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Speleothems in karstic caves beneath paleoglaciers in the Central Pyrenees

Espeleotemas en cuevas kársticas bajo paleoglaciares en el Pirineo Central

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ABSTRACT

We explore the potential of various caves and karst systems of the Central Pyrenees (Lecherines-Collarada-Monte Perdido-Escuaín-Vignemale-Cotiella-Aneto-Maladeta) that could host speleothems that grew in karstic caves under glaciated areas. The requirements for the formation of speleothems in caves under areas covered by ice are: i) warm-based glaciers and ii) the presence of sulfides in the host rock. Springs and drip water were analysed to measure the presence of sulfates. Also, the presence of gypsum speleothems, pyrite, or other sulfides in the caves has been explored. Speleological observations, geological descriptions, and hydrochemical analyses have allowed the identification of caves and karst systems that may host these types of subglacial cave speleothems.

Key-words: *Glaciation, Speleothem, Sulfur, Pyrenees, cave.*

RESUMEN

Se explora el potencial de diferentes cuevas y sistemas kársticos localizados en el Pirineo Central (Lecherines-Collarada-Monte Perdido- Escuaín- Vignemale- Cotiella- Aneto-Maladeta) que podrían albergar espeleotemas que crecieron en cuevas karsticas bajo glaciares. Los requisitos para la formación de espelotemas en cuevas subglaciares son: i) glaciares de base cálida y ii) la presencia de sulfuros en la roca encajante. Se analizaron aguas de surgencias y goteos para medir la presencia de sulfatos. Además, se exploró la presencia de espeleotemas de yeso, piritas u otros sulfuros en las cuevas. Las observaciones espeleológicas, así como las descripciones geológicas, y los análisis hidroquímicos han permitido reconocer cuevas y sistemas kársticos que pueden albergar este tipo de espeleotemas subglaciares.

Palabras clave: *Glaciación, Espeleotema, Azufre, Pirineos, Cueva.*

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Introduction

The formation of speleothems in caves is generally associated with humid and warm conditions when soil development and vegetation growth over the caves are common. This process results in the acidification of water (due to soil CO_2) that percolates through the soil, leading to the dissolution of carbonate rocks (Carbonic Acid Dissolution, CAD). Once this carbonate-saturated water reaches the cave, it degasses into the cave atmosphere, resulting in the precipitation of carbonate that forms speleothems. However, speleothem formation can also occur in the complete absence of soil and vegetation. This is the case for speleothems formed in caves beneath glaciers (e.g. Castleguard Cave, Canada; Gascoyne and Nelson, 1983). The requirements for these speleothems formation and preservation are: i) warm-based glaciers, ii) cave galleries relatively protected from glacial meltwater floods that could destroy the speleothems, and iii) the presence of sulfur (e.g., pyrites) disseminated in the carbonates where the cave develops (Spötl et al., 2024). The presence of glaciers can inhibit the formation of permafrost by insulating the rock from cold atmospheric conditions during the glacial periods. On the other hand, warm-based glaciers provide liquid water that interacts with the carbonate rocks. This subglacial water infiltrates through the bedrock, and when sulfides are present (e.g. pyrite) can oxidate to form sulfuric acid, which dissolves the carbonate rocks (Sulfuric Acid Dissolution, SAD), potentially saturating the waters with carbonate and subsequently forming speleothems when entering the caves and CO_2 degassing occurs. The oxidation reaction of sulfides (e.g., pyrite) and the dissolution of carbonate rock are defined by the equations (1) and (2) (Taylor and Wheeler, 1993):

(1) $4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3- + 8H_2SO_4$
(2) $2Ca_xMg_{(1-x)} + CO_3 + H_2SO_4 \rightarrow 2_xCa^{2+} + 2_{(1-x)}Mg^{2+} + 2HCO_3^- + SO_4^{2-}$

The first observations of speleothem growth in a cave beneath a glacier were made in Castleguard Cave, located in Banff National Park, Rocky Mountains, Canada. This cave is partially covered by the Columbia Icefield. In this cave, the primary process identified as responsible

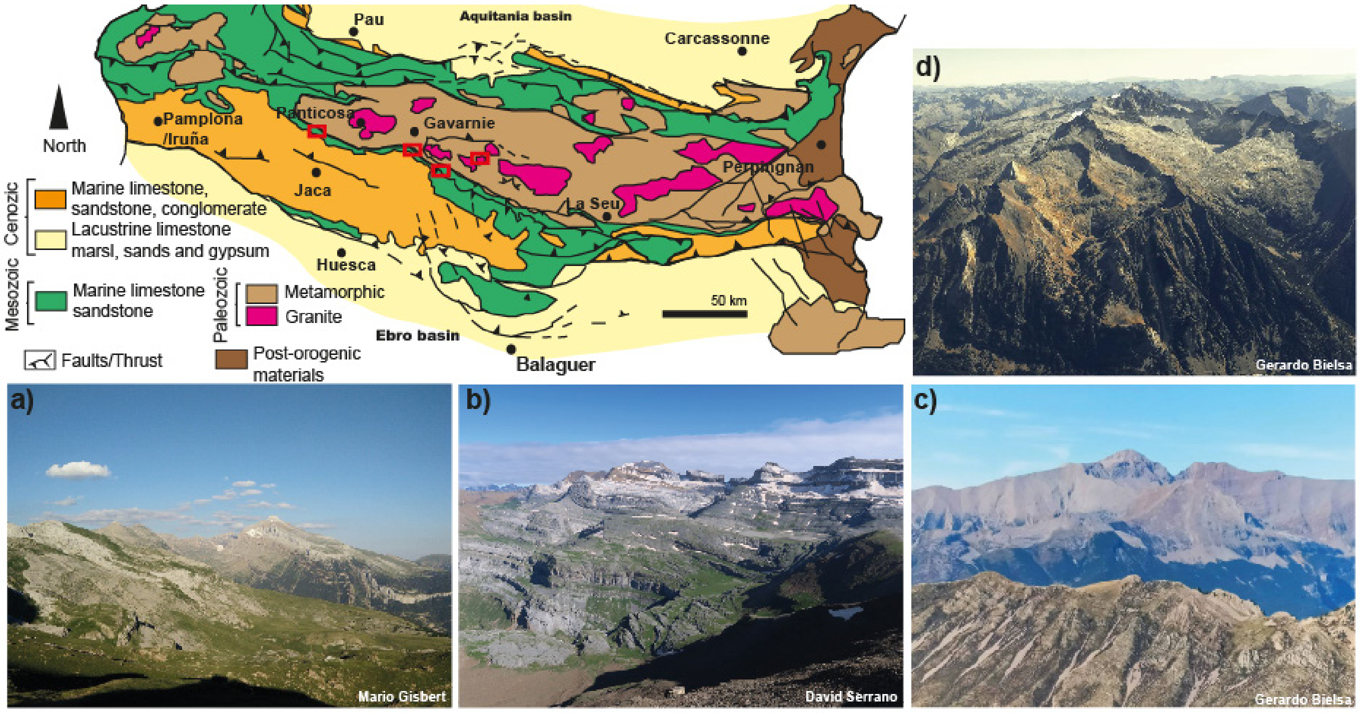

Fig. 1.-Simplified geological map of the Pyrenees, study areas (red rectangles) and photos of the study areas (partial views of a, Lecherines and Collarada massif; b, Monte Perdido massif c, Cotiella massif and d, Aneto-maladeta massifs). Detailed information on the geology of each massif can be found in sheets 144, 145, 146, 147, 179, 180, and 212 on http://info.igme.es/cartografiadigital/geologica/Magna50.aspx. See the color figure in the web version.

Fig. 1.- Mapa geológico simplificado del Pirineo, zonas de estudio (rectángulos rojos) y fotografías de las áreas de estudio (vistas parciales de a, macizo de Lecherines y Collarada; b, macizo de Monte Perdido c, macizo de Cotiella y d, macizo de Aneto-Maladeta). La informacion detalla de la geología de cada macizo puede consultarse en las hojas 144, 145, 146, 147, 179, 180 y 212 en http://info.igme.es/cartografiadigital/geologica/Magna50.aspx. Ver la figura en color en la versión web.

for speleothem deposition is oxidation of pyrite. In certain rock units, macroscopic pyrite crystals and small nodules (concretions) have been observed (Atkinson, 1983), along with secondary sulfate minerals, like gypsum (Harmon et al., 1983). In the Alps, Spötl et al., (2024) and references therein, have reported stalagmite growth in several caves during glacier stages, iincluding Marine Isotope Stages (MIS) 2, 3, 4, 6, 8, 10 and 12. These speleothems show considerably high $\delta^{13}C$ values (e.g. >0 ‰) compared to conventional speleothems (e.g. -5 to – 10 ‰), in the range of $\delta^{13}C$ carbonate values of the host rock (e.g. Skiba et al., 2023; Spötl et al, 2024). These kind of subglacial cave speleothems represent the unique potential high resolution paleoclimate archives during glacial stages in continental areas, where most of the speleothems show hiatus related to the decline of vegetation and/or dry conditions.

Like in the Alps, karstic areas in the Central Pyrenees have been strongly glaciated during the Quaternary, with the maximum ice extension during the MIS 4 in the Last Glacial Cycle (LGC) (e.g. Lewis et al., 2009, García-Ruíz et al., 2013; Bartolomé et al., 2021).

Here, we explore potential speleothems formed in subglacial karstic caves in the Central Pyrenees (Fig. 1). We conducted a review of previous publication about the regional geology, the presence of sulfides in the host rock and related gypsums speleothems, explored the limits of the area of Pyrenean glaciations, and carried out hydrochemical analyses of springs from different caves and karstic systems in the Central Pyrenees (Lecherines and Collarada massifs, Monte Perdido, Escuaín and Vignemale massifs, and Cotiella and Aneto-Maladeta massifs) (Fig. 1) in order to find evidence for sulfide oxidation.

Study site

The Pyrenees is a N100º trending orogen due to the collision of the Iberian and European plates from late Cretaceous to Early Miocene. On the north side, the North Pyrenean Zone is a narrow north-verging fold and thrust belt. In the axis of the orogen, the Axial Zone is made of Paleozoic rocks structured in an antiformal stack of different thrusts. Finally, to the south, the South Pyrenean Zone is made of a wide system of south-verging thrusts. All these different geological units contain in some extent limestone massifs or outcrops. The main ones are those included in the Axial Zone (mostly Devonian and Carboniferous in age) and the South Pyrenean Zone (with limestones from Cretaceous to Eocene). The main calcareous massifs and outcrops in the Central Pyrenees reach altitudes over 2500 and up to 3355 m a.s.l., due to the stacking of several thrusts. The sulfate formations (e.g Keuper), which in the case of the Pyrenees act as a detachment level for thrusts at the base of the chain, are not interbedded with the carbonate formations. This leads to a conjunction of factors favourable to karst development: limestone intensely affected by folds and faults, high altitude and an important supply of water coming both from direct precipitations and snow melting.

Methods

Geological maps were revised focussing on the description of carbonate formations with the presence of disseminated sulfides (e.g., pyrite, chalcopyrite). Additionally, caving reports and previous studies documenting the presence of oxidation stains, pyrites, or sulfate speleothems were reviewed. Samples of cave drip water, river water, and springs were analysed for major ions using ion chromatography at the Pyrenean Institute of Ecology (Zaragoza) laboratories. Carbonate alkalinity was determined by titration within 24 hours after sampling.

Results and discussion

Lecherines and Collarada massifs

The caves and karstic systems are open in Paleocene and Eocene materials (Fig. 1a). Water samples from the springs draining both massifs (Güixas and Esjamundo springs) show low sulfate concentrations (1.9 – 5.4 mg/l). However, the presence of gypsum speleothems, as well as calcite speleothems in some areas, has been reported in a number of galleries in both massifs (Barbier, 1970; Cuchí et al., 2012). Cuchí et al., (2012) suggested the most plausible origin of gypsum by sulfide oxidation in Lecherines system. These massifs were glaciated several times since MIS 8 (García-Ruíz et al., 2013).

Monte Perdido, Escuaín and Vignemale massifs

Most caves and systems open in Paleocene-Eocene materials in the Monte Perdido and Escuain massifs, while in Vignemale, Devonic limestones and impermeable materials comprise the bedrock (Fig. 1b). In Bujaruelo Valley (Monte Perdido-Vignemale), the Granito cave (1270 m a.s.l) shows a wide presence of speleothems. The river water inside the cave and dripwater, show low sulfate concentration (2.1 - 4.8 mg/l). Stalagmite growth between 153 to 130 ka, during MIS 6, MIS 5 and Holocene has been reported for this cave (Bartolomé et al. 2021). In Devaux cave (France-Spain border), located at 2836 m a.s.l in the Monte Perdido massif, and within the mountain permafrost, a recent study by Bartolomé et al. (2023) reveals the presence of high sulfate concentrations in the water (5.1-269.3 mg/l), both in drips and cave river. $\delta^{34}S$ analysis (-11.9 to -28.5 ‰ VCDT (Vienna Canyon Diablo troilite), Bartolomé et al., 2023) suggest the sulfur originates from pyrite (visible at naked eye in the host rock) oxidized by water circulation through the bedrock. Additionally, cryogenic cave gypsum has been reported in this cave (Bartolomé et al., 2023). From the middle to its innermost sector, conventional speleothems have been found. In the Escuaín massif, Las Fuentes de Escuaín karstic system (40 km of development and -1150 m depth) many galleries show gypsum fibres and conventional carbonate speleothems. The analysis of water from the main spring of the system (B1) show low sulfate concentration (2.2-12.8 mg/l).

Recently, new caves decorated with speleothems have been discovered in areas above ~2900 m a.s.l in the Monte Perdido massif. These caves were covered by glaciers during the Last Glacial Cycle (e.g. Sancho et al., 2018; Bartolomé et al., 2021) and during the Little Ice Age until recent years, as suggested by historical pictures of both slopes of the Monte Perdido and Vignemale massif. The rapid retreat of the Monte Perdido and Ossoue (Vignemale massif) glaciers because of the current climate warming (Martí et al., 2015; Vidaller et al., 2021) offers potential areas for exploring subglacial caves that were covered by ice until recent times. These areas might provide opportunities to study recent and past subglacial cave speleothem formation, if speleothems are present.

Cotiella and Aneto - Maladeta massifs

Caves in Cotiella massif open mainly in Upper Cretaceous limestone (Baziero Fm), which usually pyrite is present (Fig. 1c). In some caves (e.g. Espluga Lasgüériz, Pot au Feu and Brujas, all of them developed beneath a vast glaciar cirque) gypsum crusts and flowers are abundant in some galleries (Fig. 2a, b). The dripwaters in Espluga Lasgüériz show intermediate sulfate concentration (27.17 - 73.02 mg/l, Belmonte-Ribas 2014) compared with the other cave systems survey in this study. $\delta^{34}S$ analysis in sulfate formations (-23.8 to -26.3 ‰ VCDT, Belmonte-Ribas 2014) suggest the sulfur originates from pyrite. Moreover, speleothem growths were reported at 190-184 ka at the beginning of MIS 6 by Belmonte-Ribas and Sancho (2012). In Aneto- Maladeta massif, the Alba cave opens in Carboniferous marble limestone which is in contact with the Maladeta batholith (Fig. 1d). The cave shows well-developed speleothems, and

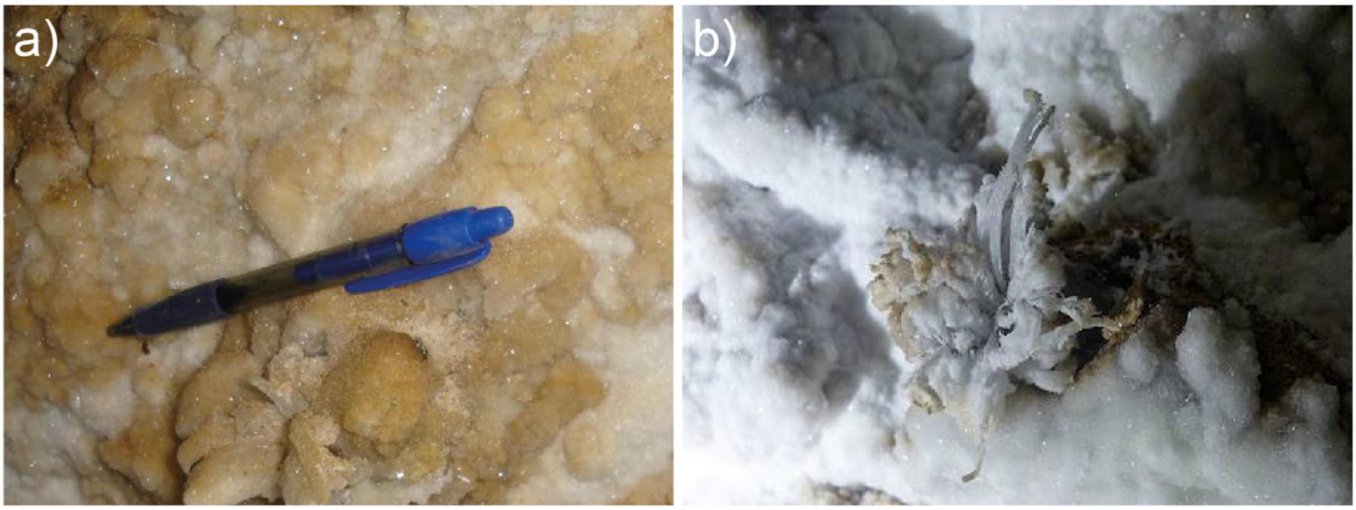

Fig. 2.-a) Gypsum crusts in the Espluga Lasgüériz. b) Gypsum flower in the Brujas cave at -920 m deep (foto: ACEC). See the color figure in the web version.

Fig. 1.- a) Revestimiento de yeso en la Espluga Lasgüériz. b) Flor de yeso en la cueva de las Brujas a -920 m de profundidad (foto: ACEC). Ver la figura en color en la versión web.

the area was strongly glaciated at least since MIS 4 (e.g. Vidaller et al., 2024).

Conclusions and future work

We have identified potential caves that may host speleothems formed beneath paleoglaciers in the Central Pyrenees. This area and cave/systems exhibit favourable conditions, such as have been affected by glaciers in the past, the presence of pyrite in the host rock and/or gypsum speleothems, as well as conventional carbonate speleothems. Altogether, it suggests the possibility to found speleothems formed during known glacial periods or older than those recognised in the Pyrenees. Future work will focus on the dating and isotopic analysis ($\delta^{18}O$, $\delta^{13}C$, $\delta^{34}S$) of speleothems, both carbonate and gypsum, to discern between presence of glaciers or vegetation, and the origin of S. The extraction of gypsum hydration water from gypsum speleothems, and fluid inclusions of carbonate speleothems will provide the original composition infiltration water (e.g. glacial meltwater), with paleoclimate implications.

Author contribution

Original draft and figures: MBa; Fieldwork: MBa, ÁB-R, RG, GC, MBi, AM. Reviewing and editing: ÁB-R, RG, MBi, GC, AM, MBa.

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