

# **Isotopic and Petrographic Evidence as a Proxy** in Paleoclimatic Reconstructions from **Flowstones in Southern Spain**

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#### Abstract

Changes in the morphology and mineralogy of speleothems (flowstones) clearly respond to climate-related phenomena, such as drip rate variability and temperature-modulated cave ventilation. Detailed petrographic observations have been coupled with  $\delta^{18}$ O and  $\delta^{13}$ C values. Fabrics may show changes related to variations in supersaturation, drip rate or input of detrital particles or organic compounds. Fabrics formed under relatively constant and regular drips (columnar compact, open and elongated) show similar  $\delta^{18}$ O and  $\delta^{13}$ C values, which are more negative than those of micrite and microsparite. The combination of internal microstratigraphy studies and isotopic data ( $\delta^{18}$ O and  $\delta^{13}$ C) from two flowstones collected from two caves in the north of Almeria province (SE Spain), suggest a spectrum of environmental conditions ranging from wetter to drier periods. Both records constitute a very useful tool for screening and interpreting high-resolution paleoclimate reconstructions.

## **Keywords**

Speleothems, Flowstones, Fabrics, Isotopic Characterization, Cave, Paleoclimatic Changes

# 1. Introduction

Speleothems have been widely recognized, over the past one to two decades, as

critical archives of terrestrial climate due to their preservation of continuous or semi-continuous climate signals over prolonged periods (centuries to hundreds of thousands of years), absolute and precise date ability, occurrence over a large range of latitudes, and potential preservation of orbital, millennial, decadal, annual, or even sub-annually occurring processes [1].

Speleothem  $\delta^{18}$ O values have been used to track the response of global, regional and local hydroclimate to climate change events, including variation in precipitation amount, changes in the seasonality of precipitation, and shifts in moisture sources and trajectories (e.g. [2] [3] [4] [5]).

Paleoclimatic reconstructions based on isotopic analyses of speleothems can be further improved by supplementing with petrographic and textural studies. The stratigraphic features may indicate under what climatic conditions these materials grew. So as  $\delta^{18}$ O and  $\delta^{13}$ C values reveal changes in temperature, seasonality, and carbonate source, the alternation of fabrics in speleothems reflects climate-related parameters, such as changes in drip rate and degassing [6] [7] [8].

The growth of calcium carbonate speleothems from supersaturated dripwaters is linked via site-specific relationships to several climatic parameters such as temperature and rainfall amount and provenance, making them excellent candidates as highly sensitive natural archives [9] [10]. If a drip has not achieved full equilibrium with respect to gaseous CO<sub>2</sub> (and so not achieved supersaturation either) when it reaches the cave floor/stalagmite, deposition will not begin at the impact point, but will occur after the drip has traveled for a long enough time for equilibrium to occur [11]. The growth of crystals requires nucleation to occur, which always occurs under thermodynamic disequilibrium, as the supersaturation of drip waters with respect to calcium carbonate is a necessary condition for nucleation, and this is a departure from thermodynamic equilibrium as the drip water is no longer of uniform composition. Supersaturation must persist, or nuclei will become unstable and redissolve. The number of nuclei, and consequently the number of crystals increases with increasing supersaturation [6]. Speleothems are expected to grow through "synchronous crystallization", in which each successive growth layer precipitates at almost the same time as the layer before it. Speleothems precipitate as syntaxial overgrowths, in which the c-axis is generally perpendicular to the growth surface [12].

Flowstones are laminated deposits which form on cave floor and walls that accrete roughly parallel to the host surface and may occur tens or hundreds of metres downstream of the water source [13]. They have in common a tendency to display undulations in surface morphology and the lamina structure is dominantly parallel and continuous with a flowing water film that is slightly supersaturated with respect to calcium carbonate [6] or from relatively strong conduit/fissure flows [14]. An advantage for palaeoenvironmental study is that flowstones can be cored with relatively little damage to the cave environment, and they can grow over tens of thousands of years. They are commonly formed of stacked layers of crystals elongated normal to the substrate [6]. Flowstones

often cease to grow during dry and/or cold intervals [15], making them very useful for constraining the timing of glacial to interglacial transitions and of warm events during glacial [16] [17].

Petrographic studies of thin sections by optical microscopy prior to isotopic analyses are also essential to detect diagenetic modifications that may alter the original geochemical signal [8] [14] [18] [19]. If the carbonate in the thin sections does not show significant post-depositional processes, then the speleothem is a suitable candidate for paleoclimatic studies.

This type of work was pioneered in a speleothem-based European Holocene paleoclimate reconstruction [20] that highlighted that certain fabrics, such as dendritic fabric, coincided with systematic shifts to <sup>13</sup>C-enriched calcite. [21] and [22] used microstratigraphic logs and stable isotope time series to find out about glacier mass fluctuations in the Swiss Alps and to distinguish, in speleothems from NE Italy, between hydrologic and hydroclimatic components. [8] proposed a logical system of creating fabric time series from a speleothem microstratigraphic log. Fabrics develop under certain environmental parameters, the most important being fluid flow and presence of impurities, which influence a certain spatial arrangement of crystals with a dominant form. Speleothem fabrics include columnar types, dendritic, micrite, microsparite and mosaic calcite [6]. Their closed crystalline nature also means that speleothems are not usually susceptible to contamination or degradation [10], or other forms of secondary alteration [9], and so are often preserved as relatively pure calcium carbonate [23].

The aim of this study is to combine stable isotopic ( $\delta^{48}$ O and  $\delta^{43}$ C) and petrographic signals of two flowstones from two caves in the north of Almeria province (SE Spain). Both records constitute a very useful tool for screening and interpreting high-resolution paleoclimate reconstructions.

### 2. Geographical and Geological Setting

The studied samples correspond to flowstone type precipitates, whose formation is due to the movement of a sheet of laminar water, which flows on the cavity walls as a consequence of gravity, forming a crust that covers its surface. The samples were extracted in two caves: the cave of Cuartillico del Agua, near El Cerro del Roquez (situated 4 km away from Chirivel), and Sima del Saliente, around La Sierra del Saliente (situated at the western edge of La Sierra de Las Estancias).

Both caves are located in the northern part of the province of Almería, near the border of Granada (Figure 1). The area is characterized by a semi-arid climate, and the average precipitation is about 300 - 350 mm per year. Both caves are formed in dolomites and limestones of the Alpujárride Complex, attributed to the middle-upper Triassic. [24] suggest a gravitational origin for these caves, due to paleo-landslides generated by extensional fractures. Sample extraction was carried out with a rock drill ROY, with a diamond grinding wheel (2 in) and maximal sampling depth of 50 cm. Thick flowstones cover their walls and, in



Figure 1. Geographic location of study areas. Map modified from IBERPIX (http://www.ign.es/web/ign/portal).

some areas, there is a spectacular occurrence of speleothems broken by gravitational movements of bedrock. Two cores of flowstone were extracted during the same sampling campaign at the studied area: core CCA was collected near the entrance of the cave of Cuartillico del Agua, and the core SSPD was collected at the base of a 10 meter-deep pit of the Sima del Saliente.

## 3. Methods

The "flowstones" speleothem records vary from 30 to 40 cm (Figure 2). The samples were sectioned longitudinally using a diamond saw to expose their internal structure and permit a check for secondary alteration. The mineralogical composition of the samples was determined by X-ray diffraction, using a PANa-lytical X'pert Pro X-ray diffractometer (PW3071) operating at 40 kV and 30 mA, and employing monochromatic Cu-Ka radiation, at the IACT. The XRD spectra were obtained from 10° to 60°  $2\theta$  using X'PerHigh Score (PANalytical) software. The diffraction data were analyzed using the XPOWDER\* software [25]. Petrographic examination was performed using a polarizing microscope LEITZ WETZLAR standard WL and OLIMPUS DP-20 equipped with microphotographic OLIMPUS BX60 on polished thin sections prepared from each flowstone using plane polarized and cross polarized. Growth discontinuities were identified and calcite textures were recognized and classified following the criteria proposed



**Figure 2.** Polished surfaces of flowstones CCA and SSPD. Black rectangles indicate where the samples were cut to make thin sections. The black dots indicate drilling sites along growth layers for analyses of stable isotopes.

in [8], although the protocol by [26] has been followed, in which they have simplified and rearranged the fabrics recognized. Optical microscopy revealed the presence of primary growth fabrics. Observations were made using scanning-electron-microscopy utilizing AURIGA (FIB-FESEM Carl Zeiss SMT).

Stable isotope subsamples were taken along the flowstone cross section with a bench micro-drill (0.5 mm diameter bit). Additionally, subsamples were taken along individual growth layers to perform a "Hendy test" for to know if the deposition of carbonate was in the isotopic equilibrium with precipitating waters [27]. A total eighty-five measurements of carbon and oxygen isotope were performed by conventional isotope-ratio mass spectrometry using a "Dual Inlet" SIRA-II model. All  $\delta^{18}$ O and  $\delta^{13}$ C values were calibrated against the international standard, and reported as the per mil (‰) deviation ( $\delta^{18}$ O,  $\delta^{13}$ C) of sample <sup>18</sup>O/<sup>16</sup>O, or <sup>13</sup>C/<sup>12</sup>C ratios relative to VPDB (Vienna PeeDee Belemnite) through certified reference carbonate materials. Analytical reproducibility of duplicates was better than 0.1‰ for  $\delta^{18}$ O and 0.05‰ for  $\delta^{13}$ C.

## 4. Results and Discussion

Prior to isotopic and petrographic studies, it is necessary to know the mineralogical composition of the flowstones. The XRD analyses show that the flowstones are mostly composed of calcite, in the all cases the calcite have a low Mg content (low-magnesium calcite LMC).

#### 4.1. Petrographic Study

For fabric analyses, the methodology proposed by [8] was adopted, but in addition we have followed the protocol by [26] and [28] in which they have simplified and rearranged the fabrics recognized. The analysis and characterization of the growth layer sets is constructed by assignation of a code (CC columnar, CCo columnar open, CCe columnar elongated, M micrite and D dentritic) to each portion of the flowstone. Optical microscopy revealed the presence of primary growth fabrics such as 1) compact columnar calcite in which the crystals present a compact aggregate, formed under relatively stable dripping conditions and lower drip rates (CC, **Figure 3(a)** and **Figure 3(d)**), 2) elongated columnar calcite resulted from the preferential growth of the acute rhombohedron and formed in very stable conditions (CCe, **Figure 3(b)**), 3) dendritic calcite characterized by milky, opaque appearance due to high intercrystalline porosity (D, **Figure 3(e)**), 4) open columnar calcite where the intercrystalline boundaries are marked by the presence of linear inclusions (CCo, **Figure 3(c)**), and 5) micrite fabric consisting of carbonate mud with crystals less than 2 - 4  $\mu$ m (M, **Figure 3(d)**). We have observed an increased presence of non-diagenetic fabrics in relation to the low proportion of diagenetic textures such as microsparite with crystals > 2  $\mu$ m (Ms, **Figure 3(f)**). The flowstones studied are composed of calcite crystals that frequently showing continuous growth, suggesting that they were deposited from continuously dripping water. Locally the growth of the crystal is interrupted by thin layers of milky-white or beige micro-crystalline calcite or detrital material.



**Figure 3.** Microphotographies under optic microscope (PPL) and SEM of the stalagmitic flowstones CCA (a-d) and SSPD (e-f). Elongated columnar calcite (CCe) is the most common fabric type observed in the thin sections (**Figure 3(b)**), commonly developed from parent water that has probably percolated through dolomitic limestones (middle-upper Triassic dolomitic rocks for these cores). In CCA, this type of fabric alternates with CCo, CC, M, Ms and Cd (**Figures 3(a)-(d)**). In SSPD, the alternation of micrite and microsparite with columnar types (**Figure 3(e)**, **Figure 3(f)**) is frequent.

#### 4.2. Isotopic Characterization of the Fabrics

 $\delta^{18}$ O and  $\delta^{13}$ C values were measured for 149 calcite subsamples drilled at discrete 1 - 3 mm intervals down the growth in the two flowstones. All results are plotted in **Figure 4** showing the isotopic compositions data obtained in this study.  $\delta^{18}$ O and  $\delta^{13}$ C measurements range from -4.05‰ to -8.55‰ and -4.37‰ to -9.87‰ respectively by flowstone CCA and -4.69‰ to -9.13‰ and -3.24‰ to -10.39‰ respectively by flowstone SSPD. The flowstones were tested (mainly columnar fabrics) with the Hendy test for isotopic equilibrium. Our results indicate that in general there is no enrichment of  $\delta^{18}$ O towards the outer end, and there is no clear relationship between  $\delta^{18}$ O and  $\delta^{13}$ C along the same layer, and thus the flowstones were formed under the isotopic equilibrium [27]. Using the paleotemperature equation of [29] the CCA record shows an average variation in temperature of ~15°C (given the  $\delta^{18}$ O<sub>VSMOW</sub> value of local water -7‰) [30] [31] [32] [33] [34]. For the stalagmitic flowstone SSPD, the mean value of paleotemperature for this stage is ~16°C.

A microstratigraphic log of three thin sections from flowstone CCA and SSPD predominantly consists of columnar (CC), columnar open (CCo), columnar elongated (CCe) and micrite fabrics. The construction of microstratrigraphic log of fabrics in flowstones allows for the recognition of changes through time (vertical dimension) of environments of deposition (Figure 5(a) and Figure 5(b)). The succession of fabrics is shown and directly compared with the series of stable isotopic data. It is observed that there is a correlation between the different fabrics and isotopic values. All columnar fabric types and dendritic have similar  $\delta^{18}$ O and  $\delta^{13}$ C values, which are more negative than the micrite and microsparite. The correlation between  $\delta^{13}$ C and  $\delta^{18}$ O from calcite fabrics is  $R^2 = 0.82$ (Figure 6). This correlation plot shows that columnar fabrics have similar  $\delta^{13}$ C and  $\delta^{18}$ O signatures, with columnar elongated fabric (CCe) characterized by the lowest values, followed by compact (CC) and open columnar calcite fabrics (CCo). Micrite and microsparite show the more positive isotope ratios values. The regression line shows that there is progressive kinetic modification of the isotope signals from columnar fabrics to microsparite, possibly due to combined degassing and evaporation process. A one-way analysis of variance was performed with the isotopic values obtained for each of the recognized fabrics. Differences between the group means were detected by an analysis of the variance (one-way ANOVA) and the post-hoc comparison between the means was carried out with the Fisher LSD test. The relationship between variables was analyzed by regression analysis. Values with P < 0.05 were considered significant. The statistical treatment of the data was carried out using the statistical package IBM SPSS Statistics v. 23 (IBM). A significant difference among the fabrics was found for each isotope (P < 0.05). Comparison between groups shows that the  $\delta^{13}C$  values for micrite and microsparite fabrics (M/Ms) and those of columnar calcite elongated fabric (CCe) are significantly different from the rest (P < 0.05), being less negative than the values of M/Ms fabrics and more negative than those of CCe fabrics, whereas those corresponding to the compact and



**Figure 4.**  $\delta^{18}$ O ‰ VPDB vs  $\delta^{13}$ C ‰ VPDB plot showing the isotopic compositions of data points measured on two flowstones CCA and SSPD.



**Figure 5.** Vertical variation and evolution of the fabrics and stable isotopic data obtained for every thin section of the stalagmitic flowstones CCA (a) and SSPD (b). Black horizontal scale bars are 200 µm.



**Figure 6.** Isotopic characterization of the fabrics observed in the thin sections of the stalagmitic flowstones.

open columnar fabrics (CC and CCo) are not significantly different (P > 0.05). For the  $\delta^{18}$ O values it is possible to confirm that there are statistically significant differences (P < 0.05) with M/Ms fabrics being the less negative, significantly different for the rest (P < 0.05) while for CCo, CCe and CC no differences were found (P > 0.05).

#### 4.3. Paleoclimatic Implications

Speleothems in caves grow only when the effective precipitation during the rainy season is positive [14]. The study reveals different paleoenvironments of deposition deduced from the variability observed in calcite fabrics and stable isotope data [35] [36]. According to [8], the speleothem fabric is a useful, complementary tool to recognize the presence, and evaluate the intensity, of disequilibrium isotopic fractionation.

In most cave systems, the carbonates often are formed in quasi-isotopic equilibrium, that is from waters at relatively low supersaturation, constant drip rate, and cave relative humidity of near 100%. Changes in some of these factors by kinetics effects [37] produced disequilibrium isotopic fractionation and affect the fabric of the crystals which precipitate [6]. The fabric of flowstones changes under different physical and hydrochemical conditions (hydrological stress, supersaturation state of the dripwater, progressive increase in Mg and impurities, and diagenesis) and provides additional information on the environment of formation. This information can facilitate the interpretation of the stable isotope signal in these materials [6] [8] [22] [38] [39].

The textural variations in speleothems may be related to drip-water availability [16], the nature of flow or transport of water [40] [41] [42] and/or evaporation [35]. However, it is important to show that changes in crystallography or petrography are synchronous throughout a particular region before using them to aid interpretation of stable isotope data, as they may have been influenced by drip-or cave-specific hydrological routing effects [23]. [39] has indicated that drip interval plays a fundamental role in the type of calcite fabric, and that the Mg concentration in drip water possibly influences fabric development: a longer drip interval can cause the calcite  $\delta^{13}$ C ratios to increase, which corresponds to lower Sr and higher Mg concentration, also resulting in higher defects and smaller-dimension of the calcite crystallites.

Fabric codes recognized, from bottom to top, suggests that a regime of relatively constant drip rate, although is possible to observed fabrics result from growth processes that imply a combination of low/high drip rate and high/low degassing. Compact (Cc) and open columnar calcite (Cco) form at relatively low supersaturation of dripwater and concentrations of foreign ions, and relatively constant flow conditions [9]. Elongated columnar calcitic fabric (Cce), of large acute crystals, is common in this flowstones that developed from parent waters whose catchment intersected dolomitic or Mg-rich rocks. This fabric requires relatively fast flow to the substrate and higher dripping rate than compact and open calcite [8], and is indicative of high flow in interglacial periods, where the protruding terminations of crystals promote turbulent flow and to generated degassing, changes the precipitation rate and development of linear inclusions. Flat terminations, or rhombohedra terminations should be due to action low flow [43]. This is congruent with the most negative  $\delta^{18}$ O values and the highest temperatures observed for this fabric: low values of stable isotope data are due to the "amount effect" (increased precipitation may be decrease of  $\delta^{18}$ O).

Micrite and microsparite commonly appear together as microsparite is a diagenetic product of micrite. Microsparite forms when a saturated flow enters in contact with micrite [44], by dissolution and re-precipitation. Thus, microsparite is associated with wet periods. Micrite, however, forms during relatively dry periods, and some authors associate micrite with bio-influenced precipitation (by cyanobacteria [45]). Micrite is more common in these flowstones than microsparite, recording the heaviest values of  $\delta^{18}$ O (less "amount effect").

Dendritic calcite, observed in CCA, is associated with periods of rapid dripping alternating with long periods of extremely slow dripping, common in speleothems located near the entrance of the cave. This remarkable variability in the environment of formation has not been recorded in the isotopic signal, because only one sample has been analyzed. This calcite fabric normally associated with strong kinetic isotope fractionations, in the case of carbon isotopes. Both  $\delta^{13}$ C and fabric changes appear to be directly related to changes in hydrology. In this way, drip-rate variations influence the duration of degassing, which can result in enrichment in <sup>13</sup>C in the solution covering the flowstone [11].

The  $\delta^{13}$ C record roughly follows the same trend as  $\delta^{18}$ O and this suggests a clear correlation between subsurface hydrology and vegetation growing at land surface above the cave [46]. High values of  $\delta^{13}$ C reflect lower dripping rate and a decline on vegetative productivity, values found in micrite [14]. In regions with semi-arid climate, evaporative processes lead to heavier  $\delta^{18}$ O isotopic composition of the cave drip-waters than the isotopic composition of precipitation [47].

Changes in seasonality of rainfall, varying cave air temperatures and evaporation are factors that influence the morphology and stratigraphy of speleothems. In synthesis, the data shown here suggest that both the combination of  $\delta^{18}$ O and  $\delta^{13}$ C trends and the changes in the petrography (fabrics log) provide information about the climatic conditions which prevailed during the flowstone formations. The combination of coded fabrics and stable isotope ratio values could be a useful tool for an adequate global interpretation in terms of paleoclimate. In the future, we wish to verify, by running scheduled trials both in the cave and in the laboratory, the relationship between controlling parameters and fabrics observed during precipitation. These trials would allow knowing the isotopic values present in predominant fabrics and which are the main parameters that control calcite precipitation.

## **5.** Conclusions

Speleothems are good proxy to understand the environmental condition above the cave where they form. The variability observed in crystallization of calcite crystals and stable isotope data constitute a useful and reliable tool for depositional conditions that form speleothems and extract paleoclimate information. There is a need to better understand the relationship between crystal microstructures, fabrics and their environment of formation, and geochemical properties, in order to test the validity of speleothems as paleoclimate indicators.

From the studied sections in the flowstones we found that the presence of micrite and microsparite has revealed relatively dry growth conditions, as micrite is much more frequent than microsparite. The more stable growth conditions correspond to fabrics: compact and open columnar calcite forms at constant dripping rate, while elongated columnar calcite requires relatively fast dripping rate.

The isotopic record supports the information obtained by the fabrics. Columnar types are characteristic of relatively warm and wet periods (most depleted values of  $\delta^{18}$ O but the highest temperatures, consequence of the "amount effect"), while micrite (M) and microsparite (Ms) form during colder and relatively dry periods (heaviest values of  $\delta^{18}$ O and the lowest temperatures). High values of  $\delta^{13}$ C also reflect a decline on vegetative productivity, as  $\delta^{13}$ C and  $\delta^{18}$ O records roughly follow the same trend.

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## **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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## **Abbreviation Note List**

CCA Core Cave of Cuartillico del Agua SSPD Core Sima Saliente Pared Derecha CC Calcite Columnar CCo Calcite Columnar Open CCe Calcite Columnar Elongated M Micrite Fabric D Dentritic Fabric Ms Microsparite Fabric