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Comparison of ^{14}C and U-Th ages of two Holocene phreatic overgrowths on speleothems from Mallorca (Western Mediterranean): Environmental implications

Paola Tuccimei¹, Mark Van Strydonck², Angel Ginés^{3,*}, Joaquín Ginés³,
Michele Soligo¹, Igor M. Villa^{4,5}, Joan J. Fornós³

Abstract:

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This investigation reports on the comparison between ICP-MS U-Th and AMS ^{14}C ages of Phreatic Overgrowths on Speleothems (POS) from two different caves on the island of Mallorca (Spain). These speleothem encrustations form at the water table of coastal caves in a low-amplitude tide-controlled microenvironment and are used to reconstruct past sea level changes. The aim of this study is to evaluate if this particular type of speleothem is datable using ^{14}C method and to investigate possible problems connected with the incorporation of dead carbon inherited from the dissolution of ^{14}C -free limestone. The results show that ^{14}C ages are strongly site dependent and appear related to local residence time of water infiltration through the soil and epikarst. When short transit time and limited interaction with soil and bedrock, as in Cova de Cala Varques A, the so-called “reservoir” effect is negligible and ^{14}C and U-Th ages corresponds within the error range. When the residence time is longer, as in Cova des Pas de Vallgornera, ^{14}C ages are steadily 2,300-2,400 years older than the U-Th data, as shown by the mean value (25%) of estimated percent dead carbon proportions and by higher and better correlated contents of major and trace elements in the vadose support of this speleothem encrustation. The potential use of this multi-method approach to paleoenvironmental studies is also suggested.

Keywords: ^{14}C , U-Th dating, Holocene, speleothem, coastal karst, Mallorca

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INTRODUCTION

The use of radiocarbon dating in speleothem chronology is considered problematic, principally because of potential variability in the contribution of “dead carbon” from the host limestone (Hendy, 1970). Precipitating waters may contain a proportion of carbon inherited from the dissolution of ^{14}C -free limestone through the karst system that varies according to the extent of open system conditions and incongruent dissolution (Wigley et al., 1978). Where soil organic matter (SOM) turnover rates is longer than 10 years, soil $^{14}\text{CO}_2$ cannot be considered in equilibrium with the atmosphere and uncorrected ^{14}C

ages overestimate the true age of deposition (Genty et al., 1999). Because of these problems, relatively few speleothem chronologies are based on ^{14}C ages. However, where independent ages were calculated, the dead carbon proportion (dcp), due to the dissolution of the limestone and to “slow” oxidation of SOM was found to range between 10 and 20% (Bastin & Gewalt, 1986; Holmgren et al., 1994; Genty et al., 1998; Beck et al., 2001), although much greater values were also observed (Vogel & Kronfeld, 1997).

Another problem could arise from the contamination of speleothems with younger carbon from soil organic matter that might be deposited in the original structure of porous speleothems and subsequently decay, releasing CO_2 that could precipitate as carbonate (Goslar et al., 2000). In addition to that, bomb- ^{14}C may affect modern speleothems leading to an apparent age that is younger than corresponding U-Th age (Genty et al., 1998).

This study reports on the comparison between Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) U-Th and Accelerator Mass Spectrometry (AMS) ^{14}C ages of two Holocene POS from Mallorca (Spain). U-Th ages of POS are increasingly gaining attention from the scientific community because they allow to precisely constrain sea-level change

¹ Dipartimento di Scienze Geologiche, Università “Roma Tre”, Largo San Leonardo Murialdo 1, 00146 Roma, Italy

² Institut Royal du Patrimoine Artistique, Parc du Cinquantenaire 1, B-1000 Bruxelles, Belgium

³ Departament de Ciències de la Terra, Universitat de les Illes Balears, ctra. Valldemossa km 7.5, Palma de Mallorca, 07122, Spain. email: agines.gracia@yahoo.es

⁴ Institut für Geologie, Universität Bern, Baltzerstrasse 3, 3012 Bern, Switzerland

⁵ Dipartimento di Scienze Geologiche e Geotecnologie, Università di Milano - Bicocca, Piazza dell'Ateneo Nuovo 1, 20126 Milano, Italy

during the Holocene (Tuccimei et al., 2010) and Late Pleistocene (Vesica et al., 2000; Tuccimei et al., 2006; Dorale et al., 2010). These speleothem encrustations form a bulky belt-like band deposited at the water table of caves in unique karstic coastal settings having morphologies that can be directly related to sea level at the time of formation (see for details Ginés et al., 1981; Pomar et al., 1979; Vesica et al., 2000). U-Th ages of these samples -found at current sea level in the range of tidal fluctuation- have been recently reported by Tuccimei et al. (2009, 2010). These studies demonstrated that POS can readily be dated using U-series method, if the closed system condition can be verified. The aim of this study is to estimate if Holocene POS from two coastal caves in Mallorca are datable using ^{14}C method and to assess potential problems related to future application of radiocarbon dating to speleothem overgrowths studies. Finally, this investigation highlights several environmental implications concerning water-soil-rock interaction processes, climatology and hydrology of coastal karst.

GEOLOGICAL SETTING AND SAMPLES DESCRIPTION

In the context of the Western Mediterranean plate tectonics, Mallorca was affected by two tectonic phases: the former -compressive- acting from the Paleogene to the Middle Miocene, the second -extensive- Upper Miocene in age, resulting in a structure formed by horsts and grabens (Gelabert et al., 1992) bounded by Upper Miocene normal faults. Both tectonic phases affect all carbonate lithologies occurring almost continuously since the Permo-Triassic to the present (Fornós & Gelabert, 1995). The horsts correspond to the mountain ranges (Serra de Tramuntana and Llevant) and consist of an imbricate thrust sheet system facing NW. The grabens correspond to the basins (Pla and Migjorn) filled with tabular postorogenic sediments, mainly Upper Miocene to Quaternary in age. Sediments deposited after the Middle Miocene are considered post-orogenic and do not present evident compressive structures. Consequently, Mallorca must be considered stable since the Upper Miocene (Fig. 1).

The two speleothems chosen for this investigation are VA-D1 and VL-D3 from two coastal caves in Mallorca (Spain): Cova de Cala Varques A and Cova des Pas de Vallgornera, respectively (Fig. 1). Both caves are developed within very porous calcarenites of the Upper Miocene Reef Complex (Fornós & Gelabert, 1995). The first one is located within 50 m from the coast line whereas the latter one at several hundreds meters inland.

Cova de Cala Varques A is located only few metres from the eastern coast of Mallorca and belongs to a system of three neighbour caves interconnected through underwater passages. The presence of bulky calcite overgrowths along the margins of extensive brackish water pools is noteworthy (Fig. 2a).

Cova des Pas de Vallgornera is the largest cave in Mallorca, with a passage development exceeding 63 km (Fornós et al., 2010). It consists of an impressive

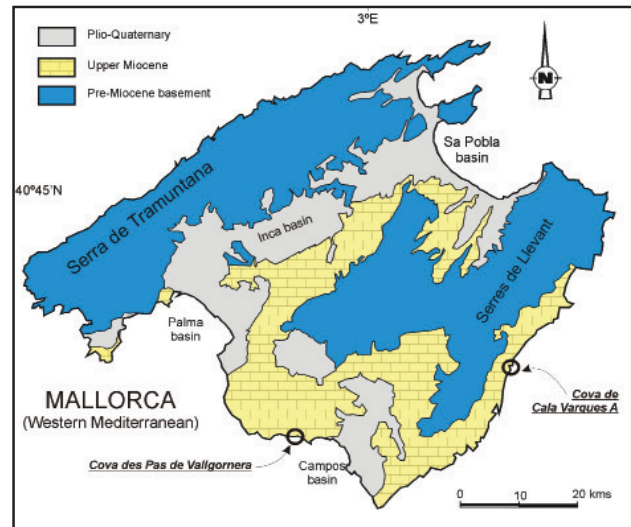


Fig. 1. Geological map of Mallorca Island (Western Mediterranean) with the location of the studied caves.

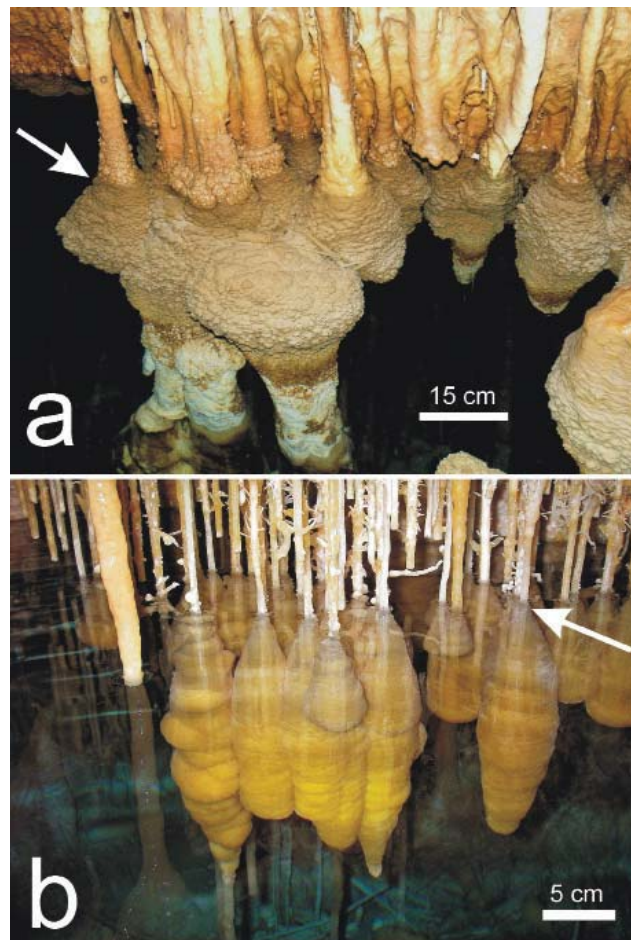


Fig. 2. Carbonate crystallisations at the water table of coastal caves. a: calcite belt of POS in Cova de Cala Varques A (Manacor); white arrows emphasise water table position when the picture was taken, which was slightly higher than present mean sea level (Photo: B.P. Onac). b: aragonite belt of POS from Cova des Pas de Vallgornera (Llucmajor); the thickest part of the overgrowth band corresponds to the mean sea level; white arrows emphasise water table position when the picture was taken (Photo: A. Merino).

maze of passages and chambers developed roughly on two main levels (Ginés et al., 2009), of which, the lower is partially drowned by brackish waters. Among the many carbonate precipitates found in the cave, there are abundant aragonite deposits, formed at the surface of the subterranean pools. They include abundant delicate stalactites with tips coated by smooth yellowish aragonite overgrowths (Fig. 2b).

Speleothem VA-D1 is a stalactite encrusted by a globular phreatic precipitate of 3–10 cm thickness, consisting of mm-scale elongated rhombohedral calcite crystals. Speleothem VL-D3 is a vadose stalactite covered by a globular phreatic overgrowth with a thickness of 0.5–2 cm. It is composed of 20 μm wide and 1 mm long acicular aragonite crystals with flat orthorhombic terminations, arranged in 0.3–1 mm thick successive growth bands of radial fan crystals (Tuccimei et al., 2010).

METHODS

Sampling

Five samples were selected from speleothem VA-D1 (Cova de Cala Varques A), one from the inner vadose support (subsample 14) and four (subsamples 1, 2, 3 and 4) from the phreatic overgrowth along a transect parallel to the growth axis, in correspondence with the larger thickness of the overgrowth (Fig. 3).

Three other samples (subsamples 2, 4 and 5) were obtained from speleothem VL-D3 (Cova des Pas de Vallgornera) along a transect parallel to the growth axis (Fig. 4). Finally, thin sections were cut from both speleothems along horizontal planes perpendicular to the inner vadose support for electron microprobe analyses.

Radiocarbon dating

CO_2 was extracted from the samples with phosphoric acid without any pre-treatment. Part of the released CO_2 was used for stable isotope measurements ($\delta^{13}\text{C}$) using a Finnigan-Mat- δ . The results are expressed in ‰ vs. V-PDB. The remaining CO_2 was used for the graphitization (with H_2 over a Fe catalyst) (Van Strydonck & Van der Borg, 1990-91) and preparation of an AMS target. ^{14}C content of the graphite was measured using a 3 MEV Tandemron 4130 AMS machine (High Voltage Engineering) (Nadeau et al., 1998). Radiocarbon ages and $\delta^{13}\text{C}$ values are reported in Table 1. Errors associated to the ages are quoted as 1σ according to Stuiver & Polach (1977).

U-Th dating

Carbonate samples were spiked with a mixed ^{236}U – ^{229}Th tracer and dissolved in concentrated distilled HCl. The dried chloride was then converted to nitrate. U and Th were separated on miniaturized PTFE columns containing U-TEVATM resin using HNO_3 and HCl. As the Th eluate is strongly bound to rather volatile organic matter washed from the resin, the Th fraction was evaporated at $<50^\circ\text{C}$ to avoid loss by evaporation. Organic molecules were oxidised according to the protocol described in Tuccimei et al. (2010). After oxidation, U samples were dissolved

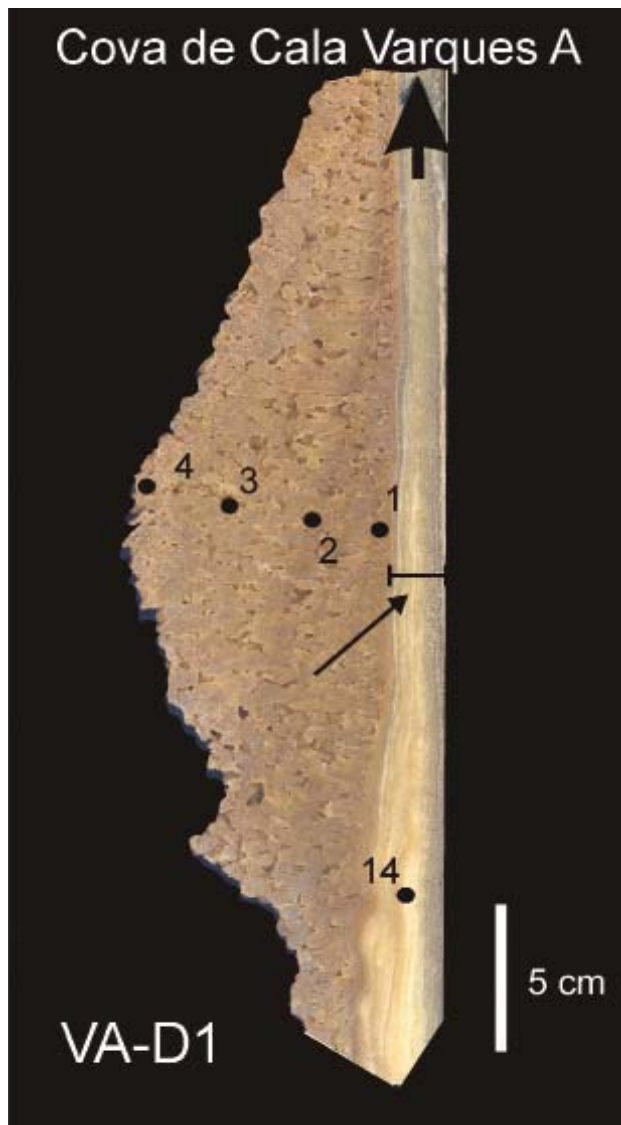


Fig. 3. Location of subsamples from speleothem VA-D1 (Cova de Cala Varques A) analysed for U-Th and ^{14}C dating, as well as trace elements and calcium profiles included in Fig. 5.

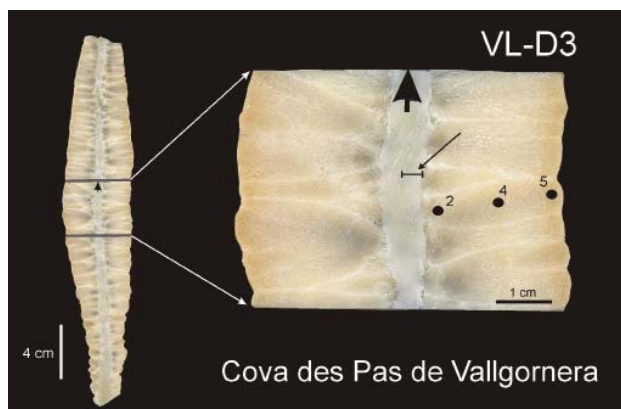


Fig. 4. Location of subsamples from speleothem VL-D3 (Cova des Pas de Vallgornera) analysed for U-Th and ^{14}C dating, as well as trace elements and calcium profiles included in Fig. 5.

Table 1. U-Th, ^{14}C ages and dead carbon proportion results on VA-D1 and VL-D3 speleothems.

Sample name	U-Th age years (BP)	^{14}C age years (BP)	$a^{14}\text{C}_{\text{atm.meas}}$ pMC	$a^{14}\text{C}_{\text{meas}}$ pMC	dcp (%)	$\delta^{13}\text{C}$ V-PDB (‰)
VA-D1-1	2800±20	2820±30	71.15±0.35	70.36±0.26	1.11±0.79	-3,9
VA-D1-2	2300±700	2185±30	76.01±12.44	76.18±0.30	-0.22±23.15	-3,2
VA-D1-3	1500±35	1700±25	82.24±0.71	80.93±0.24	1.59±1.26	-3,14
VA-D1-4	1100±250	315±25	86.11±5.20	96.14±0.28	-11.65±8.55	-3,42
VA-D1-14	7700±100	7750±45	42.35±1.04	38.10±0.22	10.04±3.52	-8,42
VL-D3-2	1840±10	4120±35	78.94±0.20	59.89±0.27	24.13±0.58	-4,73
VL-D3-4	1350±5	3615±30	83.28±0.10	63.79±0.25	23.40±0.43	-5,23
VL-D3-5	610±5	3005±30	93.02±0.12	68.79±0.27	26.05±0.43	-5,19

$^{14}\text{C}_{\text{atm.meas}}$ = ^{14}C activities of the atmosphere obtained by converting the U-Th age into a ^{14}C activity by means of the calibration curve (intCal09, Reimer et al., 2009);
 $a^{14}\text{C}_{\text{meas}}$ = measured ^{14}C activities;
dcp = dead carbon proportions;
 $\delta^{13}\text{C}$ values are referred to the standard V-PDB;
 ^{14}C activities are expressed as pMC (percent modern carbon). For VA-D1 and VL-D3 subsample locations see Figures 3 and 4 respectively. All errors quoted as 1σ .

in 0.5 mol L⁻¹ HNO₃, Th samples in 3 mol L⁻¹ HCl, and measured on a Nu Instruments™ multicollector plasma source mass spectrometer equipped with an APEX™ desolvating nebulizer. Measurement protocols are as described by Fleitmann et al. (2007). Activity ratios for ICP-MS data were calculated with the decay constants described in Cheng et al. (2000). The ages of all samples were calculated by means of Isoplot/Ex (version 3.0), a plotting and regression program designed by Ludwig (2003) for radiogenic-isotope data. U-series data reported by Tuccimei et al. (2010) are listed in Table 1; errors are quoted as 2σ in the original publication, and as 1σ in the present study, in order to ease the comparison with the ^{14}C data.

Electron microprobe analyses

Thin sections were analysed using a JEOL JXA-8200 electron microprobe, equipped with five wavelength-dispersive spectrometers, at an average spatial resolution of 200 – 300 μm . The measurements were focused on calcium, magnesium, strontium, sodium and phosphorus abundances of the vadose support of both speleothems in order to infer the interaction of the percolating water as it passes through the soil and epikarst.

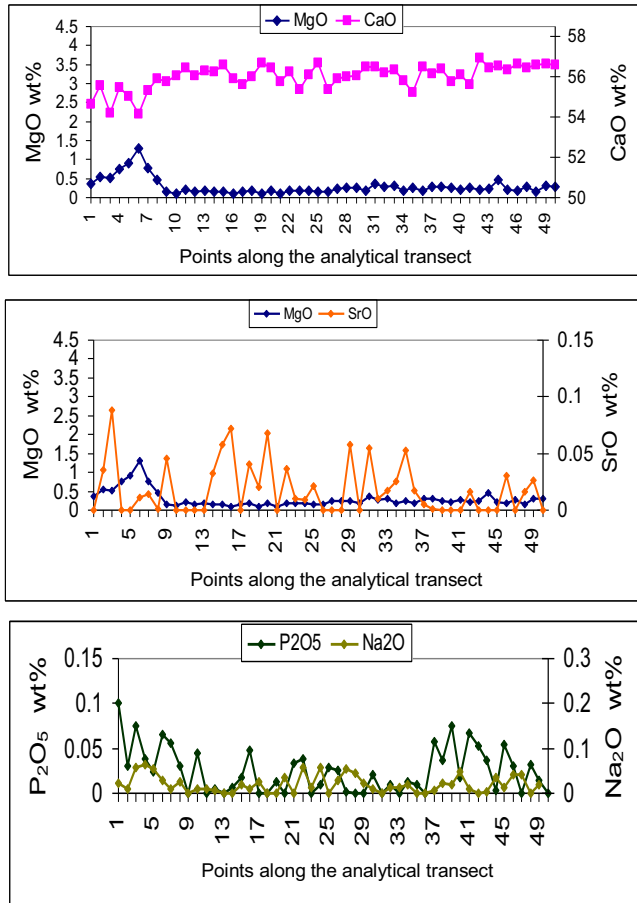
RESULTS AND DISCUSSION

^{14}C data were not calibrated because the source of carbon is unknown, possibly being a mixture of carbon from different reservoirs: air, dissolved rock, SOM and plants. In addition, mother solutions are phreatic brackish waters resulting from a mixture of fresh-groundwater and seawater; the mixing proportion at Cova de Cala Varques A is ~ 40% (Tuccimei et al., 2010), and possibly different ratio at Cova des Pas de Vallgornera. Age data are reported in Table 1, along with dead carbon proportion and $\delta^{13}\text{C}$ values.

U-Th ages of subsamples from speleothem VA-D1 were corrected for the presence of a detrital component containing inherited ^{230}Th according to a 3-D isochron approach, as shown in Tuccimei et al. (2010); measured $^{230}\text{Th}/^{232}\text{Th}$ activity ratio ranged between 0.4 and 7.1. U-Th ages of subsamples from VL-D3 speleothem, affected by a very minor contamination, were corrected for an initial ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio of 0.85 ± 0.36 (upper crust value, Wedepohl, 1995). In this case, measured values of $^{230}\text{Th}/^{232}\text{Th}$ activity ratio ranged between 145 and 510 (Tuccimei et al., 2010).

Older samples from Cova de Cala Varques A speleothem encrustation (VA-D1-1, VA-D1-2 and VA-

VA-D1 vadose support



VL-D3 vadose support

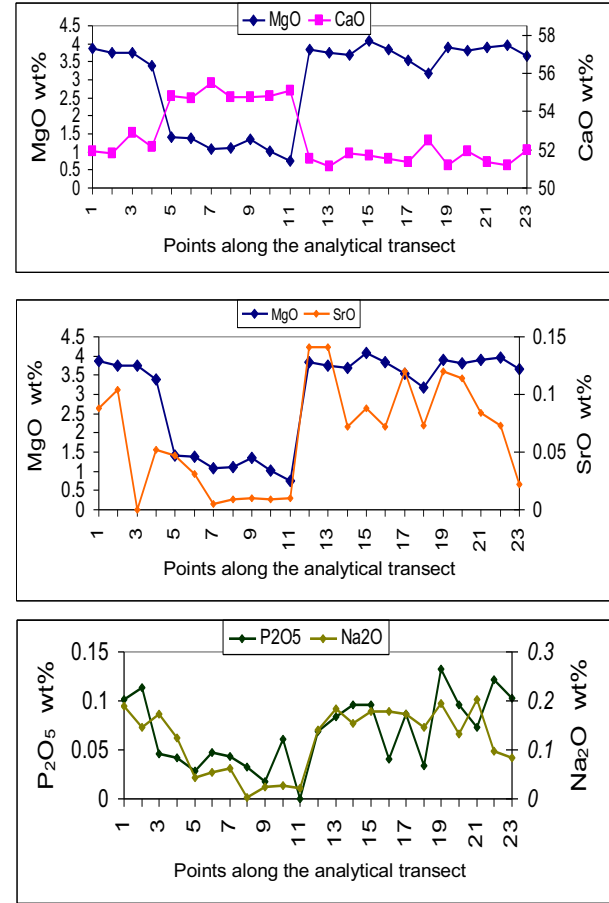


Fig. 5. Major (Ca, Mg, Na) and trace elements (Sr, P) profiles across the vadose supports of VA-D1 and VL-D3 speleothems. All Y-axes are similar to better illustrate different abundances and changes. Profile locations are shown in Figures 3 and 4.

D1-3) provided reasonably consistent U-Th and ^{14}C ages, including the vadose support (sample VA-D1-14). U-Th ages are generally slightly younger than related ^{14}C ages, while the youngest portion of the phreatic overgrowth (VA-D1-4) displays a ^{14}C age younger than that obtained by U-Th method. In principle, this could be due to contamination with modern carbon from very young organic matter deposited in the original structure of porous speleothem and degraded by the microbial activity, but its $\delta^{13}\text{C}$ composition does not record any significant change when compared to other subsamples from the overgrowth. Actually, the $\delta^{13}\text{C}$ values of all subsamples from POS VA-D1 are quite constant (from -3.14 to -3.90 ‰ V-PDB), showing that the carbonate was deposited under the same conditions over time and assuming that the environment can be considered stable. Finally, the carbon isotopic composition of the vadose support (-8.43 ‰ V-PDB) is more negative than that of POS, indicating its meteoric origin.

The speleothem from Cova des Pas de Vallgornera (VL-D3-2, VL-D3-4, VL-D3-5) displays systematically older ^{14}C ages that are steadily about 2,300-2,400 years older than U-Th data. The constant difference suggests that the system was stable over the entire period of speleothem precipitation. The temporal shift

between the two dataset could be due to the so-called “reservoir effect” according to which the speleothem precipitates from a solution containing more ^{14}C -free carbon from leached carbonate rocks or old SOM.

This observation is confirmed by magnesium, strontium, sodium and phosphorus contents of calcite vadose supports of VA-D1 and VL-D3 speleothems (Fig. 5), which reflect abundances of these elements in the mother solutions and thus an estimate of the interaction with the soil and bedrock.

VL-D3 speleothem is characterised by higher concentration of magnesium and sodium and markedly less strontium and phosphorus compared to VA-D1. The fluctuations of all these elements along growth profiles are evidently correlated for VL-D3 and apparently random for VA-D1. These findings argue for a higher residence time in the soil and epikarst above Cova des Pas de Vallgornera (VL-D3) than above Cova de Cala Varques A (VA-D1). This is so because in temperate regions, solute acquisition by karst waters generally depends on water residence time and tends to increase during drier periods when residence times are longer (Fairchild et al., 2000). This seems to be true for Cova des Pas de Vallgornera, which is located farther inland under a bush Mediterranean scrub-cover, alternating with cultivated grassland, whereas

Cova de Cala Varques A opens very close to the coast line, beneath a rocky supralittoral karrenfield covered by a discontinuous and thin soil with very scarce natural vegetation. Furthermore, the thickness of the rock cover is greater above Cova des Pas de Vallgornera (approximately 20 m) compared to Cova de Cala Varques A where only reaches a few metres. Finally, looking at the carbon isotopic composition of VL-D3 POS, it is possible to observe that it is slightly more negative (from -4.73 to -5.23 ‰ VPDB) than that of Cova de Cala Varques A, but fairly homogeneous.

If a long residence time in the soil and epikarst of Cova des Pas de Vallgornera and a shorter one at Cova de Cala Varques A are inferred, the relative dead carbon proportion (dcp) in all subsamples, can be calculated from the following equation by Genty et al. (1999):

$$dcp = \left[1 - \left(\frac{a^{14}C_{init}}{a^{14}C_{atm.init}} \right) \right] \cdot 100\%$$

where $a^{14}C_{init}$ is the initial ^{14}C activity of the calcite and $a^{14}C_{atm.init}$ is the atmospheric ^{14}C activity at time of deposition.

Since the initial ^{14}C activity of calcite is equal to:

$$a^{14}C_{init} = \frac{a^{14}C_{meas}}{\exp(\lambda \cdot t)}$$

where $a^{14}C_{meas}$ is the measured radiocarbon activity corrected for isotopic fractionation, λ is the ^{14}C decay constant, calculated from the Libby half-life and t is time, and the initial ^{14}C activity of the atmosphere is given by the following equation:

$$a^{14}C_{atm.init} = \frac{a^{14}C_{atm.meas}}{\exp(\lambda \cdot t)}$$

where $a^{14}C_{atm.meas}$ represents the ^{14}C activity of the atmosphere obtained by converting the U-Th age into a ^{14}C activity by means of the calibration curve (intCal09) (Reimer et al. 2009), then, the first equation becomes:

$$dcp = \left[1 - \left(\frac{a^{14}C_{meas}}{a^{14}C_{atm.meas}} \right) \right] \cdot 100\%$$

Calculated dead carbon proportion values are reported in Table 1 and displayed in Fig 6. Table 1 also reports $a^{14}C_{atm.meas}$ and $a^{14}C_{meas}$ data used to calculate the values of dcp.

The pooled mean of percent dcp values calculated for subsamples from the phreatic overgrowth of Cova de Cala Varques A is 1.08 ± 0.35 (1 σ) and there is 95 % probability that all of them represent the same true value (t-test). The pooled mean takes into account the precision of data (standard deviation) and consequently the weight of dcp calculated for subsamples VA-D1-2 and VA-D1-4 is low because of the large uncertainties. This highlights the negligible

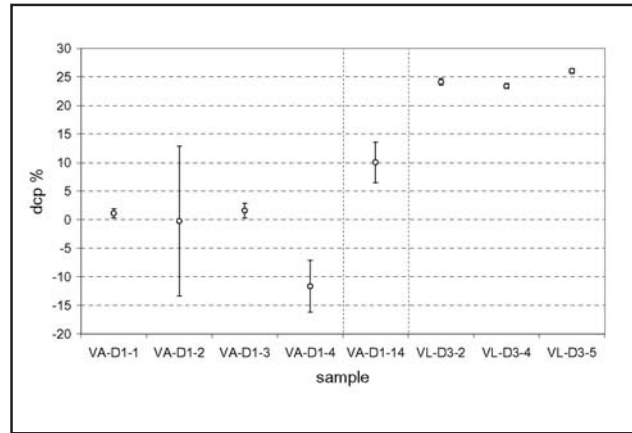


Fig. 6. Dead carbon proportions (dcp %) of dated subsamples from VA-D1 and VL-D3 speleothems.

effect of water-soil-rock interaction has on ^{14}C data of the carbonate encrustation (subsamples 1, 2 and 3). The negative proportion of dead carbon recorded by subsample 4 is not statistically different from that of other subsamples. Consequently, no consideration on the addition of modern carbon from organic matter to the porous structure of outermost layers of this overgrowth can be advanced and documented.

Values of percent dead carbon proportion calculated from speleothems VL-D3 are very constant and the pooled mean is 24.61 ± 0.25 . This mean value is significantly higher than that obtained for POS VA-D1. Our results approach the range in dcp of 10-20 % reported by Bastin & Gewalt (1986), Holmgren et al. (1994), Genty et al. (1998) and Beck et al. (2001) for Holocene and Pleistocene speleothems from different parts of the world.

The values of dcp confirm a stronger water-soil-rock interaction of precipitating water in Cova des Pas de Vallgornera compared to Cova de Cala Varques A. A longer residence time of percolation water is in turn related to a stronger solute acquisition by karst waters that presumably favoured the precipitation of aragonite instead of calcite at Cova des Pas de Vallgornera. Actually, the precipitation of aragonite was probably promoted by the high magnesium content of precipitating waters, as clearly inferred from the electron microprobe analyses of VL-D3 vadose support (Fig. 5). The intense water-soil-rock interaction caused a strong enrichment in magnesium, which may have inhibited calcite precipitation over the vadose support. This hypothesis agrees with Berner's (1975) experiments, where dissolved magnesium appears to decrease the rate of calcite crystal growth but have no effect on aragonite crystallization.

CONCLUSIONS

U-Th ages of phreatic overgrowths on speleothems from coastal caves of Mallorca (Spain) are increasingly gaining attention from the scientific community because they allow to precisely constraining sea-level changes during the Holocene (Tuccimei et al., 2010) and Late Pleistocene (Vesica et al., 2000; Tuccimei et al., 2006; Dorale et al., 2010).

Here we investigate the potential of these speleothem encrustations to be ^{14}C dated by comparing radiocarbon age results of Holocene speleothems with U-series data. ^{14}C data were not calibrated because the source of carbon is unknown, possibly representing a mixture of carbon from different reservoirs.

The outcomes of ^{14}C ages are strongly site dependent and appear related to the local residence time of water infiltration through the soil and epikarst. When the water transit is fast and has limited interaction with soil and bedrock, as seem to be the case at Cova de Cala Varques A, the so-called "reservoir" effect is negligible and ^{14}C and U-Th ages corresponds within the error range. However, when the residence time is longer (as probably occurs in Cova des Pas de Vallgornera), ^{14}C ages are significantly older, as shown by the high values (25%) of dcp; these data, as well as the $\delta^{13}\text{C}$ composition of speleothems, result quite constant demonstrating the stability of these chemical systems over the last 2,800 years. This investigation provides a first contribution to assess potential problems related to future application of radiocarbon dating to speleothem overgrowths (POS) studies. Environmental implications concerning water-soil-rock interaction processes, climatology and hydrology in coastal karst systems are suggested.

In conclusion, it is worth noting that studies on POS chronology based on ^{14}C dating should be integrated with investigation on trace elements distribution along growth profiles of vadose supports in order to collect information on the interaction among the freshwater component of precipitating solutions, the soil and the epikarst. Abundances and correlations among elements could provide further evidence of longer residence time and possible incorporation of dead carbon.

This study shows that the use of radiocarbon dating in generating POS chronologies is promising, but in some situations still problematic, whereas U-Th dating remains the best approach to study these speleothem encrustations.

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REFERENCES

- Bastin B. & Gewalt M., 1986 - *Analyse pollinique et datation ^{14}C des concrétions stalagmitiques Holocènes: Apports complémentaires des deux méthodes.* Géographie Physique et Quaternaire, **40**: 185-196.
- Beck J.W., Richards D.A., Edwards R.L., Silverman B.W., Smart P.L., Donahue D.J., Herrera-Osterheld S., Burr G.S., Calsoyas L., Jull A.J.T. & Biddulph D., 2001 - *Extremely large variations of atmospheric ^{14}C concentration during the last glacial period.* Science, **292**: 2453-2458.
- Berner R.A., 1975 - *The role of magnesium in the crystal growth of calcite and aragonite from sea water.* Geochimica et Cosmochimica Acta, **39**: 489-494.
- Cheng H., Edwards R.L., Hoff J., Gallup C.D., Richards D.A. & Asmero Y., 2000 - *The half-lives of uranium-234 and thorium-230.* Chemical Geology, **169**: 17-33.
- Dorale J.A., Onac B.P., Fornós J.J., Ginés J., Ginés A., Tuccimei P. & Peate D.W., 2010 - *Sea level high stand 81,000 years ago in Mallorca.* Science, **327**: 860-863.
- Fairchild I.J., Borsato A., Tooth A., Frisia S., Hawkesworth C.J., Yiming H., McDermott F. & Spiro B., 2000 - *Control on trace elements (Sr-Mg) compositions of carbonate cave water: implications for speleothem climatic records.* Chemical Geology, **166**: 255-269.
- Fleitmann D., Burns S.J., Mangini A., Mudelsee M., Kramers J., Villa I.M., Neff U., Al-Subbary A.A., Buettner A., Hippler D. & Matter A., 2007 - *Holocene ITCZ and Indian monsoon dynamics recorded in stalagmites from Oman and Yemen (Socotra).* Quaternary Science Reviews, **26**: 170-188.
- Fornós J.J. & Gelabert B., 1995 - *Lithology and tectonics of the Mallorcan karst.* In: Ginés A. & Ginés J. (Eds.) - *Karst and Caves of Mallorca*, Endins, **20**: 27-43.
- Fornós J.J., Ginés A., Ginés J., Gràcia F., Merino A., Cifre J. & Hierro F., 2010 - *Hypogene speleogenetic evidences in the development of Cova des Pas de Vallgornera (Mallorca island, western Mediterranean).* In: Andreo B., Carrasco F., Durán J.J. & LaMoreaux J.W. (Eds.) - *Advances in Research in Karst Media.* Springer-Verlag: 349-354.
- Gelabert B., Sàbat F. & Rodríguez-Perea A., 1992 - *An structural outline of the Serra de Tramuntana of Mallorca (Balearic Islands).* Tectonophysics, **203**: 167-183.
- Genty D., Vokal B., Obelic B. & Massault M., 1998 - *Bomb ^{14}C time history recorded in two modern stalagmites - importance for soil organic matter dynamics and bomb ^{14}C distribution over continents.* Earth Planetary Science Letters, **160**: 795-809.
- Genty D., Massault M., Gilmour M., Baker A., Verheyden S. & Keppens E., 1999 - *Calculation of past dead carbon proportion and variability by the comparison of AMS ^{14}C and TIMS U/Th ages on two Holocene stalagmites.* Radiocarbon, **41** (3): 251-270.
- Ginés J., Ginés A., Fornós J.J., Merino A. & Gràcia F., 2009 - *On the role of hypogene speleogenesis in shaping the coastal endokarst of southern Mallorca (Western Mediterranean).* In: Klimchouk A.B. & Ford D.C. (Eds.) - *Hypogene Speleogenesis and Karst Hydrogeology of Artesian Basins.* Ukrainian Institute of Speleology and Karstology, Special Paper **1**: 91-99.
- Ginés J., Ginés A. & Pomar L., 1981 - *Morphological and mineralogical features of phreatic speleothems occurring in coastal caves of Majorca (Spain).* Proc. of 8th International Congress of Speleology, Bowling Green, USA, **2**: 529-532.
- Goslar T., Hercman H. & Pazdur A., 2000 - *Comparison of U-series and radiocarbon dates of speleothems.* Radiocarbon, **42** (3): 403-414.
- Hendy C.H., 1970 - *The use of ^{14}C in the study of cave processes.* Twelfth Symposium Radiocarbon Variations and Absolute Chronology. Almqvist and Wiksell, Stockholm and Wiley and Sons, New York: 419-443.

- Holmgren K., Lauritzen S.E. & Possnert G., 1994 - $^{230}\text{Th}/^{234}\text{U}$ and ^{14}C dating of a Late Pleistocene stalagmite in Lobatse II Cave, Botswana. *Quaternary Science Reviews*, **13**: 111-119.
- Ludwig K.R., 2003 - *Using Isoplot/Ex, version 3. A geochronological toolkit for Microsoft Excel*. Berkeley Geochronology Ctr. Spec. Pub, **4**.
- Nadeau M.-J., Grootes P.M., Schliecher M., Hasselberg P., Rieck A. & Bitterling M., 1998 - *Sample throughput and data quality at the Leibniz-Labor AMS facility*. *Radiocarbon*, **40**: 239-245.
- Pomar L., Ginés A & Ginés J., 1979 - *Morfología, estructura y origen de los espeleotemas epiacuáticos*. *Endins*, **5/6**: 3-17.
- Reimer P.J., Baillie M.G.L., Bard E., Bayliss A., Beck J.W., Blackwell P.G., Bronk Ramsey C., Buck C.E., Burr G.S., Edwards R.L., Friedrich M., Grootes P.M., Guilderson T.P., Hajdas I., Heaton T.J., Hogg A.G., Hughen K.A., Kaiser K.F., Kromer B., McCormac F.G., Manning S.W., Reimer R.W., Richards D.A., Southon J.R., Talamo S., Turney C.S.M, van der Plicht J. & Weyhenmeyer C.E., 2009 - *IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP*. *Radiocarbon*, **51 (4)**: 1111-1150.
- Stuiver M. & Polach H., 1977 - *Reporting ^{14}C data*. *Radiocarbon*, **19 (3)**: 355-365.
- Tuccimei P., Ginés J., Delitala M.C., Ginés A., Gracia F., Fornós J.J. & Taddeucci A., 2006 - *Last interglacial sea level changes in Mallorca island (Western Mediterranean). High precision U-series data from phreatic overgrowth on speleothems*. *Zeitschrift für Geomorphologie*, **50**: 1-21.
- Tuccimei P., Soligo M., Fornós J.J., Ginés A., Ginés J., Onac B.P. & Villa I.M., 2009 - *Precipitation of phreatic overgrowths at the water table of meteoric-marine mixing zones in coastal cave systems: a useful tool in sea level change reconstruction*. In: White W.B. (Ed.), *Proc. of 15th International Congress of Speleology*, Kerrville, USA, symposia, part 1: 554-560.
- Tuccimei P., Soligo M., Ginés J., Ginés A., Fornós J., Kramers J. & Villa I.M., 2010 - *Constraining Holocene sea levels using U-Th ages of phreatic overgrowth on speleothems from coastal caves in Mallorca (Western Mediterranean)*. *Earth Surface Processes and Landforms*, **35**: 782-790.
- Van Strydonck M. & Van der Borg K., 1990-91 - *The construction of a preparation line for AMS-targets at the Royal Institute for Cultural Heritage Brussels*. *Bulletin Kon. Inst. v. h. Kunstpatrimonium*, **23**: 228-234.
- Vesica P., Tuccimei P., Turi B., Fornós J.J., Ginés A. & Ginés J., 2000 - *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)*. *Quaternary Science Reviews*, **19**: 865-879.
- Vogel J.C. & Kronfeld J., 1997 - *Calibration of radiocarbon dates for the late Pleistocene using U/Th dates on stalagmites*. *Radiocarbon*, **39**: 27-32.
- Wedepohl K.H., 1995 - *The composition of the continental crust*. *Geochimica Cosmochimica Acta*, **59**: 1217-1239.
- Wigley T.M.L., Plummer L.N. & Pearson F.J., 1978 *Mass transfer and carbon isotope evolution in natural waters systems*. *Geochimica Cosmochimica Acta*, **42**: 1117-1140.