

# Characteristics of cryogenic carbonates in a Pyrenean ice cave (northern Spain)

## Caracterización de carbonatos criogénicos en una cueva helada del Pirineo

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### ABSTRACT

We provide micromorphological, isotopic and chronological data on cryogenic cave carbonates (CCC) from Sarrios-6 ice cave (2780 m a.s.l.) in the Monte Perdido Massif (central Pyrenees). It is the first report of such speleothems on the Iberian Peninsula. Millimeter-sized white skeletal calcite rhombohedrons overgrown by brown rhombohedral crystals are present within a perennial ice body. The morphology of two carbonate generations suggests an early stage of fast carbonate precipitation followed by a second phase formed at a slower precipitation rate. The two generations show distinct isotopic compositions (skeletal cores: mean  $\delta^{13}\text{C} = 4.8\text{‰}$ , mean  $\delta^{18}\text{O} = -20.8\text{‰}$ ; overgrowths: mean  $\delta^{13}\text{C} = 5.3\text{‰}$ , mean  $\delta^{18}\text{O} = -21.3\text{‰}$ ). A preliminary radiocarbon date of a seed found in the same ice layer suggests that the precipitation of CCC likely occurred during the Medieval Climate Anomaly.

**Key-words:** Cryogenic cave carbonate, ice cave, Medieval Climate Anomaly, Pyrenees.

### RESUMEN

Se aportan datos micromorfológicos, isotópicos y cronológicos de carbonatos criogénicos CCC de la cueva helada Sarrios-6, situada a 2780 m s.n.m. en el macizo de Monte Perdido (Pirineo central). Es el primer estudio de este tipo de espeleotemas en la Península Ibérica. En una masa de hielo aparecen cristales romboédricos de calcita de tamaño milimétrico constituidos por un núcleo interno de cristales esqueléticos rodeados por un crecimiento externo de color pardo-rojizo. Indican una fase rápida inicial de precipitación de calcita y otra posterior más lenta. Los dos tipos de calcita presentan composición isotópica diferente (núcleo: valor medio de  $\delta^{13}\text{C} = 4,8\text{‰}$  VPDB, valor medio de  $\delta^{18}\text{O} = -20,8\text{‰}$  VPDB; crecimiento externo: valor medio de  $\delta^{13}\text{C} = 5,3\text{‰}$  VPDB, valor medio de  $\delta^{18}\text{O} = -21,3\text{‰}$  VPDB). La datación de una semilla incluida en la masa de hielo indica que la formación de la CCC tuvo lugar durante la Anomalía Climática Medieval.

**Palabras clave:** Carbonato criogénico, cueva helada, Anomalía Climática Medieval, Pirineos.

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### Introduction

The cryogenic cave carbonates (hereafter CCC) are a specific type of speleothems formed by the segregation of solutes during freezing of mineralized karst waters in ice caves (e.g., Žák *et al.*, 2008). CCC occurs in ice cave as fine-grained powder or as coarse (millimeter- to centimeter-sized) crystals aggregates. These two types of CCC form in different environments and are characterized by distinct isotopic signatures (Žák *et al.*, 2008). In Europe, research on CCC has been focusing on the central re-

gions (Richter *et al.*, 2013; Žák *et al.*, 2012) and on the Alpine range (Luetscher *et al.*, 2013; Spötl and Cheng, 2014). These carbonates, if radiometrically dated, provide interesting palaeo-environmental information at high latitudes and high-altitude regions subjected to permafrost conditions where other archives are rare.

Sarrios-6 is a cave in the Monte Perdido karstic massif (Central Pyrenees) which is part of the Ordesa and Monte Perdido National Park (Huesca Province, northeastern Iberian Peninsula). The cave hosts remnants of congelation ice deposits (Luetscher and

Jeannin, 2004) containing cryogenic carbonates. Here, we report the first micromorphological, isotopic and chronological data of CCC from the Spanish mountains. These insights allow exploring the origin and environmental significance of these peculiar speleothems.

### Study area

Sarrios-6 is located at 2780 m a.s.l. (42° 41' 9" N, 0° 1' 32" W, geographic coordinates) (Fig. 1A). The cave has two main entrances at the foot of the Faja de los Sarrios,

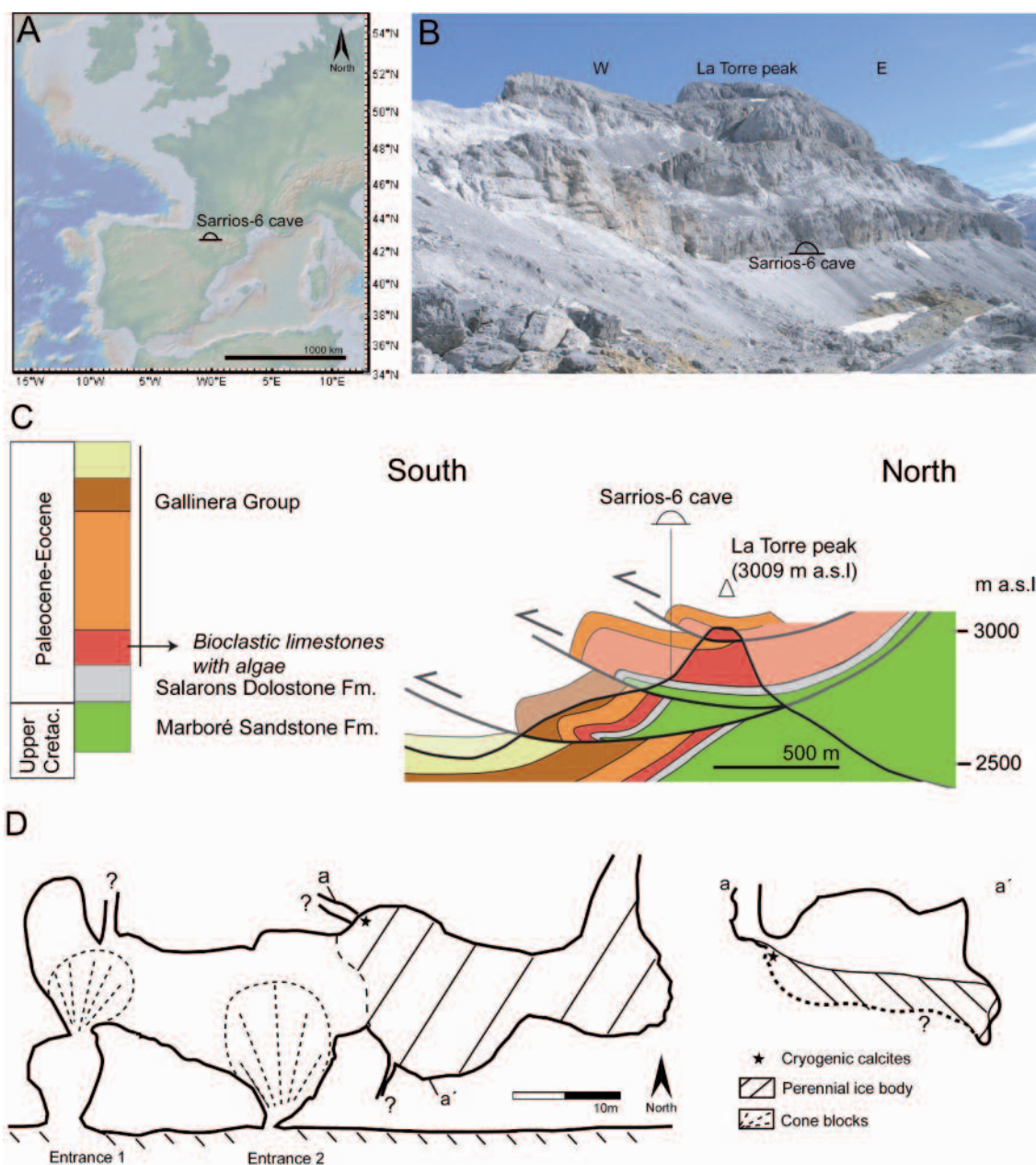


Fig. 1.- Location of the Sarrios-6 ice cave in the Central Pyrenees (A), cave entrance at the base of the Sarrios rock cliff (B), geological cross-section (C) and plan view and longitudinal section of the cave showing the location of the ice deposits and cryogenic carbonates (D).

Fig. 1.- La cueva helada Sarrios-6. Localización en los Pirineos centrales (A), entrada de la cueva en la Faja de los Sarrios (B), corte geológico (C) y planta y sección de la cueva con la posición del hielo y los carbonatos criogénicos (D).

a west-east facing rock cliff (Fig. 1B) made of bioclastic limestones of Paleocene age. These rocks constitute the basal unit of the Gallinera Group (Robador, 2005) integrated in the Larra-Monte Perdido fold and thrust system (Pyrenean Internal Sierras) (Teixell, 1992) striking WNW-ESE and thrusting towards the South (Fig. 1C). Bedding is slightly tilted towards the North and the bedrock is affected by a closely spaced cleavage striking WNW-ESE and tilted to the North (40-50°). Sarrios-6 cave shows a west-east trending main gallery with sev-

eral north-south passages (Fig. 1D). Some old phreatic dissolution features are preserved and breakdown deposits and cryoclasts are very abundant. Besides, some congelation ice is present which contains CCC.

### Methodology

Field work carried out in Sarrios-6 cave included a geological and geomorphological survey of the cave, a description of the ice bodies and CCC sampling. Micromor-

phological observations of CCC were done using a binocular microscope and by scanning electron microscopy (JEOL JSM 6400). Samples for stable isotope analyses were handpicked using a binocular microscope, measured using isotope ratio mass spectrometry and the results are reported on the VPDB scale with an analytical precision of 0.06 and 0.08‰ for  $\delta^{13}C$  and  $\delta^{18}O$ , respectively (Spötl and Vennemann, 2003). A seed found in the cave ice was radiocarbon-dated at the Laboratory of Direct AMS Radiocarbon Dating System of Seattle (USA).

The INTCAL13 calibration curve (Reimer *et al.*, 2013) was used to calibrate the age.

## Results

Ice in the Sarrios-6 cave occurs as bodies partially filling some passages and covering the floor of the main gallery. The origin of the ice seems to be related to the freezing of infiltrated water in cave pools. The ice body hosting the CCC is a side-wall slab 3.5 m thick and 4 m wide, attached to the bedrock. Most of the ice is banded and laminated but unconformities are also present. The sampled CCC occurs as loose crystals, concentrated in a patch located within a 80 cm-thick layer in the ice body (Fig. 2A). A plant seed (mm-sized) was sampled within this unit for radiocarbon dating.

### Micromorphological features

In this reconnaissance study we focus on one type of CCC, i.e. rhombohedral crystals up to 4 mm in diameter, which are composed of a core and an outer zone. The core consists of fragile, skeletal and porous rhombohedral crystals aggregates which are creamy to orange colored and up to 1.5 mm in size (Figs. 2B and 2C). These cores are overgrown by brownish-orange crystals showing rhombohedral growth steps (Figs. 2B and 2C).

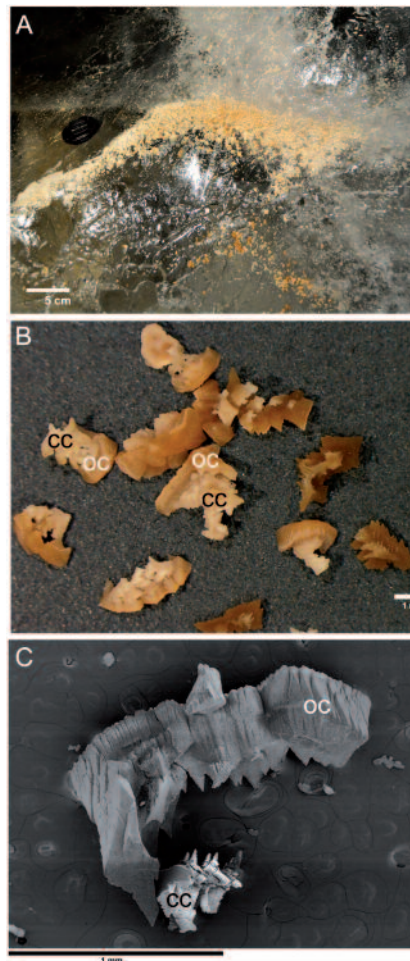
### Isotopic data

The two generations of three CCC<sub>coarse</sub> crystals were separated for the isotopic analysis. The skeletal cores show mean  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of 4.8‰ and -20.8‰, respectively, slightly different from the overgrowths whose values are 5.3‰ and -21.3‰, respectively.

The overgrowths are enriched in  $^{13}\text{C}$  and depleted in  $^{18}\text{O}$  with respect to the cores (Fig. 3). These compositions fall within the range of published data CCC<sub>coarse</sub> elsewhere (Žák *et al.*, 2012).

### Chronology

A plant seed found within the ice body in the same stratigraphic level yielded a radiocarbon date of  $783 \pm 23$  BP (1149-1177 cal AD; 2-sigma range; laboratory code D-AMS 008324). Assuming that the seed is



**Fig. 2.- Occurrence of cryogenic calcites in Sarrios-6 ice cave. Patch of cryogenic calcites within the ice (A) and rhombohedral morphologies of cryogenic carbonate crystals seen under binocular microscope (B) and SEM (C). cc: core crystals (in fact they are probably crystal aggregates, not single crystals); oc: overgrowth crystals.**

*Fig. 2.- Carbonatos criogénicos de la cueva helada Sarrios-6. Masa de carbonato criogénico dentro de la masa de hielo (A) y morfologías romboédricas de cristales de carbonato criogénico vistos en la lupa binocular (B) y en el SEM (C). cc: cristales centrales; o: cristales externos.*

approximately of the same age as the ice in which it was embedded, CCC formed during the Medieval Climate Anomaly (MCA).

## Discussion

### Formation of cryogenic cave carbonate

Coarse CCC is linked to slow freezing of cave water pools enclosed in the ice (Žák *et al.*, 2008; Spötl and Cheng, 2014). Although the crustal morphology and isotopic composition of the CCC<sub>coarse</sub> from the Sar-

rios-6 cave are consistent with those from other CCC occurrences in Europe, the Spanish samples exhibit some interesting details with respect to their two step growth: the skeletal crystals of the core formed at a rather high growth rate, as suggested by the predominance of edges and vertices. During a second growth phase, the overgrowths formed at a slower growth rate.

The isotope composition of the two calcite generations is consistent with a two-stage evolution, whereby the second phase is slightly depleted in  $^{18}\text{O}$  and enriched in  $^{13}\text{C}$  compared to the first one. The shift towards higher  $\delta^{13}\text{C}$  and lower  $\delta^{18}\text{O}$  values during the freezing of water and subsequent CCC precipitation has been previously observed in isotopic profiles across individual CCC<sub>coarse</sub> crystals (Žák *et al.*, 2004; Luetscher *et al.*, 2013). In our case, the isotopic difference between the two phases is small, which suggests that the two growth phases were closely related.

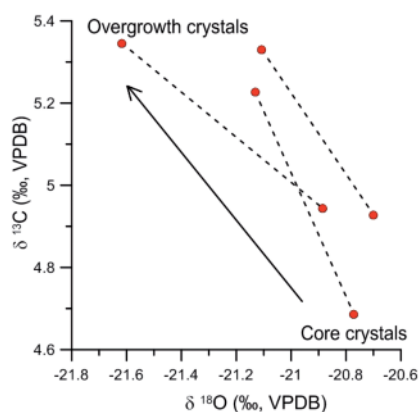
### Palaeoclimatic conditions

According to the radiocarbon age, the ice containing CCC in the Sarrios-6 ice cave likely accumulated during the MCA. This period was characterized by warm and arid climatic conditions in the Mediterranean side of Iberian Peninsula (Moreno *et al.*, 2012). In the Pyrenees, melting of the winter snow above the caves allowed water to infiltrate into the karst system. The low temperatures inside the cave favored the freezing of seepage water leading the accumulation of ice and, eventually, the precipitation of CCC. In Alpine ice caves, CCC<sub>coarse</sub> has been assigned to relative warm temperatures during the Medieval Warm Period and the Roman Warm Period (Luetscher *et al.*, 2013) but also to lower temperatures at the onset of the Little Ice Age (Spötl and Cheng, 2014).

## Conclusions

Preliminary insights into cryogenic calcites from Sarrios-6 ice cave (central Pyrenees) based on micromorphological, isotopic and chronological data can be summarized as follows:

a) CCC<sub>coarse</sub> crystals composed of a skeletal core and brown overgrowths were found in situ in the layered ice. These petro-



**Fig. 3.- Stable isotopic composition of cryogenic carbonates in Sarríos-6 ice cave.**

*Fig. 3.- Composición isotópica del carbonato criogénico de la cueva helada Sarríos-6.*

graphic features point to a two-stage growth at slightly different precipitation rates.

b) This two-stage formation is also supported by the isotopic composition of the two calcite generations, reflecting the isotopic fractionation observed during the freezing of water and associated precipitation of CCC<sub>coarse</sub>.

c) According to a radiocarbon date of a seed found in the same ice layer, these processes occurred at the end of the MCA coinciding with a climatic amelioration that likely favored the infiltration of water into the Sarríos-6 cave and the subsequent re-freezing leading to the precipitation of CCC.

To our knowledge it is the first report of CCC<sub>coarse</sub> from a cave in the Pyrenees.

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