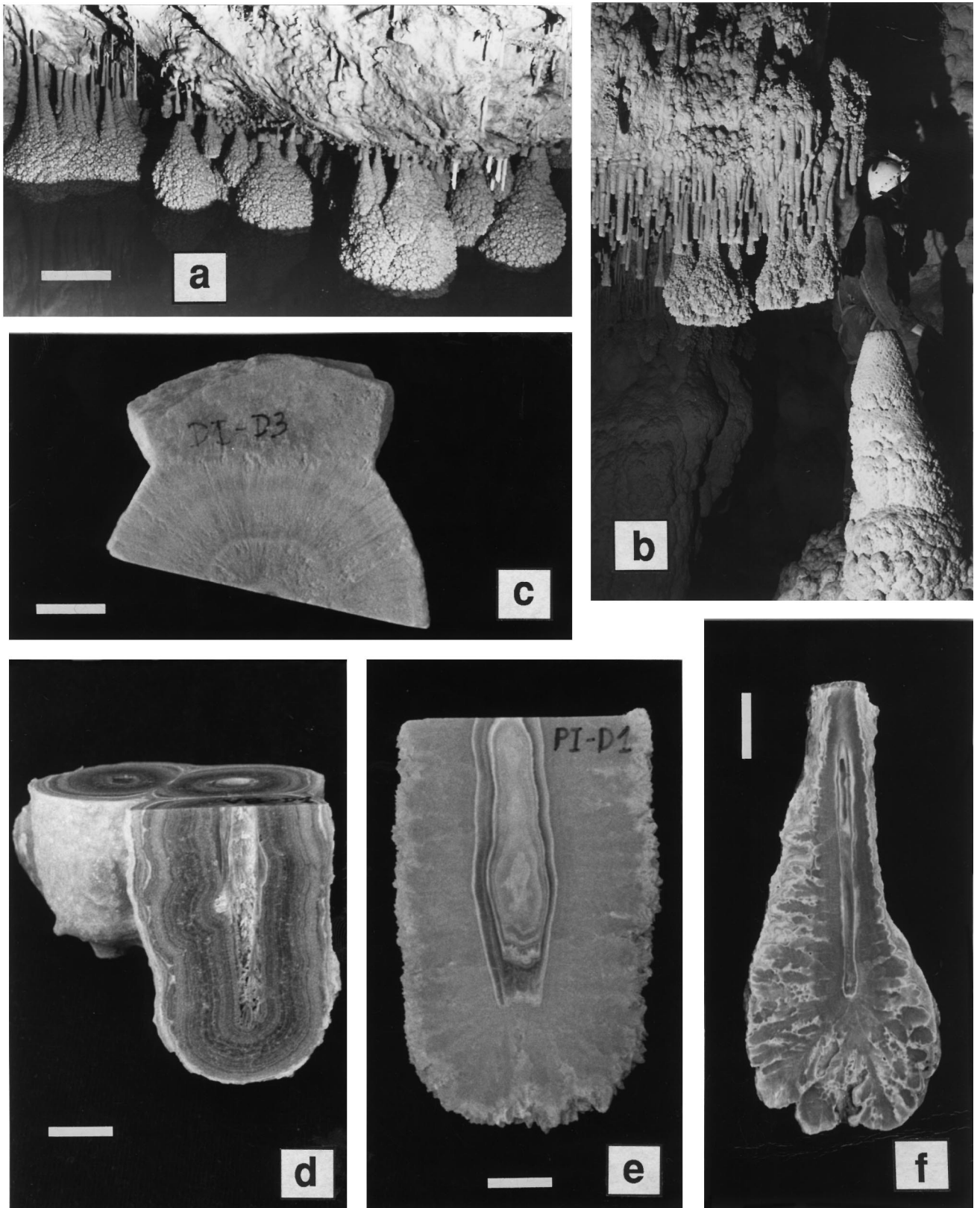
Fig. 3. (a) Present-day formation of calcite phreatic speleothems in the littoral brackish water pools in Cova de Cala Varques, related to the present sea level. Scale bar, 20 cm; (b) Paleolevels of calcite phreatic speleothems covering the ceiling of Cova de sa Bassa Blanca. See caver at the right-hand side for scale; (c) Transverse section of an aragonite phreatic speleothem from Cova del Dimoni (sample DI–D3). Scale bar, 1.2 cm; (d) Longitudinal and transverse section of stalactites with phreatic overgrowth from Cova de Cala Varques-B (sample VB-D2). Scale bar, 1.4 cm; (e) Longitudinal section of a stalactite with phreatic overgrowth from Coves del Pirata (sample PI-D1). Scale bar, 1.2 cm; (f) Longitudinal section of a stalactite with calcite phreatic overgrowth from Cova del Dimoni. Scale bar, 4 cm.

permit identification of former high sea levels (Fig. 3b). Generally, coastal phreatic overgrowths are similar to other subaqueous speleothems, but specific morphological and textural properties differ. According to Pomar et al. (1976), they can be classified into three types depending on their external textural features: smooth surfaces, coralloidal formations and needle-like crystal surfaces; the first type being aragonitic (Fig. 3c) and the other two calcitic.

Most of the overgrowths form around pre-existing vadose speleothems, thus adopting bulky forms. Sometimes they are belt-like around stalagmites and columns. In many cases, especially when the overgrowth affects the tip of stalactites (Figs. 3d and e), the original speleothem morphology can be modified substantially (Fig. 3f). Occasionally, calcite rafts are also trapped between the growth layers of these coatings.

Although there is still much that needs to be understood about the geochemistry of coastal karsts, it appears that these speleothems originate within the range of oscillation (usually 50 cm) of the surface of such subterranean pools. The proximity to the pool surface favours the precipitation process as the carbon dioxide degassing occurs preferentially close to the water surface. In the following discussion, these phreatic overgrowths are referred to as brackish water speleothems.

4. Analytical procedures

Samples of brackish water speleothems, vadose speleothems formed in the subaerial environment, and waters from the brackish pools were collected from nine caves located on the southeastern coast of Mallorca (Fig. 1).

The speleothems were sectioned and single growth layers were selected using a variety of motor-driven dental tools followed by sonic cleaning in double-distilled water to perform U/Th dating, as well as isotopic and X-ray analyses. For isotopic analyses the samples were reacted in 100% H_3PO_4 at 25°C (McCrea, 1950) and the carbon and oxygen isotopic ratios from the obtained CO_2 were determined on a Finnigan MAT 252 mass spectrometer. Results are reported in the normal δ (per mil) notation relative to the PDB and SMOW standards for carbon and oxygen, respectively. The precision of carbon and oxygen isotopic data was ± 0.05/mil.

Water from the brackish pools was analysed to determine the oxygen isotopic composition and $\delta^{13}C$ of the total dissolved carbonate species. The precipitation method (Bishop, 1990) for the $\delta^{13}C$ analyses of natural water involves adding $SrCl_2$–NH_4OH solution (Friedman, 1970) to promote precipitation, with subsequent filtration and drying of the carbonate sample under vacuum. Isotopic analyses were performed on the CO_2 gas

liberated from the precipitate with the procedures mentioned above. The isotope composition of oxygen in water samples was determined by analysis of the CO_2 that was isotopically equilibrated with the water sample at a known temperature.

Samples for Th/U analysis were prepared according to the analytical procedures described in Edwards, Chen and Wasserburg (1986, 1987). Before dissolution, speleothems for TIMS analyses were spiked with a ^{235}U-enriched solution prepared by diluting the National Bureau of Standards (NBS) U-500 standard ($^{235}U/^{238}U$ atomic ratio of 0.99970 ± 0.00006) and with a ^{232}Th enriched tracer obtained by diluting the "Roma-standard" ($^{232}Th/^{230}Th$ atomic ratio of $1,857,900 \pm 6,700$, (Voltaggio et al., 1995,1997).

Another tracer containing ^{228}Th in secular equilibrium with ^{232}U was used for α-counting analyses. Isotopic compositions were measured on a Finnigan MAT 262 mass spectrometer equipped with a retarding potential quadrupole (RPQ) and by α-counting.

The total procedural blank for mass spectrometric analyses is about 100 pg ^{232}Th and ^{238}U. No corrections were made for the blanks in this study since the U and Th in the samples are normally about 1000 times larger than the blanks. A series of measurements of the $^{234}U/^{238}U$ atomic ratio in solutions prepared by dissolving NBS standard reference material 960 yielded a mean ratio of $5.25 \times 10^{-5} \pm 2.01 \times 10^{-7}$ for the $^{234}U/^{238}U$. This shows that the measurements are reproducible and that the error estimates for each individual mass spectrometer runs are reasonable. Another set of twelve measurements was also performed on the above mentioned "Roma-standard" (a solution prepared from a Th nitrate produced at the beginning of this century by G. A. Blanc, one of the discoverers of ^{228}Th), yielding values of $^{232}Th/^{230}Th$ atomic ratio within the roughly ± 8 /mil error of each measurement (mean ratio of $1,857,900 \pm 6,700$).

Typical run precisions for U and Th isotopic ratios measured on our samples by mass spectrometry and α-counting are generally better than 1 and 3%, respectively. The corrections for spikes impurities and uncertainties resulted in larger errors for $^{230}Th/^{234}U$ activity ratios. The consequent ages have large uncertainties, more than 10% in 2σ for ages older than 200 ky.

5. Speleothem mineralogy

Some of the brackish water speleothems studied in this work have been analysed by X-ray diffractometry. Calcite, low Mg-calcite, high Mg-calcite and aragonite mineralogies are all present. As suggested by many authors (Pomar et al., 1987; Ford and Williams, 1989; Frank and Lohmann, 1996 and references included in Rao, 1996), the mineralogical nature of carbonate precipitates is

strongly affected by the temperature and the availability of some cations (mainly Sr and Mg) in the system. Rao and Adabi (1992) have found a clear relationship between the mineralogical nature of carbonate precipitates and temperature. In particular, aragonite and high Mg-calcite are favoured by warmer temperatures, while low Mg-calcite and calcite preferentially form at colder temperatures.

It must be noted that differences in the mineralogical nature of calcium carbonate affects the isotopic fractionation of oxygen and carbon between precipitate and solution (Faure, 1986).

6. Th/U data for speleothems

Fifteen brackish water speleothems and one vadose sample have been analysed using the Th/U method in order to date high sea stands of the Mediterranean during the Middle and Late Quaternary.

Obtained ages of phreatic overgrowths for individual localities are shown in Fig. 4 and range from 71.3 to ⩾350 ka (Table 1) showing good agreement with the OIS 5a, 5c, 5e and 7 corresponding with periods of high sea level. Mix and Ruddiman (1984) and Shackleton (1987) explain that ocean isotopic composition is not a linear function of ice volume and hence is not a linear function of sea level. Consequently, in the following discussion oxygen isotopic stages are used solely for reference and the high sea stands recognized in this work are not expected to match exactly the peaks of associated isotopic stages. Two samples from Cova de na Mitjana and Coves del Drac (Fig. 1), whose ages (> 301 and > 350 ka, respectively) approach the dating limits of the Th/U method, could pertain to OIS 9, or could represent an even earlier event. The vadose speleothem, VB-D, has given an age of 36 ka that corresponds to the end of

OIS 3, a period of low sea stand connected with cold environmental temperature.

Data from the brackish water speleothems mainly document Mediterranean sea levels at heights between 1.4 and 2.5 m a.s.l. in correspondence with the Last Interglacial (OIS 5e).

Goy et al. (1993) and Zazo et al. (1997) report at least two high sea stands during OI substage 5e in Balearic Islands and in peninsular Spain, and Hillaire-Marcel et al. (1996) recognize two different high sea stands in OIS 5e dated at 135 and 117 ka, represented by three sedimentary units from Campo de Tiro in the Bay of Palma de Mallorca. Similar consideration has been made by Dai Pra and Ozer (1984) on the coast of central Italy and by Hearty and Kindler (1995), Hearthy (1998) and Chen et al. (1991) on the Bermudas–Bahamas Islands.

In the southern part of Migjorn area (Cova de Cala Varques B and Cova des Serral) the 117 ka high sea stand is located at about 1.4–1.5 m above present sea level (samples VB-D1-2 and SE-D2), but records of the same episode have been found at a higher position, 2.5 m a.s.l. (samples DI-D1-1 and DI-D1-2), in a cave of the northern Migjorn (Cova del Dimoni). This suggests that the height of this stage is progressively decreasing towards the SW. This is probably due to a tectonic tilt which has lowered the south-western sector of Migjorn with respect to the north-east.

In Coves del Pirata and in Cova de na Barxa speleothems formed during OIS 5e have been recognized, but it is not possible to refer them to the 117 or 135 ka sea level fluctuations because of the large uncertainties affecting their ages.

The occurrence of speleothems of the same age at different heights is also documented by deposits that can be correlated with other isotope substages: 5c and 5a. With regard to deposits referred to as OIS 5c, they have been recognized in Cova des Serral (Ginés and Ginés, 1993) and Cova del Dimoni, at 1.5 and 2.5 m a.s.l., respectively (samples Serr10 and DI-D3). For marine levels correlated with substage 5a, they occur at 1.4 and 1.9 m a.s.l., respectively in Cova de Cala Varques B and Cova de Cala Falcó (samples VB-D2 and FA-D3-4).

The high sea stands recognized in this work for the OIS 5e range from 2 to 2.5 m a.s.l. in the Eastern Mallorca, from Cova de na Barxa to Coves del Pirata. Such data match those reported in Stearns and Thurber (1967) and Cuerda (1989) regarding Th/U measurements on marine terraces located in the same sector of the coast, from Cova de na Mitjana to Cova del Dimoni. In particular, two *Strombus bubonius* samples from Ses Rotes de Sa Cova, collected at + 2 m a.s.l. can be associated with the high sea stands of 5e. No comparison can be made with older material because of the large uncertainties affecting ages close to the dating limit of the Th/U method.
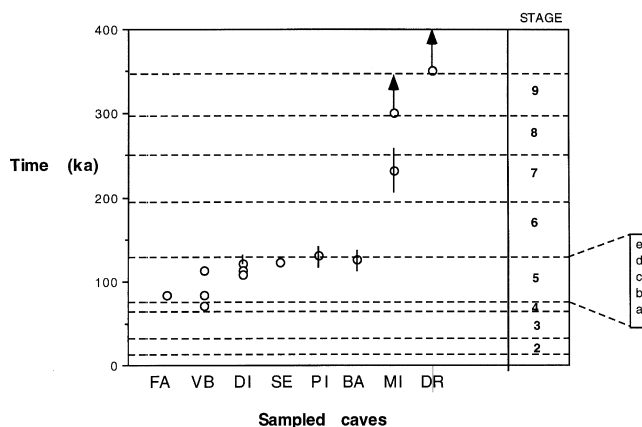

Fig. 4. Th/U ages of phreatic overgrowths on speleothems. Cave labels as in Fig. 1. Limits between Oxygen Isotope Stages (OIS) from Shackleton and Opdyke (1973).

Table 1
U-series data of speleothems. * indicates mass spectrometric analyses. Vadose speleothems are indicated with °. Speleothems whose growth layers have been analysed are underlined. Errors are 2σ for both mass spectrometry and α-counting ages.

Cave	Sample	Heigth a.s.l. (m)	U (ppb)	$^{234}U/^{238}U$	$(^{234}U/^{238}U)0$	$^{230}Th/^{232}Th$	$^{230}Th/^{234}U$	Age (ka)
Cova de Cala Falcó	FA-D3-4*	+ 1,9	542 ± 5	1,378 ± 0,003	1,528 ± 0,037	112,3 ± 0,2	0,554 ± 0,023	83,9 ± 5,0
Cova de Cala Varques B	VB-D°*	–	58 ± 2	2,110 ± 0,087	2,229 ± 0,110	164 ± 29	0,289 ± 0,019	36,0 ± 2,8
	VB-D2*	+ 1,4	228 ± 10	2,113 ± 0,099	2,41 ± 0,13	inf.	0,567 ± 0,025	83,4 ± 5,1
	VB-D1-1*	+ 1,4	234 ± 3	2,10 ± 0,09	2,358 ± 0,120	112,1 ± 0,7	0,505 ± 0,008	71,3 ± 1,5
	VB-D1-2*	+ 1,4	252 ± 4	1,519 ± 0,081	1,71 ± 0,08	inf.	0,632 ± 0,020	111,9 ± 5,7
Cova des Serral	SE-D2	+ 1,5	200 ± 4	1,453 ± 0,032	1,639 ± 0,046	240 ± 45	0,705 ± 0,019	121,3 ± 5,6
Cova del Dimoni	DI-D3	+ 2,5	1887 ± 45	1,108 ± 0,015	1,147 ± 0,020	inf.	0,638 ± 0,020	107,9 ± 5,7
	DI-D1-1	+ 2,5	2640 ± 77	1,185 ± 0,013	1,255 ± 0,018	257 ± 25	0,660 ± 0,020	112,9 ± 5,8
	DI-D1-2	+ 2,5	1273 ± 48	1,090 ± 0,018	1,126 ± 0,025	inf.	0,676 ± 0,032	119,7 ± 10,0
Coves del Pirata	PI-D1	+ 2,1	262 ± 9	1,663 ± 0,062	1,959 ± 0,092	inf.	0,745 ± 0,035	130,4 ± 14,0
Cova de na Barxa	BA-D3	+ 2,4	423 ± 19	1,430 ± 0,070	1,612 ± 0,103	inf.	0,715 ± 0,045	124,7 ± 14,0
Cova de na Mitjana	MI-D1 a	+ 3,9	128 ± 9	0,791 ± 0,067	–	inf.	1,340 ± 0,112	–
	MI-D1 b	+ 3,9	52 ± 6	2,091 ± 0,257	–	inf.	10,403 ± 1,098	–
	MI-D2	+ 4,9	146 ± 4	1,057 ± 0,019	1,110 ± 0,037	47 ± 5		231,9 ± 28,0
	MI-D3	+ 5,8	169 ± 1	0,972 ± 0,028	0,937 ± 0,035	51 ± 2	0,894 ± 0,024 0,972 ± 0,035	> 300,7
Coves del Drac	DR-D4	+ 3,3	2888 ± 84	1,039 ± 0,016	⩾ 1,139	inf.	1,038 ± 0,040	> 350

The high sea stands recorded in the eastern coast of Mallorca for OIS 5e are comparable with those of Campo de Tiro in the Bay of Palma (Hillarie-Marcel et al., 1996) which is considered a subsiding area at least from the Pliocene (Goy et al., 1993). In other sites of the island, records of the same events occurs at higher elevations, with the heights of maxima transgressive between + 12 and + 2.5 m (Goy et al., 1993). Hence, it appears that neotectonics have played an important role (Del Olmo and Alvaro, 1984; Gelabert et al., 1992) in the recent evolution of Mallorcan coast.

Uranium series disequilibrium analyses have also permitted the calculation of the uranium contents and the $^{234}U/^{238}U$ initial activity ratios of speleothems (Table 1). $^{234}U/^{238}U$ initial activity ratios reflect the lithological nature of the rocks where the caves develop. Cova de Cala Falcò, Cova de Cala Varques B, Cova des Serral, Cova del Dimoni, Coves del Pirata, Coves del Drac and Cova del Pont are located in calcarenites, and Cova de na Barxa and Cova de na Mitjana are located in dolomitic limestones and limestones, respectively. In particular, ratios lower than about 1.25 (data from Andrews et al., 1989; Ginés and Ginés, 1993) are representative of speleothems from caves formed in limestones and dolomitic limestones, whereas ratios higher than this limit belong to samples from caves located in calcarenites.

Uranium content of speleothems depends on the concentrations of this element in parental solutions: fresh water, sea water and mixing in different proportions between them, sea water being strongly enriched in U. This is well documented when comparing U abundances of vadose speleothems (see sample VB-D: 58 ppb) with those of brackish water speleothems that can reach uranium contents in the order of ppm.

Brackish water speleothems show extremely variable uranium concentrations in relation to the amount of sea water constituting the parental solution of the cave pools. The highest contents have been found for Cova del Dimoni and Coves del Drac, where $^{234}U/^{238}U$ initial activity ratios approaching the marine value (1.15), confirm a notable sea water component in the system. Although these caves are located inside calcarenite formations and thus should have $^{234}U/^{238}U$ initial ratios higher than 1.25, their low ratios are justified and are strongly affected by the presence of sea water with a significant U content and low $^{234}U/^{238}U$ initial ratios.

7. Stable isotope data for speleothems

Oxygen and carbon isotope data for brackish-water speleothems and vadose samples are reported in Table 2 and plotted in Fig. 5. In Table 2 data of host rocks are also included. $\delta^{18}O$ and $\delta^{13}C$ show a positive covariance. The data points are fitted by a regression line with a correlation coefficient of 0.890, clearly indicating an almost perfect linear relationship. The same correlation between $\delta^{18}O$ and $\delta^{13}C$ has been found for the marine-meteoric mixing zones of many areas (Allan and Matthews, 1982; Frank and Lohmann, 1996).

The observed covariance cannot be explained only in terms of isotopic fractionation due to temperature variations because of the large spread of isotopic values. It cannot be explained in terms of lithological differences of host rocks because speleothems with the lowest and highest $\delta^{18}O$ and $\delta^{13}C$ occur in caves formed in the same kind of rock, calcarenites (Cova del Pont, Coves del Pirata and Cova del Dimoni) (Table 2).

The U-content of the speleothems (from 50 ppb to 2.9 ppm) is positively correlated with $\delta^{13}C$ (Fig. 6) and also with $\delta^{18}O$ because of the linear correlation between C and O (Fig. 5). The observed covariances among such parameters could be interpreted as a mixing between two end-members enriched or depleted in ^{18}O, ^{13}C and uranium, respectively, in sea water and ground water.

In Fig. 5 brackish water speleothems with the high $\delta^{18}O$ and $\delta^{13}C$ values have a heavier composition which can be interpreted as due to a higher sea water contribution, while those with lower values record a lower sea water component. Clearly their low ^{18}O and ^{13}C values could also be justified by meteoric diagenesis, but this process is not evidenced by the petrographic analysis of these samples. Moreover, as pointed out by Allan and Matthews (1982) and Frank and Lohmann (1996), calcites or limestones altered by meteoric diagenesis have a characteristic pattern with a wide range of $\delta^{13}C$ compositions and much narrower range of $\delta^{18}O$ compositions, which is not that shown by our samples. Such pattern results from the fact that the $\delta^{13}C$ value of recrystallization products is taken from a combination of two carbon reservoirs (soil gas and unstable carbonate minerals) whereas the $\delta^{18}O$ value is dominated by a single reservoir (the water in which open system recrystallization occurs). The positive covariance also detected for this speleothem group suggests an impoverishment in ^{18}O and ^{13}C of the parent solution.

Vadose speleothems are precipitated from fresh water which has relatively high isotopic ratios (Fig. 5) that can be explained by relatively high isotopic values for the seepage waters from which they were deposited. Heavy isotopic composition of seepage waters are favoured by isotopically heavy lowstand rainfall, which was ultimately derived from ^{18}O-enriched lowstand oceans. Cooler atmospheric temperatures which are likely to have pre-
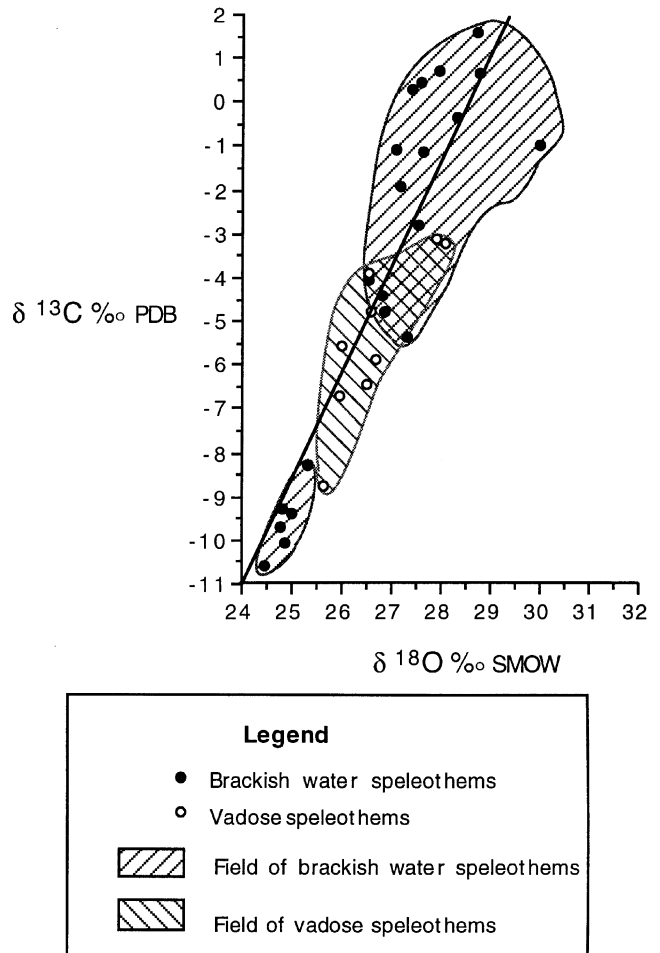

Fig. 5. $\delta^{18}O$ vs. $\delta^{13}C$ of different kinds of speleothems and their relative fields. The correlation coefficient of the regression line is 0.89.

vailed during lowstand periods further enhanced the shift toward heavier $\delta^{18}O$ values.

In light of this, the only vadose speleothem (VB-D) that has been dated shows an age of 36 ka. This sample has the same isotopic composition as a brackish-water speleothem (SE-D2) formed 121.3 ka B.P. This demonstrates that during the cold climate at the end of OIS 3, seepage waters reached an isotopic composition heavier than that of brackish waters during warmer interglacial periods.

Growth layers from three samples of the brackish water speleothems, FA-D3, DI-D1 and VB-D1, sampled in Cova de Cala Falcó, Cova del Dimoni and Cova de Cala Varques B respectively, have been analysed to detect the variation in isotopic ratios over time.

In sample FA-D3 the evolutionary trend (Fig. 7) starts with a decrease in $^{18}O/^{16}O$ and an increase in $^{13}C/^{12}C$ ratios between levels 5 and 4, then a subsequent positive covariance between the two variables from 4 to EC is shown. The path found from level 5 to 4 could be justified by the different mineralogical nature (Faure, 1986; Rao,

Table 2
Stable isotopic compositions of speleothems and host rocks. Symbols as in Table 1. The host rocks are in bold: **CA** stands for calcarenites, **CD** for dolomitic limestone and **CZ** for limestone.

Cave	Sample	$\delta^{18}O(\%_{\circ})$ SMOW	$\delta^{13}C(\%_{\circ})$ PDB
Cova de Cala Falcó	FA-D2	+ 26,85	− 1,87
	FA-D3-1	+ 27,95	+ 0,68
	FA-D3-2	+ 27,61	+ 0,41
	FA-D3-3	+ 27,42	+ 0,30
	FA-D3-4	+ 27,16	− 1,94
	FA-D3-5	+ 27,54	− 2,81
	FA-D3-EC	+ 28,74	+ 1,58
	FA-D5°	+ 26,59	− 4,77
	FA-D6°	+ 25,94	− 6,73
	FA-CA	+ 26,58	− 3,26
Cova de Cala Varques B	VB-D2	+ 26,84	− 4,41
	VB-D1-1	+ 27,30	− 5,35
	VB-D1-2	+ 26,87	− 4,77
	VB-D°	+ 26,56	− 3,89
	VB-D3-1°	+ 25,62	− 8,77
	VB-D3-EC°	+ 28,11	− 3,23
Cova des Serral	SE-D2	+ 26,55	− 4,04
Cova del Dimoni	DI-D3	+ 28,33	− 0,35
	DI-D1-1	+ 28,77	+ 0,62
	DI-D1-2	+ 27,09	− 1,06
	DI-CA	+ 26,22	− 4,77
Coves del Pirata	PI-D1	+ 25,33	− 8,30
Cova de na Barxa	BA-D3	+ 30,01	− 1,00
	BA-CD	+ 28,47	− 0,31
Cova de na Mitjana	MI-D2	+ 24,85	− 10,04
	MI-D3	+ 24,81	− 9,26
	MI-D1 a	+ 24,79	− 9,71
	MI-D1 b	+ 24,46	− 10,60
	MI-CZ	+ 26,01	+ 0,70
Coves del Drac	DR-D4	+ 27,62	− 1,12
	DR-D1°	+ 26,50	− 6,45
	DR-D2°	+ 26,68	− 5,90
	DR-D7°	+ 25,99	− 5,55
	DR-D8°	+ 27,89	− 3,12
Cova del Pont	PO-D1	+ 25,02	− 9,37

Fig. 6. $\delta^{13}C$ vs. U ppb of speleothems, that is $\delta^{18}O$ vs. U ppb because of the linear correlation between C and O (Fig. 5). Data points are fitted by a hyperbola representing a two-component mixing curve defined by an isotopic ratio ($\delta^{13}C$ or $\delta^{18}O$) and the concentration of another element (uranium), end members being sea water and ground water.

1996) of the two layers, calcite in 5 and Mg calcite + aragonite in 4. The subsequent ratio change, recorded on levels 4 to 1, which are progressively enriched in aragonite may be explained by an enrichment in ^{13}C and ^{18}O of parent solutions because of a higher sea water contribution, or a decrease in depositional temperature. If we assume that parent solutions have remained stable and are similar to the values of the present day pool ($\delta^{18}O = -3.64$/mil $_{SMOW}$), the obtained values indicate a temperature decrease of about 3°C (^{18}O the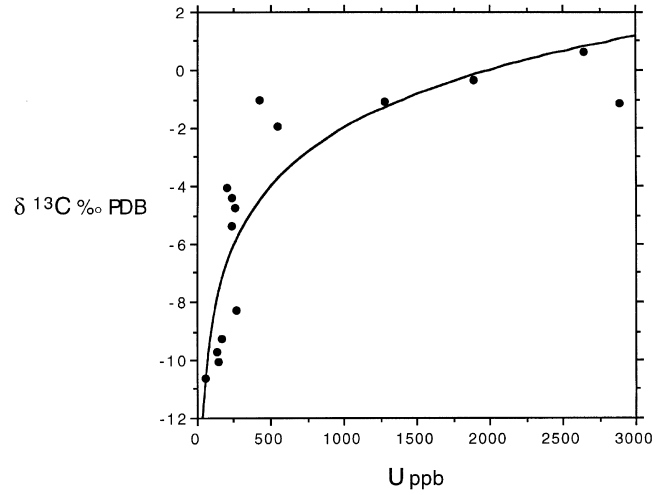rmometry equation from Friedman and O'Neil, 1977). Since the aragonitic component of these layers increases progressively, it is reasonable to accept that this trend is due exclusively to the gradual enrichment in ^{18}O of the parent solution, associated with a relative increase of sea water in the system. The external layer (EC) which is made of calcite, is enriched in ^{18}O by 0.8/mil with respect to the adjacent aragonitic level (1) (Fig. 7). This difference can be explained in terms of a temperature decrease of about 3°C and is in agreement with the changed mineralogical nature of the speleothem, since calcite forms at lower temperatures than aragonite (Rao, 1996).

In DI-D1 it is possible to note a positive covariance from level 2 (119.7 ka) to level 1 (112.9 ka), with a strong enrichment in ^{18}O and ^{13}C. This path resembles that of sample FA-D3 from layers 4 to 1 (Table 1) and in this case also the difference in isotopic composition between the two layers would involve a strong temperature decrease. If we assume that parent solutions have retained the same isotopic composition, equal to that of the present day pool ($\delta^{18}O = +1.32$/mil $_{SMOW}$), the recorded values are compatible with a temperature decrease of more than 9°C between levels 2 and 1. It is possible that such a decrease is too great to have occurred during the last interglacial in a cave, an isolated environment not experiencing extremes of temperature, although higher resolution records have shown a greater climatic instability in Mallorca from isotopic data (Rose et al., 1999) and from pollen and ice core evidence elsewhere (Field et al., 1994; Johnsen et al., 1995). The enrichment in ^{13}C and ^{18}O from 119.7 to 112.9 ka is likely to be connected with a relative increase of sea water in the pool, connected with a phase of climatic amelioration. This interpretation is supported by the strong enrichment in uranium content of layer 1 compared with 2, due to the high U
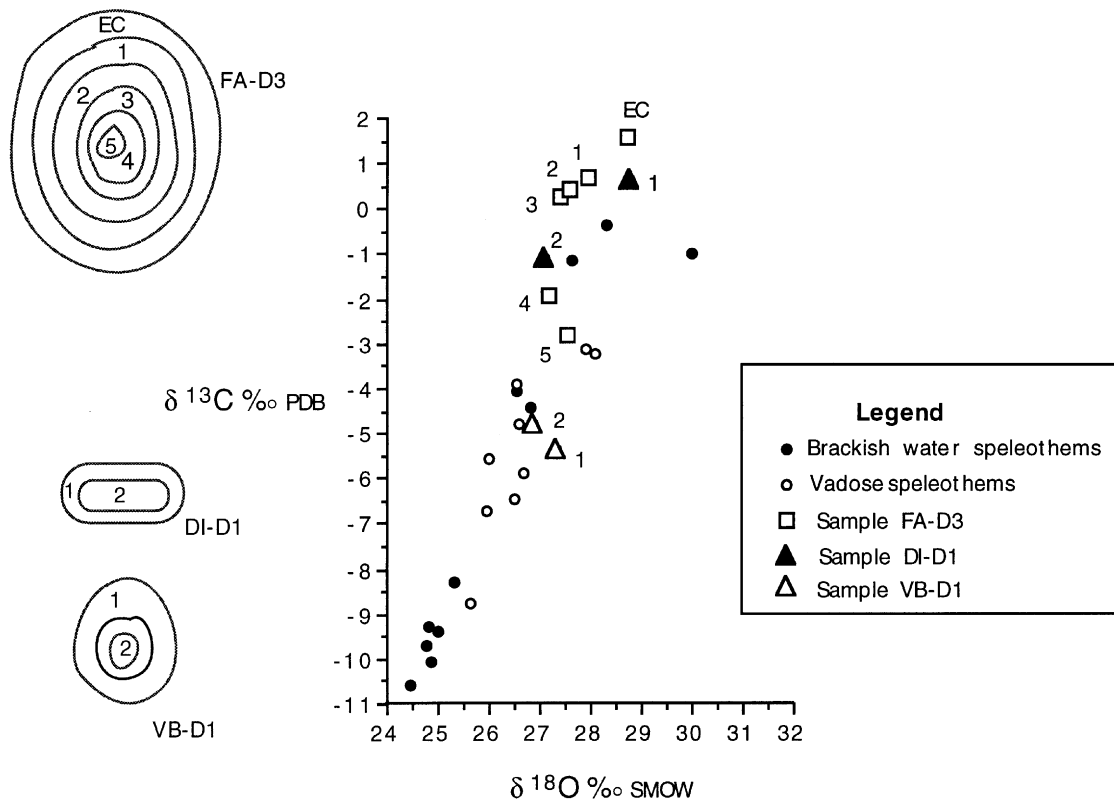
Fig. 7. $\delta^{18}O$ vs. $\delta^{13}C$ of speleothems. The growth layers of three of them have been analysed. Numbering increasing towards the nucleus of the speleothems, as depicted in the drawing.

concentration of sea water (Table 1). The aragonitic nature of layer 1 with respect to the calcitic composition of layer 2 also confirm the hypothesis of climatic amelioration (Tuccimei et al., 1998).

Finally, in speleothem VB-D1 levels 2 (111.9 ka) and 1 (71.3 ka) have been analysed. The apparent age gap between these two layers is well explained by the occurrence of an intermediate level which has not been possible to sample. These two layers show a path characterized by a decrease in ^{13}C and an increase in ^{18}O that could be justified by different mineralogical nature (Faure, 1986; Rao, 1996) of the two layers (Mg calcite in 2 and calcite in 1), caused by a temperature decrease. This is the same situation, encountered for levels 5 and 4 of FA-D3 sample, also attributable to a mineralogical change. In sample VB-D1, level 1, depleted uranium concentrations and higher $^{234}U/^{238}U$ initial activity ratio (Table 1) have also been recorded. This could indicate a relatively lower sea water component in the system at 71.3 ka.

8. Stable isotope data of brackish-pools waters

In Table 3 the oxygen and carbon isotopic compositions of cave waters, calcite rafts (CR) and total dissolved carbonate species (TDC) are reported, together with data on water temperatures and pH levels, plus calculated $\delta^{13}C$ values of CO_{2gas} in equilibrium with $HCO_{3dissolved}^{-}$ (for TDC) and $CaCO_{3solid}$ (for CR). For these last calculations the equations of Deines et al. (1974) have been used.

The $\delta^{18}O$ values of cave-pool waters show a strong variability ranging from $+1.32$ (Cova del Dimoni) to -5.66/mil (Cova del Pont). Such variations can be correlated with the amount of sea water in the system and, in turn, with the distance between the caves and the open coast. Cova del Dimoni is today directly connected with the sea, making its oxygen isotopic composition close to that of the Mediterranean which is normally higher than 0/mil (Scudeler Baccelle et al., 1994; Voltaggio et al., 1997 and references therein). Thus, the pool of Cova del Dimoni, characterized also by the heavier carbon isotopic value ($\delta^{13}C_{TDC} = -2.83$/mil) approaches, more than others, that of seawater (Kroopnick, 1985). Cova del Pont and Coves del Pirata are located further away from the coast and are less affected by sea water, and this is reflected in the $\delta^{13}C$ of TDC and CR.

The isotopic composition of TDC and CR permits the evaluation (Deines et al., 1974) of the $\delta^{13}C$ of CO_2 gas in equilibrium with bicarbonate and carbonate species, respectively. Analogous values can be obtained considering

the fractionation of the carbon isotopes in the equilibrium system $CO_2(gas)$–HCO_3^- (dissolved)–$CaCO_3$(solid) from Emrich et al. (1970). These authors have found the following fractionation factors: $+10.17 \pm 0.18$/mil between solid carbonate and gaseous carbon dioxide, $+1.85 \pm 0.23$/mil between carbonate and bicarbonate and $+8.38 \pm 0.12$/mil between bicarbonate and carbon dioxide. Recently Zhang et al., (1995) have obtained values of isotope fractionation between HCO_3^- and CO_2 similar to those of Emrich et al. (1970) and Deines et al. (1974). Different values have been found in the system $CaCO_3$–CO_2, but considering the temperature and pH data of the Mallorca cave pools, the fractionation factors correspond (within the error limits) to those given above.

The $\delta^{13}C$ of CO_2 gas ranges from -11.66 to -1872/mil. Clearly these values can give us information about possible sources of gaseous carbon dioxide: soil gas (Allan and Matthews, 1982; Deines et al., 1974), metastable sedimentary rocks (see Table 2) and seawater.

The fields of such sources are described together with the $\delta^{13}C$ compositions of speleothems which result from the mixing of carbon from the above-mentioned sources. Two different $\delta^{13}C$-fields are shown in Fig. 8. Precipitates with higher $^{13}C/^{12}C$ ratios are essentially linked with a carbon of metasedimentary and marine origin.

Isotopically lighter calcites of Coves del Pirata, Cova del Pont and analogously Cova de na Mitjana (where CO_2 data are not avalaible), are explained by parent solutions composed of higher volumes of ground water derived from rainfall enriched in ^{16}O with respect to seawater. Additionally, since they have recharged through thick terrestrial soils, rich in organic material, they are also enriched in ^{12}C.

9. Paleoclimatic implications

The stable isotopic values of the brackish water speleothems considered in this work cannot be used to reconstruct a single paleoclimatic curve of Late Quaternary because they come from different caves whose pools are characterized by waters of different composition and provenance. Only in the case of a single cave, would it be theoretically possible to make a curve analogous to those found in publications such as Shackleton and Opdyke (1973) and Martinson et al., (1987) which are based on other paleoclimatic indicators such as corals or forams, where a continuous record was available.

In Fig. 9 $\delta^{18}O$ values of brackish water speleothems (full circles) from any cave are plotted over time, along with one vadose sample from Cova de Cala Varques B (open square). Dashed lines are representative of high sea stand periods in Mediterranean Sea as known in literature (Martinson et al., 1987; Goy et al., 1993; Hillaire-Marcel et al., 1996; Zazo et al., 1997) and full lines, drawn on the basis of dated speleothems, indicates cold periods (Martinson et al., 1987). The above-mentioned authors have recognized at least two different high sea stands during OIS 5e, dated at 117 and 135 ka. Brackish water speleothems older than OIS 5 have not been included in the figure because of the larger errors

Table 3
Temperature, pH and $\delta^{18}O$ values of waters. $\delta^{13}C$ of TDC and CR (TDC is total dissolved carbon and CR is calcite rafts). $\delta^{13}C$ values of CO_2 gas in equilibrium with brackish pools waters as deduced from the equations of Deines et al., 1974. Calculated $\delta^{18}O$ of present precipitates in brackish pools according to the geothermometric calculations of Friedman and O'Neil (1977).

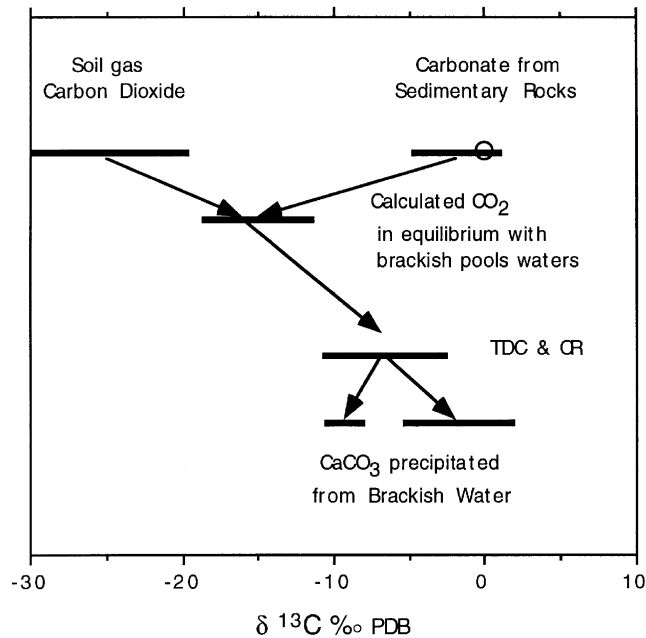| Cave	Sample	T (°C)	pH	$\delta^{18}O$(‰) SMOW	$\delta^{13}C$ (‰) PDB	$\delta^{13}C$(‰) (CO_2) PDB	$\delta^{18}O$(‰) ($CaCO_3$) calculated SMOW
Cova de Cala Falcó	H₂O	18	7,8	− 3,64	–	–	+ 26,70
	TDC	–	–	–	− 9,68	− 17,98	–
Cova de Cala Varques B	H₂O	16	7,8	− 3,15	–	–	+ 27,58
	CR	–	–	–	− 5,53	− 16,06	–
Cova de Cala Varques C	H₂O	16	7,3	− 2,48	–	–	–
	CR	–	–	–	− 4,76	− 15,28	–
Cova des Serral	H₂O	15,5	7,4	− 2,67	–	–	+ 28,18
	CR	–	–	–	− 5,22	− 15,8	–
Cova del Dimoni	H₂O	12,8	7,5	+ 1,32	–	–	+ 32,96
	TDC	–	–	–	− 2,83	− 11,66	–
Coves delPirata	H₂O	20	7,1	− 3,17	–	–	+ 26,63
	TDC	–	–	–	− 10,67	− 18,72	–
Cova de na Barxa	H₂O	16,5	7,0	− 3,54	–	–	+ 27,06
	TDC	–	–	–	− 6,71	− 15,17	–
Cova del Pont	H₂O	16,3	7,9	− 5,66	–	–	+ 24,92
	TDC	–	–	–	− 7,13	− 15,57	–

Fig. 8. $\delta^{13}C$ fields of gaseous carbon dioxide sources. Open circle represents the average $\delta^{13}C$ of sea water (Kroopnick, 1985). Data of soil gas CO_2 from Allan and Matthews (1982); Deines et al. (1974). $\delta^{13}C$ composition of sedimentary rocks from this work. Calculated CO_2 in cave pools from equations of Deines et al. (1974). TDC and CR stand for total dissolved carbon and calcite rafts in cave waters, respectively. Brackish water speleothems compositions are also reported.

associated with their age. Samples from Cova de na Barxa and Coves del Pirata can be ascribed to a high sea stand of OIS 5e, but it is not possible to refer them to the 117 or to the 135 ka line because of the large error associated with their age.

Samples from Cova des Serral (SE-D2), Cova de Cala Varques B (VB-D1-2) and Cova del Dimoni (DI-D1-1 and DI-D1-2) record the 117 ka high sea stand. In particular the sample of Cova del Dimoni (DI-D1-2) has an isotopic composition lower than that of the subsequently formed layer dated at 112.9 ka. Since level DI-D1-1 has been associated with the 117 ka high sea stand, the older sample can be referred to a previous relatively cooler phase, presumably characterized by a relatively lower sea water component in the system. This is also confirmed by the lower U-content and the calcitic composition of the 119.7 ka sample, as pointed out in a previous section. Only sample DI-D3 from Cova del Dimoni can be related to the following line at 103 ka, corresponding to OIS 5c.

Speleothems FA-D3-4 from Cova de Cala Falcó and VB-D2 from Cova de Cala Varques B can be associated to the line at about 80 ka, corresponding to OIS 5a. If we compare the isotopic composition of this last sample with that of the speleothem from the same cave associated with the high seastand of 117 ka, it is clear that they have the same isotopic composition, reflecting sim-

ilar sea water components in the system and analogous environmental temperatures. Therefore it is possible that the final part of OIS 5e and OIS 5a had similar climatic conditions.

The full line at 71.3 ka indicates a cold period (OIS 4). It is representative of one sample from Cova de Cala Varques B (VB-D1-1) which is the layer formed after that dated at about 112 ka (VB-D1-2). As shown previously, the different isotopic compositions of these two samples from the same speleothem can be explained in terms of a changed mineralogical nature (from Mg-calcite to calcite), connected with a decrease in temperature. In fact, OIS 4 is colder than OIS 5e.

The full line at 36 ka, obtained by the age of a vadose speleothem from Cova de Cala Varques B, is placed in a cold period (at the end of OIS 3).

This vadose speleothem (VB-D) shows the same isotopic composition of a brackish-water sample (SE-D2) formed at 121.3 ka demonstrating that during cold periods ground waters can reach an isotopic composition heavier than that obtained by brackish waters during interglacial periods.

The calculated $\delta^{18}O$ values of the present day precipitates are also plotted in Fig. 9. They have been obtained using the geothermometer calcite-H_2O (Friedman and O'Neil, 1977), considering the oxygen isotopic composition and the temperature measured in brackish water pools (Table 3).

Standard oceanic curves show that the present warm period is characterized by low $^{18}O/^{16}O$ ratios due to the high temperature of deposition. However, values calculated for present day precipitates should be higher than the past value, due to the differences between warm periods with a relatively higher sea-water component in the cave pools, and heavier isotopic composition during the earlier warm period, assuming the fractures network connecting the cave with the sea has not changed.

10. Conclusions

(a) Th/U dating and carbon and oxygen isotope analyses of phreatic overgrowths on speleothems have identified past high sea stands of the Mediterranean sea around the Balearic Islands for OIS 9 or older, 7, 5e, 5c and 5a.

(b) A phreatic overgrowth on speleothem for cold OIS 4 (71.3 ka) has been also recognized, indicating that environmental conditions were still favourable for carbonate precipitation, but the calcitic nature of the crystallization accounts for a colder climatic phase.

(c) Oxygen and carbon isotopic ratios from speleothems have demonstrated that heavier isotopic compositions record a relatively higher sea water component in the cave pools during warm climatic
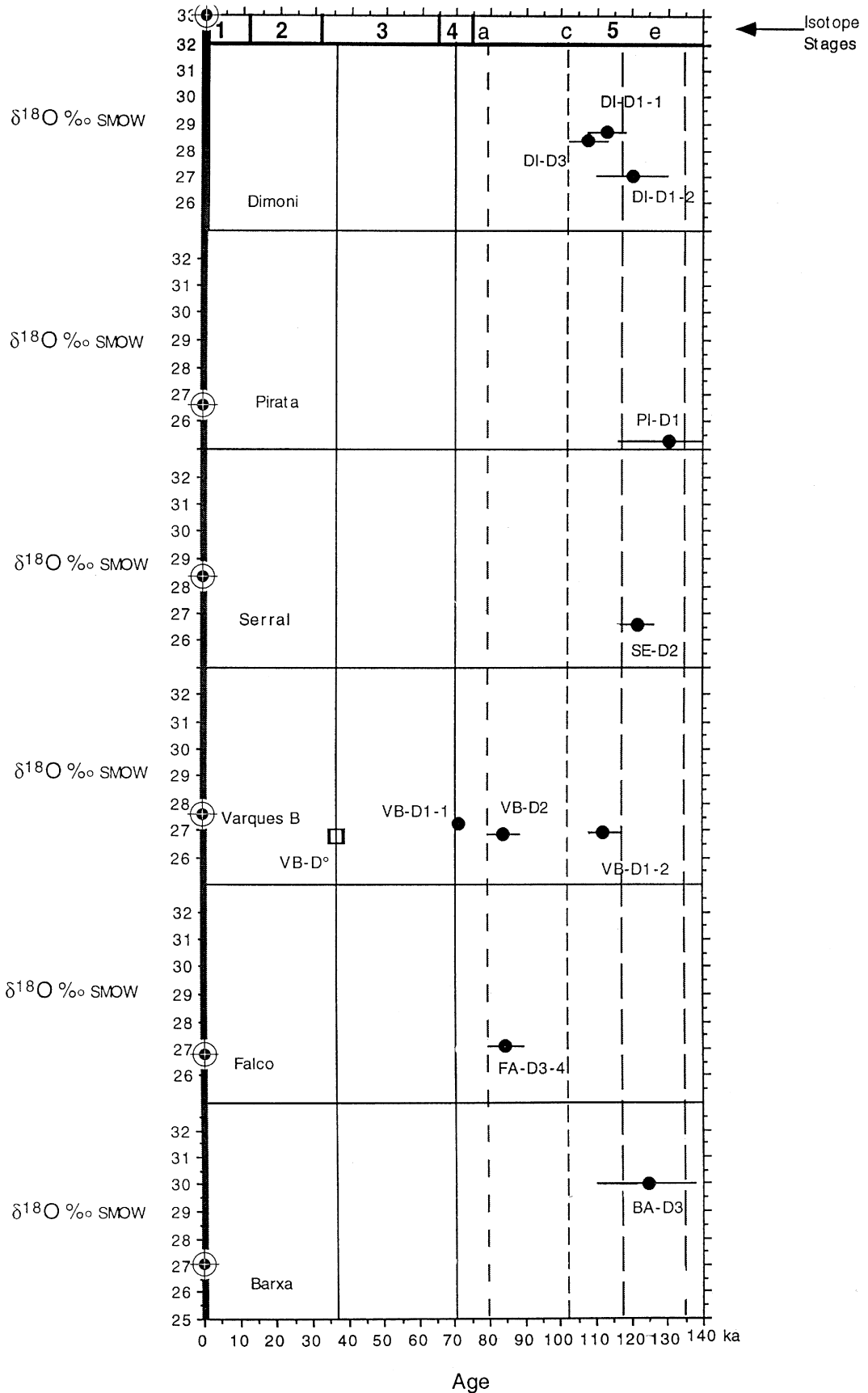
Fig. 9. $\delta^{18}O$ values of dated speleothems. Full circles represent brackish water speleothems and the open square indicates a vadose sample. Dashed lines are peaks of high seastands, while full lines stand for cold periods. Double-crossed circles are representative of the present precipitates as deduced from the geothermometers of Friedman and O' Neil (1977). Oxygen Isotope Stages of oceanic chronology as in Martinson et al. (1987) except for the lines at 117 and 135 ka (Hillaire-Marcel et al., 1996).

episodes. The changes in the marine component, associated with climatic fluctuations are also recorded by the U content. Detailed analyses of successive growth layers of some speleothems indicate that isotopic fractionation of carbon and oxygen is influenced by changes in mineralogy.

(d) The higher sea water component recorded by phreatic overgrowths on speleothems during warm periods could be explained in terms of a greater marine intrusion in the system. This relative increase of sea water in the cave pools could be explained by a decrease in the fresh ground-water component.

(e) Vadose speleothems deposited in subaerial environments are formed either in warm or cold periods. It has been demonstrated that during cold periods, they can assume isotopic compositions as heavy as those of brackish water speleothems.

(f) The geothermometric calculations indicate that present precipitates, in equilibrium with temperatures and $^{18}O/^{16}O$ ratios of waters in the cave pools, show that at present conditions are warmer than OIS 5e.

Brackish water speleothems represent a new and very powerful tool to obtain quantitative information about climatic fluctuations. This permits inferences about past continental and oceanic climate changes. Similar studies about phreatic overgrowths on speleothems could be applied to other areas of the world where analogous cave deposits occur.

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