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Geochemistry of speleothems affected by aragonite to calcite recrystallization — potential inheritance from the precursor mineral

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Abstract

Formerly aragonite speleothems recrystallized to calcite result from solutions subsaturated in aragonite and supersaturated in calcite that infiltrate into the speleothem through the interconnected porosity. In most cases, the crystal replacement takes place through a thin solution film. This diagenetic process can occur under open or semi-closed geochemical conditions. Thus, secondary calcite crystals record the composition of the fluid at the time of diagenesis affected by calcite partition coefficients and fractionation factors (open system) or partly inherit the composition of the primary aragonite (semi-closed system). So, whether or not recrystallized aragonite speleothems can record reliable geochemical signals from the time of speleothem primary deposition

still is an open debate. We studied a stalagmite from Eagle Cave (Spain) predominantly composed of secondary calcite that replaced aragonite, although a core of primary aragonite extending 45 mm along the growth direction was preserved at the base of the sample. We obtained Mg and Sr compositional maps, paired U-Th dating and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles across the diagenetic front. Additionally, two parallel isotope records were obtained along the speleothem growth direction in the aragonite and calcite sectors. Our results support that recrystallization of this speleothem took place in open system conditions for $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg and Sr, but in semi-closed system conditions for U and Th. The recrystallization of this sample took place during one or several events, likely after the Younger Dryas as a result of climate change influencing drip water composition. Based on compositional zoned patterns, we suggest that the advance of diagenetic fronts in this speleothem had an average rate of $50 \pm 45 \mu\text{m/yr}$. Such recrystallization rate can transform any aragonite speleothem into calcite within a few centuries. We suggest that the volume of water interacting with the speleothem at the time of recrystallization is of critical importance for inheritance of different elements. The volume of solution is controlled by (1) the discharge of water passing through the sample and (2) the lapse time between aragonite dissolution and calcite precipitation. Hydrology and hydrochemistry of the interacting solution, together with the mineralogy and texture of the speleothem are the essential controls for the diagenesis of the speleothem. Recrystallization of aragonite speleothems does not follow stratigraphical levels of the sample but occurs along sites with preferential flow paths in any sector of the speleothem. In these cases the relationship between age and distance from base is not preserved. However, alternation of periods of recrystallization with periods of aragonite precipitation causing speleothem accretion can result in recrystallized speleothems with coherent distance from the base-age relationship. Thus, early

diagenesis of speleothems affected by seasonal or inter-annual oscillation of drip waters supersaturated and subsaturated in aragonite may provide best-scenario conditions for dating and preservation of paleoenvironmental records along recrystallized speleothems. However, even in this scenario, the variable discharge and the diagenetic rate control the geochemical inheritance from the primary aragonite crystals.

Key words: Speleothem; diagenesis; aragonite; calcite, open system

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1. INTRODUCTION

Carbonate minerals precipitate in caves from waters supersaturated with respect to those minerals (Hill and Forti, 1997). The geochemical composition of these carbonates depends on the precipitated carbonate mineral, the chemistry of the solution that formed them and the cave atmosphere conditions (Tarutani et al., 1969; McDermott, 2004; Fairchild and Treble, 2009). These parameters depend greatly on the environmental and climate conditions (e.g., Ayalon et al., 1998; Fairchild et al., 2006). Thus, speleothems potentially record along their growth axis a geochemical signal related to changes of the environment and/or the climate during their period of formation. However, diagenesis of carbonate speleothems modifies their primary geochemical signature, limiting the reliable dating from these samples (Railsback et al., 2002; Ortega et al., 2005) as well as the interpretation of their geochemical record in terms of variations of past environment or climate (e.g., Frisia et al., 2002; Hopley et al., 2009; Lachniet, 2015).

Diagenesis of speleothems was already mentioned in early speleothem studies (Murray, 1954) and pioneer studies focusing on diagenesis were published decades ago (Folk and Assereto, 1976; Cabrol and Coudray, 1982; Bar-Matthews et al., 1991; Frisia, 1996; Railsback, 2000; Kendall and Iannace, 2001). Although speleothem dissolution is in itself a diagenetic process (Csoma et al., 2006; Martín-García et al., 2011; Martín-Pérez et al., 2012; Shtober-Zisu et al., 2014), most studies focused on speleothem diagenesis describe recrystallization processes, where a secondary mineral replaces a precursor mineral. The polymorphs of CaCO_3 , calcite and aragonite, are the most common carbonate minerals in speleothems (Hill and Forti, 1997). Recrystallization processes in carbonate speleothems may include non-carbonate minerals (Woo et al., 2008), or replacements from calcite to calcite, aragonite to aragonite or aragonite to calcite (Cabrol and Coudray, 1982; Perrin et al., 2014). However, most speleothem diagenetic studies describe the replacement of aragonite by calcite (e.g., Railsback, 2000; Spötl et al., 2002; Frisia et al., 2002; Lachniet et al., 2012; Zhang et al., 2014; Frisia, 2015). Different terms can be found in literature to describe this process in speleothems (i.e., secondary calcite replacing aragonite crystals): recrystallization, replacement, inversion, transformation, calcitization or neomorphism (Bischoff and Fyfe, 1968; Railsback et al., 2002; Woo and Choi, 2006; Martín-García et al., 2009; Perrin et al., 2014). All these terms are correctly applied to name the process here described, although they are not synonyms. Detailed definitions of these terms can be found in previous studies (Martín-García et al., 2009; Perrin et al., 2014). In environments with temperature $<100^\circ\text{C}$, the recrystallization of aragonite to calcite resulting from a solid-state reaction is negligible (Tarutani et al., 1969), since it would require several million years to be completed (Fyfe and Bischoff, 1965). This recrystallization process is much faster when the

reaction is triggered by a fluid solution (Bischoff, 1968). So, in most environments, aragonite to calcite recrystallization is considered to occur from the interaction of fluid solutions with aragonite crystals (Perdikouri et al., 2008). Aragonite to calcite recrystallization in speleothems can result from (1) the formation of voids due to dissolution of primary aragonite crystals and subsequent cementation with calcite crystals (Folk and Assereto, 1976; Martín-García et al., 2014). However, in most cases recrystallization results from (2) the nearly simultaneous dissolution of aragonite and precipitation of calcite through a solution film $<1\text{ }\mu\text{m}$ thick (Pangitore, 1976). For the latter mechanisms to occur, the solution has to be subsaturated with respect to aragonite and supersaturated with respect to calcite (Folk and Assereto, 1976; Frisia et al., 2002).

The distribution coefficients of elements such as Mg, Sr and U differ between aragonite and calcite (Rimstidt, et al., 1998; Fairchild and Treble, 2009). Thus, under similar hydrochemical and environmental conditions, aragonite incorporates more U and Sr than calcite, whereas the latter incorporates more Mg than aragonite (Speer, 1983; Reeder et al., 2000; Wassenburg et al., 2012). In a chemically open system where solutions interact with the speleothem, not all the elements have the same solubility. For example, U preferentially leaches compared to Th, which affects the age determination of speleothems (Richards and Dorale, 2003). So, calculated dates in speleothems affected by aragonite to calcite recrystallization are usually older than expected in open system conditions (Railsback et al., 2002; Lachniet et al., 2012; Scholz et al., 2014). Fractionation factors of carbon and oxygen stable isotopes between the solution and the precipitated mineral also differ in the case of this mineral being aragonite or calcite (Tarutani et al., 1969). Therefore, recrystallization from aragonite to calcite also implies modifications of the isotope record (Zhang et al., 2014). However, the isotopic

composition, the content of U, Mg and Sr as well as the dates of primary aragonite compared to those from secondary calcite crystals suggest that, under certain circumstances, recrystallization can take place in a semi-closed system, where the secondary minerals partially preserve the composition of the precursor mineral (Frisia et al., 2002; Woo and Choi, 2006; Martín-García et al., 2009; Perrin et al., 2014). In these studies, the compositional overlap between primary and secondary minerals often results from the large variability of measured parameters. Such large variability results from (1) the integration of data from a series of speleothem samples or even type of speleothems formed from solutions with very different hydrochemistry, and/or (2) comparison of asynchronous levels from the same speleothem, neglecting the importance of hydrochemical variability through time. Therefore, the suggestion from many previous studies considering recrystallization under a semi-closed system and the partial preservation of the primary geochemistry should be taken with caution.

Here we present a research focused on EA5 stalagmite from Eagle Cave (central Spain). This speleothem has clear processes of aragonite to calcite recrystallization. Most of the sample is composed of secondary calcite, although a core of primary aragonite is preserved. In this exceptional sample we can compare primary aragonite and secondary calcite crystals from the same stratigraphic levels, limiting uncertainty related to the variability introduced when comparing different samples or periods. Thus, the aim of this paper is to evaluate the preservation of the original geochemistry in recrystallized speleothems and to better understand the aragonite to calcite diagenetic processes.

2. MATERIAL AND METHODS

This research is based on a speleothem from Eagle Cave, located in Avila province, central Spain (40°9'15''N, 5°4'20''W; 427 m above sea level). This cave is formed in marbles that constitute the topmost unit of a metasedimentary series of Cambrian age composed of schists and quartzites (Martín Escorza, 1971; Odriozola et al., 1980). The essential minerals of these marbles are dolomite and magnesite (Krklec et al., 2016). A meteorological station at this site (data from 2009 to 2014) records mean annual temperature of 14.7 °C and mean annual precipitation of 797 mm. The climate is Mediterranean-continental with dry summers (precipitation in June-July-August <40 mm) and 19 °C difference between maximum and minimum mean monthly temperatures.

The cave has a main hall with a stable temperature of 15.6 ± 0.2 °C and relative humidity near 100 % (Domínguez-Villar et al., 2013a). A multitude of speleothems decorates Eagle Cave. Mineralogical studies of two stalagmites from this cave showed that they are composed of calcite and aragonite (Domínguez-Villar et al., 2013b). In 2007, the stalagmite EA5 was collected from the main room. EA5 is a 161 mm long candle-like speleothem, which external appearance is similar to most stalagmites in the cave (Fig. 1). No water was dripping over this speleothem at the time of collection. However, hydrochemistry of drip waters feeding four candle-like speleothems from the main hall were collected from 2008 to 2010, providing a Mg/Ca ratio ranging from 0.9 to 8 (n=30) showing clear seasonal variability and mean saturation indexes of calcite and aragonite ($\pm 1\sigma$) of 0.29 ± 0.19 and 0.16 ± 0.19 respectively (Domínguez-Villar et al., 2012).

Stalagmite EA5 was cut in half along the growth axis. Rock sections 100 to 300 μm in thickness were glued to glass plates and polished. These thick sections were used for their petrographic study under optical microscope, and analysed by different techniques: electron probe microanalysis (EPMA), particle-induced X-ray emission (PIXE) and electron backscatter diffraction (EBSD). Naturally broken surfaces of small aragonite and calcite speleothem fragments (<5 mm in size) were used for observation under scanning electron microscope (SEM). The samples were coated with a thin film of gold before using a JSM 6400 microscope working at 20 kV to produce SEM images. This technique was used to observe the morphology of aragonite and calcite crystals and the speleothem texture in detail. Thick sections were coated in graphite and analyzed with EPMA in a JEOL Superprobe JXA-8900 M at an accelerating voltage of 15.0 kV. We obtained compositional maps for Ca, Mg, Fe and Sr, although concentrations of Fe and Sr in our sample were below detection limits. Maps were 100×100 μm to 1500×1500 μm in size and had a spatial resolution of 1 or 1.5 $\mu\text{m}/\text{pixel}$. This technique provides compositional maps with relative units (X-ray counts/pixel). Quantitative compositional maps of Ca, Mg and Sr were obtained using the PIXE technique working with 3 MeV protons. We measured Ca and Mg with a Si(Li) X-ray detector and Sr with a X-ray iGe detector. A Kapton filter 975 μm thick was installed in the iGe detector in order to reduce the counting rate of Ca and lighter elements in the recorded spectrum. Due to a presence of strong Ca tail in the spectrum, Mg could not be measured in all samples. Analytical uncertainties for Mg and Sr determinations were <350 ppm and <10 ppm respectively for selected sectors. The compositional maps cover 0.35×0.35 mm to 2×2 mm areas at spatial resolutions ranging from 1 to 6 $\mu\text{m}/\text{pixel}$.

Using a microdrill, we collected 11 carbonate powder samples, 0.2 to 0.5 g in size, to perform X-ray diffraction (XRD) analyses and determine the mineral composition of the speleothem. These samples were analyzed in a Bruker D8 diffractometer working at 40kV and 30mA between 2 and 65° 2 θ . With this technique we can calculate the aragonite to calcite ratio in a bulk sample using the reference intensity ratio method to estimate the proportion of each mineral with an accuracy of 5% (Chung, 1974). However, the spatial distribution of both minerals was determined by phase maps using the EBSD technique applied to thick rock sections mounted on glass plates. We use an AURIGA crossbeam workstation from Carl Zeiss SMT (focused ion beam SEM with electrons produced by field emission) equipped with an EBSD detector from Oxford Instruments. Maps cover areas <1 mm² with spatial resolution ranging from 1 to 14 μ m/pixel.

Stable isotopes of oxygen and carbon were analyzed in a Finnigan MAT-252 mass spectrometer fitted with a Kiel Carbonate Device III. A total of 160 samples 50 μ g in size were collected using a microdrill with a drill bit of 0.5 mm in diameter. Two parallel vertical profiles (along the speleothem growth direction) and three transverse profiles (following same stratigraphic levels) were sampled. One of the vertical profiles follows the centre of the speleothem where secondary calcite is the dominant mineral. The second vertical profile is slightly off the centre of the speleothem, where a 45 mm long core of primary aragonite is preserved. The sampling interval of both profiles was 1 mm along the basal 45 mm. Above this point, samples were collected in a single profile along the center of the speleothem, considering a sampling interval of 2 mm. Data are reported in δ notation ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) with respect to Vienna Pee Dee Bee standards (‰ VPDB). Data were calibrated against NBS-18 and NBS-19 standards.

Analytical uncertainties for both isotopes were $<0.10\%$. We analyzed the uranium and thorium isotope composition of 10 samples from EA5. Samples ranged in size from 30 to 250 mg and their preparation was according to standard procedures (Edwards et al., 1986; Dorale et al., 2004). Six of the samples were run in an ELEMENT inductively coupled plasma mass spectrometer (ICP-MS) in 2007, and additional four samples were run in a NEPTUNE multi collector ICP-MS in 2014. Ages were calculated according to updated decay constants (Cheng et al., 2013) and assuming an initial $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio of $4.4 \pm 2.2 \times 10^6$. Analytical uncertainty is $<1\%$, except for one sample that has relatively high initial Th (i.e., its uncertainty is 6%). We calculated all ages as if the system would have been closed since deposition. Secondary calcite samples are unlikely to fulfill the requirements to obtain accurate dates from U and Th isotope determinations (Richards and Dorale, 2003; Scholz, et al., 2014). However, these inaccurate age calculations are reported together with isotope determinations to evaluate geochemical modifications of the speleothem caused by diagenetic processes.

3. RESULTS

3.1. Petrography and mineral composition

According to XRD analyses EA5 stalagmite is mostly composed of calcite (Fig. 2). A 45 mm long core of pure aragonite is preserved at the base of the sample, slightly off the central axis (Fig. 1). However, within the aragonite core, there are some euhedral secondary calcite crystals >1 mm in size that have hexagonal outlines (Fig. 1, Fig. 3B). Aragonite crystals have fibrous habit arranged in fans with preferential growth perpendicular to the speleothem surface. Width of aragonite fibres is $<50\text{ }\mu\text{m}$ and most

frequently 1 to 10 μm . These crystals often do not coalesce, which results in a speleothem with considerable porosity (Fig. 3). Off the aragonite core, the speleothem is composed of calcite with a variable proportion of aragonite, typically between 5 and 15 %. The top of the speleothem is composed of a distinct millimetre thick calcite lamina. Based on optical microscope and SEM observations, the aragonite crystals of the core at the base of the speleothem and the top millimetre lamina of calcite are primary crystals. However, most of the speleothem is composed of secondary calcite. Despite recrystallization, secondary crystals have clearly preserved structures such as speleothem banding (Fig. 1).

These secondary calcite crystals have textural relics (i.e., partially preserved textures of the precursor crystals without traces of the primary mineral) and occasionally mineralogical relics (i.e., partially preserved crystals of the primary mineral), obvious due to the fibrous texture of the precursor aragonite crystals (Fig. 4). Secondary calcite exhibits equant and columnar fabrics according to Frisia et al. (2000) classification. Length to width ratio of columnar crystals in EA5 is $<6:1$. Orientation of the columnar c-axis crystals is often perpendicular to the speleothem surface. However, c-axes of columnar crystals also have other preferential orientations such as perpendicular to diagenetic fronts or less commonly, forming clusters radiating (Fig. 4F) up to 360 degrees. Most of the relics in equant and columnar secondary calcite crystals are textural relics, with a small proportion of mineralogical relics, since the proportion of aragonite preserved in secondary calcites is limited compared to the abundant relics observed under the optical microscope (Fig. 2, Fig. 4). Relics are more common in the nucleus of some equant crystals than in their edges (Fig. 4D). When columnar crystals replace vertically oriented aragonite fans, the textural relics are more common off the

central axis of the former fan (Fig. 4B). However, the presence of relics frequently varies dramatically from one crystal to the other (Fig. 4C) and even within the same crystal. Euhedral hexagonal crystals observed under optical microscopy often show variable concentration of relics along their crystal faces at different stages of the crystal growth (Fig. 4E).

The size and fabric of secondary calcite crystals vary greatly along the sample. In some cases, the preservation of relics or the geochemical composition can be used to infer sequential stages of recrystallization (Fig. 4E), although they do not show any obvious pattern between size or fabric of the crystals and the evolution of recrystallization. Secondary calcite crystals are compact, with little porosity aside from the textural relics (Fig. 3). However, the coalescence of secondary calcite crystals is often incomplete, especially between equant crystals. Thus, although the recrystallization process has modified the original porosity of the aragonite sample, the speleothem still has substantial porosity. SEM observations show that the contact between aragonite and calcite crystals can be sharp, preserving the euhedral face of the secondary calcite at the diagenetic front, or uneven, with aragonite fibres disrupting an irregular diagenetic front (Fig. 3). In both cases aragonite fibres proximal to the diagenetic front are often partially dissolved. Enclosed in the secondary calcite, SEM images show preserved aragonite needles, as well as the porosity after their dissolution, indicating the existence of both mineral and textural relics (Fig. 3E). EBSD mineral phase images show that within secondary calcites, aragonite is preserved as isolated crystals $<10\text{ }\mu\text{m}$ in size, or as partially dissolved fibres (Fig. 5). These analyses show a proportion of aragonite within secondary calcite in agreement with XRD analyses. Calcite crystals <10 to $40\text{ }\mu\text{m}$ in size are occasionally found within primary aragonite. These crystals were not

observed in optical microscopy or during SEM imaging and we cannot discern if these are primary or secondary calcite crystals. Contrary to what is occasionally observed with textural relics, in EA5 stalagmite mineralogical relics do not concentrate preferentially along areas that were recrystallized at the same time (i.e., do not form zoned patterns of mineralogical relics).

3.2. Geochemical composition

The concentration of Mg and Sr in secondary calcite crystals of EA5 speleothem frequently differs from that of aragonite crystals. Aragonite commonly has higher Sr and lower Mg than secondary calcite (Fig. 6). This change in chemical composition can be relatively homogeneous (Fig. 6) or present a zoned pattern (Fig. 7, Fig. 8). Zoned patterns are more obvious in Mg than in Sr maps due to larger differences. The areas of these zoned pattern crystals with higher Mg have slightly lower Sr concentration and vice versa (Fig. 9). EBSD analyses have shown that this antithetic composition does not result from variable preservation of mineralogical relics (Fig. 5F). In crystals showing a compositional zoned pattern we sometimes observe a variable morphology of the diagenetic front depending on the Mg content (Fig. 8). During periods of precipitation of calcite with high Mg concentration the diagenetic front was more irregular than during periods when calcite had low Mg concentration. The distribution of Mg and Sr content is often relatively homogeneous for synchronously precipitated areas within crystals or in contiguous crystals. However, we also record sharp lateral compositional changes, even within a single crystal (Fig. 10).

Carbon and oxygen stable isotope composition of similar stratigraphical levels vary depending on the dominant mineral composition of the analyzed carbonate (Fig. 11). Values of both stable isotope ratios are more negative in secondary calcite than in aragonite samples. The parallel isotope records of the basal 45 mm of the stalagmite, have an average difference between aragonite and the recrystallized calcite of $0.72 \pm 0.34 \text{ ‰}$ and $1.49 \pm 0.63 \text{ ‰}$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ respectively ($n=44$). Aragonite and secondary calcite crystals in equivalent stratigraphical levels of the stalagmite neither were formed at the same time nor from the same solution. Thus, we compare these records only to evaluate the potential inheritance of isotopic values from the primary mineralogy after diagenesis. It should be kept in mind that most secondary calcites have $<10 \text{ ‰}$ aragonite. However, the effect of such limited aragonite proportion on the isotope composition of calcite is within analytical uncertainty for $\delta^{18}\text{O}$ values and only slightly above for $\delta^{13}\text{C}$ values. Both, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signals recorded at the base of the stalagmite parallel to its vertical axis have a clearly different structure between the series obtained in the aragonite and secondary calcite sectors (Fig. 11B). We also measured the stable isotope composition following three stratigraphical levels (i.e., laminae). Samples for these analyses were collected every 2 mm along each of the three chosen laminae, covering the top/central part of the speleothem. Two of these profiles crossed the diagenetic front at the base of the sample, whereas all samples from the third profile consist of secondary calcite with limited proportion of relic aragonite (Fig. 11C). The lateral variability of isotope composition along this third profile was $<0.3 \text{ ‰}$ for $\delta^{18}\text{O}$. The $\delta^{13}\text{C}$ variability was $<0.5 \text{ ‰}$ within 10 mm of the speleothem axis and increased by 0.06 ‰/mm beyond this point. Differences in mean $\delta^{18}\text{O}$ values between aragonite and calcite samples in the other two lateral profiles are 0.73 and 0.58 ‰ , whereas differences in mean $\delta^{13}\text{C}$ values are 1.47 and 1.20 ‰ ($n=8$ for each profile).

Considering the variability within each mineral, the isotope differences calculated along lateral profiles are in good agreement with those measured along the growth direction of the speleothem. The stable isotope composition of recrystallized calcite along the growth axis of the 161 mm of EA5 speleothem is far from homogeneous: $>1\text{‰}$ and $>2\text{‰}$ for the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variability respectively (Fig. 11A). This isotope record includes gradual as well as sharp changes in the isotope composition.

The U concentration of aragonite samples is not higher than in secondary calcite samples: both are between 0.7 and 2 ppm (Table 1; Fig. 12). On the other hand, the primary calcite from the top of the speleothem has much lower U concentration (i.e., 0.04 ppm). Aragonite and secondary calcite samples from similar stratigraphical levels have overlapping $\delta^{234}\text{U}$ values considering inter-sample variability. None of the aragonite and secondary calcite samples have low $^{230}\text{Th}/^{232}\text{Th}$ activity ratios that could impact the age calculation beyond analytical uncertainty (Richards and Dorale, 2003). Calculated ages from these U and Th isotope data do not always follow a stratigraphical order due to some reversals, although most dates follow a logical chrono-stratigraphical sequence (Fig. 12). Comparison of the calculated ages with distance from the base shows two dates clearly outside the expected stratigraphical order. One of these reversal ages was from a primary aragonite sample, whereas the other was from a secondary calcite sample. The reversal age in the aragonite sample was unexpected, although secondary calcite crystals are occasionally dispersed within the aragonite. In a subsequent sampling we collected smaller aragonite aliquots to avoid the probability of including small secondary calcite crystals within the samples and minimize the possibility of having an open system. Two aragonite samples in the proximity of the aragonite sample that has a reversal age provided nearly identical results to each other,

and both differ significantly from the reversal age. Laterally to these dates, the secondary calcite sample collected nearly at the same stratigraphical level shows an age difference only slightly above the 2σ uncertainty of the dates (<300 yr). However, the other clear reversal age corresponds to a secondary calcite sample significantly older than the primary aragonite samples at the same stratigraphical level. None of the samples with clear reversal ages had anomalously high or low U content that could be used to predict U leaching or incorporation (Scholz et al., 2014) during recrystallization. Ages in apparent stratigraphical order suggest that the base of the sample was formed during the Younger Dryas period. The accuracy of dates from secondary calcite above the aragonite core is difficult to evaluate. They do not present age reversals although, if accurate, would imply an unlikely increase in growth rate. The primary calcite lamina at the top of the stalagmite has an age ~ 10 ka younger than any of the other dates, suggesting the existence of an important hiatus at the top of the sample.

4. DISCUSSION

4.1. Recrystallization process

The recrystallization of aragonite to calcite in speleothems occurs through a fluid solution, which is subsaturated in aragonite and saturated in calcite (Folk and Assereto, 1976; Frisia et al., 2002; Perrin et al., 2014). In most cases, the recrystallization occurs through a thin film <1 μm thick (Pingitore, 1976). Aragonite crystals are dissolved in contact with the solution in one side of the thin film, whereas simultaneously in the other side, calcite crystals are precipitated due to the diffusion of calcium and carbonate ions (Carlson, 1983; Perdikouri et al., 2008). This thin film is a diagenetic front which

progressive displacement causes the expansion of the recrystallization of aragonite to calcite along the speleothem. Alternatively, although less frequently, the recrystallization can result from a sequence where aragonite is dissolved in a first stage and calcite cements fill previous pores in a subsequent stage (Folk and Assereto, 1976; Carlson, 1983). Since both carbonates are polymorphs and their chemical reactions involve the same species, saturation indexes of both minerals evolve in parallel. Thus, when saturation indexes of these minerals decreases in the solution, aragonite always reaches subsaturation in the first place, while calcite still is supersaturated. Only if the solution continues decreasing its saturation indexes calcite reaches subsaturation too. Therefore, transformation of aragonite into calcite is only possible within a narrow compositional window of the solution. Variable saturation index can result from changes in the amount of prior calcite precipitation (Martín-Pérez et al., 2012; Domínguez-Villar et al., 2016), the discharge of water (Railsback et al., 1994; Lachniet et al., 2012) and the concentration of CO₂ in the soil or in the cave atmosphere (Bar-Matthews et al., 1991; Spötl et al., 2005; Scholz et al., 2014). These variations can occur at different timescales: intra-seasonal events, seasonal, inter-annual or permanent after modifications of former conditions in the system. However, recrystallization of aragonite speleothems requires not just a certain hydrochemistry, but drip water reaching the crystals deep inside the speleothem. So, the speleothem has to be permeable to drip water (e.g., Muñoz-García et al., 2012; Shtober-Zisu et al., 2014). Aragonite speleothems have, most commonly, a fibrous texture of non-coalescent crystals that results in long pores orientated roughly perpendicular to the speleothem surface. Thus, the orientation of pores in the central axis of aragonite speleothems, where the drip water splashes, is particularly well suited for water percolation into the stalagmites.

The content of organic matter in aragonite rocks may be a significant control on their transformation to calcite (Webb et al., 2009), and oxidation of organic matter in speleothems may cause dissolution to some extent (Frisia, 1996). However, the limited content of organic matter in majority of speleothems results in most cases in a negligible impact of this control on the recrystallization of aragonite. Crystal defects, such as twins or dislocations, and impurities have also been suggested to impact the aragonite to calcite transformation (Frisia Bruni and Wenk, 1985). However, the hydrochemistry of the solution flowing through the speleothem still is the main control triggering and governing the transformation of aragonite into calcite in the sample, and in most cases, the role of other potential controls is very limited or negligible compared to the dominant role of hydrochemistry.

Speleothem samples recrystallized from aragonite to calcite were often observed to consist mostly of mosaics of equant crystals (e.g., Folk and Assereto, 1976; Frisia, 1996; Ortega et al., 2005; Hopley et al., 2009). However, columnar crystals can also result from speleothem recrystallization (Cabrol and Coudray, 1982; Railsback et al., 2002; Lachniet et al., 2012; Perrin et al., 2014; Scholz et al., 2014; Zhang et al., 2014). This is the case in EA5 speleothem, where both, equant and columnar secondary calcite crystals are recorded (Fig. 4). Evidence of dissolved aragonite crystals at the diagenetic front are observed in SEM images from EA5 stalagmite showing: (1) aragonite fibres partially dissolved, as indicated by their round morphologies in some of their crystal faces (Fig. 3F) and (2) elongated pores that resemble the last core of former aragonite needles before their final dissolution (Fig. 3E). These traces of former aragonite needles result in textural or mineralogical relics depending on their complete or partial

dissolution. In EA5 stalagmite there is a clear difference in the porosity of aragonite and secondary calcite crystals. Secondary calcite crystals are equant or columnar crystals, partially or totally coalescing with each other, whereas most of fibrous aragonite crystals do not coalesce. However, aragonite is a denser mineral than calcite (e.g., Klein and Hurlbut, 1993; Hill and Forti, 1997) and recrystallization of the same mass would occupy more space under closed system conditions. Nevertheless, this is an unlikely scenario in most cave environments. In the case of EA5 stalagmite, the porosity between secondary calcite crystals is so important in sectors of the speleothem composed of large crystals (e.g., >2 mm in size), that these crystals easily get detached from the speleothem when handling the hand specimen slabs. Thus, although porosity within secondary calcite crystals is limited, often large pores exist between crystals favouring the local permeability of water through the sample.

Speleothem structures such as growing bands are preserved in the recrystallized stalagmite despite significant redistribution of porosity. The recrystallization of aragonite through a thin film favours the preservation of structures of the precursor mineralogy (Pangitore, 1976; Bayer et al., 2013). In this speleothem we did not observe dissolution of aragonite and precipitation of calcite in pores, and therefore, all replacement took place through thin film solutions. In this stalagmite, structures are better preserved in sectors of the speleothem with smaller crystal sizes (Fig. 1). Secondary calcite crystal sizes vary along the speleothem either progressively or across sharp boundaries that follow stratigraphical surfaces of the speleothem. This evidence suggests (1) that the aragonite texture plays an important role in the texture of the secondary calcite and/or (2) that the recrystallization took place in subsequent events with drip waters having significantly different hydrochemistry. The latter option implies

that aragonite precipitation and recrystallization processes alternated during the growth of this speleothem as a result of drip waters with a saturation index with respect to aragonite fluctuating periodically or episodically between the supersaturated and subsaturated state. These conditions are recorded in many drips of the cave nowadays (Domínguez-Villar et al., 2012).

Equant and columnar crystals of secondary calcite contiguous to each other are not uncommon in EA5 stalagmite. Also, crystals of very different size or incorporating diverse density of relics are contiguous to each other (Fig. 4C). Chemical banding across secondary calcite crystals show that they were often recrystallized at the same time (not shown) and the cause of the growth inhibition of some crystals in relation to others, or the lateral textural differences is unclear. We speculate that their cause could be related to the original texture and/or the orientation of the porosity in relation to the source of percolating water. An example is provided by secondary calcite crystals replacing fans of vertically oriented aragonite fibres (Fig. 4B). In this case, the density of relics increases off the vertically oriented c-axis of the crystal due to the angle of the fan fibres diverging from vertical and limiting the water flow. Thus, the preferential flow of percolated water along these crystals affected the hydrochemistry of the solution and the preservation of relics.

4.2. Open versus semi-closed geochemical system

Concentration of Mg, Sr and U is commonly used to trace open geochemical conditions in the replacement of aragonite by calcite in speleothems. They are used due to their different partitioning coefficients in aragonite and calcite (Railsback et al., 2002, Frisia

et al., 2002; Ortega et al., 2005; Wassenburg et al., 2012). Frequently, oxygen and carbon stable isotopes are also compared between both minerals (Woo and Choi, 2006; Martín-García et al., 2009; Zhang et al., 2014). Some authors describe the recrystallization of aragonite to calcite as an open system process in which the original signature of the aragonite is lost and the secondary calcite composition is related to the parental solution (Ortega et al., 2005; Martín-García et al., 2009, 2014; Perrin et al., 2014). However, other authors suggest that recrystallization occurs in a semi-closed system due to partial preservation of aragonite composition in secondary calcites (Frisia et al., 2002; Spötl et al., 2002; Railsback et al., 2002; Woo and Choi, 2006; Zhang et al., 2014).

The distribution maps of Mg and Sr in EA5 speleothem show clear compositional variations between aragonite and secondary calcite crystals as expected from their different partition coefficients (Speer, 1983; Wassenburg et al., 2012). Secondary calcites in EA5 stalagmite have less Sr than the aragonite crystals they replace, suggesting a leaching of Sr in the system. On the other hand, Mg concentration is generally higher in secondary calcites compared to aragonite, implying that additional Mg was delivered from percolating solutions (Fig. 6). This effect is more evident when the secondary calcite has a compositional zoned pattern, since alternating bands of higher Mg content have differences in the order of 10^3 ppm. Thus, the recrystallization process of EA5 stalagmite took place in an open system in relation to these two elements, where the composition of the secondary calcite crystals is related to the parental solution. Oxygen and carbon stable isotopes also show a similar pattern. Mean composition of the profile along secondary calcite crystals at the base of the speleothem is 0.72 ± 0.34 ‰ more negative in $\delta^{18}\text{O}$ and 1.49 ± 0.63 ‰ more negative in $\delta^{13}\text{C}$ than

the profile along the aragonite core. The two profiles across the diagenetic front following speleothem growing bands show isotope shifts of similar magnitude. These results are in agreement with the isotope differences between both carbonates precipitated in experimental studies from solutions having the same initial composition. Fractionation between both minerals at 25 °C in assumed equilibrium conditions is between 0.6 and 0.8 ‰ for $\delta^{18}\text{O}$ (Tarutani et al., 1969; Grosman and Ku, 1986; Kim et al., 2007) and between 1.4 and 1.8 ‰ for $\delta^{13}\text{C}$ (Rubinson and Clayton, 1969; Turner, 1982; Romanek et al., 1992). In the transformation of aragonite to calcite, the precipitation of primary and secondary crystals is not contemporaneous and the hydrochemical composition of the solutions they were formed from may differ. In EA5 stalagmite, the clear differences in the mean isotope values between aragonite and calcite samples, together with the lack of similar structure between parallel records, support that the secondary calcite did not inherit the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition from the primary aragonite. Additionally, in this stalagmite we find that the isotopic difference between aragonite and calcite is similar to the expected difference between both minerals precipitated after the same solution and conditions. So, we can speculate that there was little difference from the solution that precipitated the primary aragonite and secondary calcite crystals. Alternatively, the $\delta^{13}\text{C}$ composition of both solutions could have been similar, while differing in their $\delta^{18}\text{O}$ composition and temperature of the solution. Thus, the secondary calcite precipitated under the latter scenario might have provided $\delta^{18}\text{O}$ values keeping the same difference with the primary aragonite crystals if the change on the isotope composition of the parental solution was compensated at the time of precipitation by a different fractionation related to a change in temperature of the solution (e.g., a less negative $\delta^{18}\text{O}$ composition of the solution accompanied by a proportional increase in temperature).

On the contrary, U and Th show a different scenario. The U concentration of primary calcite is nearly two orders of magnitude lower than in aragonite samples (Fig. 12). This is expected due to different partition coefficients between both minerals (Railsback et al., 2002; Frisia et al., 2002; Ortega et al., 2005). However, considering the inter-sample variability, the U concentration in samples of secondary calcite is similar to those from aragonite samples. Concentration of Th is in consequence also similar in secondary calcite and aragonite samples (Table 1). Although Th is expected to have a limited mobility in solution, U is highly soluble in groundwaters (Richards and Dorale, 2003). So, U has higher probability to be mobilized during the recrystallization process. However, we do not observe a significant U leaching as observed with Sr. Therefore, data from EA5 stalagmite do not support an open system but a semi-closed system for U and Th and the secondary calcite has inheritance of the composition of the precursor mineral. An additional criterion to identify important modifications of the U signature is to compare the $\delta^{234}\text{U}$ of aragonite and calcite samples or study its variability among secondary calcite samples (Lachniet et al., 2012; Scholz et al., 2014). However, the aragonite and secondary calcite samples from EA5 are indiscernible within the inter-sample variability, whereas primary calcite clearly shows a distinct signature (Fig. 12). We have calculated the ages of samples of primary and secondary carbonates from EA5. However, we do not consider that secondary calcite dates are accurate, since the closed system principle to apply this geochronological method is not fully achieved. Four of the ages calculated from the base of the speleothem in the aragonite crystals are nicely replicated and are in stratigraphical order giving us confidence on their accuracy. One of the dates in aragonite shows a reversal, likely as a result of open system conditions in this sample. Although during the collection of aragonite samples we avoided the

proximity of large euhedral secondary calcite crystals, EBSD imaging shows occasional calcite crystals (<40 μm in size) disperse within the aragonite core. Involuntary sampling of small secondary calcite crystals could have caused inaccuracy in this age determination. However, U concentration and $\delta^{234}\text{U}$ values from this sample do not provide any diagnostic evidence to support the semi-open system conditions. Two samples from secondary calcite were collected laterally to those sampled in the aragonite core. One of them shows an age almost identical to those from the aragonite core, whereas the other shows an age shifted by ~ 3 ka. The more inaccurate date is older than expected, which could support U leaching. However, U concentration is not lower than in other samples and its $\delta^{234}\text{U}$ values do not show any distinctive signature. In this case, the large variability of U and $\delta^{234}\text{U}$ values in the aragonite prevents their use to identify semi-open system conditions in EA5 speleothem.

The elements forming relatively small chemical species (i.e., C, O, Mg and Sr) show open system conditions during diagenesis in EA5 speleothem, with the secondary calcite composition depending on the solution and a negligible influence of the precursor mineral. On the other hand elements forming larger chemical species such as U and Th suggest a semi-closed system during diagenesis. Studies of REE in aragonite recrystallized to calcite also suggest that the size of the element or chemical species is relevant for its mobilization during diagenesis (Banner and Hanson, 1990; Webb et al., 2009). Under conditions of most groundwaters U mobilizes as a large chemical species $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ (Reeder et al., 2000; Ortega et al., 2005), limiting its diffusion within the thin film solution. Additionally, U chemical species are preferentially incorporated on the surface of calcite crystals when particular steps/spiral growth hillocks are available, favouring higher concentrations than expected (Reeder et al., 2001, 2004; Rihs et al.,

2004; Doudou et al., 2012). A decrease in pH values and saturation indexes similar to those occurring during the aragonite recrystallization to calcite favours the formation of these steps (Reeder et al., 2001), facilitating the incorporation of U during the diagenetic process. This mechanism explains the relatively high U content in secondary calcites that replace aragonite (Eggins et al., 2005). In agreement with geochemical models (Banner and Hanson, 1990; Maliva, 1998), we consider that during diagenesis, the volume of solution versus mineral specific surface determines secondary calcite crystals recording: (1) some inheritance from the precursor mineral for certain elements/chemical species, or (2) the chemistry of the solution affected by their particular partition coefficients/fractionation factors. Thus, the geochemical modification during aragonite to calcite recrystallization in speleothems resulting from open or semi-closed system conditions for different elements and chemical species depends on the volume of water that interacts with the mineral at the time of recrystallization and the composition of the solution at the time of secondary calcite precipitation. The volume of water is controlled by the discharge of water passing through the speleothem and the time lapse since dissolution of aragonite to precipitation of calcite.

Available examples of speleothems affected by this mineral recrystallization support the geochemical dynamics previously described. Thus, U-series geochemistry is the main criterion to justify semi-closed system dynamics (Frisia et al., 2002; Railsback et al., 2002; Spötl et al., 2002) whereas those studies focused on trace elements or light stable isotopes are frequently reporting open system conditions (Martín-García et al., 2009, 2014; Perrin et al., 2014). Zhang et al. (2014) found speleothems composed of secondary calcite with occasional cores of aragonite preserved. In some specimens the

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were affected by open system conditions, whereas in other samples $\delta^{13}\text{C}$ values recorded inheritance from the aragonite. Although this pattern is not too common, other examples exist in samples recrystallized from aragonite to calcite in environments other than caves (Rehman et al., 1994). This is not surprising since the $\delta^{13}\text{C}$ takes three orders of magnitude more water-rock interaction to reach equilibrium with the solution compared to the $\delta^{18}\text{O}$ (Banner and Hanson, 1990). Therefore, those speleothems not completely equilibrated with the solution are probably the result of a recrystallization that took place under a relatively large discharge and/or completed in a short time period. Thus, the particular case of EA5 stalagmite records semi-closed system conditions for U and Th, in relation to its specific water flow and rate of recrystallization. However, speleothems affected by different environmental dynamics might record these and other elements being affected by open or semi-closed system conditions, always following a scale of elements requiring different volumes of water-rock interaction to be mobilized (Banner and Hanson, 1990; Maliva, 1998).

4.3. Diagenetic evolution of EA5 stalagmite and interpretation of its geochemical signature

The base of EA5 stalagmite has preserved a core of 45 mm of aragonite that precipitated during the Younger Dryas. During this period the drip waters that fed this speleothem were continuously supersaturated with respect to aragonite and calcite, although the elevated Mg content of the waters (Domínguez-Villar et al., 2012) favoured the precipitation of aragonite (Bischoff, 1968; de Choudens-Sánchez and González, 2009). The drip hydrochemistry was modified at some point after 12.3 ka BP (not necessarily soon after), having solutions subsaturated in aragonite and supersaturated in calcite.

This change of drip hydrochemistry caused the progressive replacement of aragonite by secondary calcite through a thin film of water. This was possible because of aragonite texture and porosity favouring the drip water percolation through the speleothem. Despite the solution being supersaturated with respect to calcite, this mineral did not precipitate on the surface of the speleothem due to the role of dissolved Mg in the inhibition of calcite precipitation (Bischoff, 1968; Railsback, 2008). However, the stalagmite top records one millimetre thick lamina of primary calcite composed of several growing bands. The primary calcite has a dense packing with limited porosity, which likely prevented further percolation of drip water into the speleothem. The lamina has lateral continuity and covers the whole surface of the speleothem up to its base. The precipitation of this lamina was likely related to drip waters with low Mg/Ca ratio that favoured occasional precipitation of calcite ~2 ka ago. During numerous survey campaigns to the cave in the past decade, we never observed active drip over EA5 stalagmite site. Dates suggest an important hiatus between the primary calcite lamina and the rest of the speleothem. So, it is possible that this stalagmite did not receive any drip flow during most of the Holocene, and only extreme isolated flush events caused occasional drip flow. Flush events have little time to interact with the host rock causing relatively low Mg/Ca ratios that favour primary calcite precipitation. We consider that the diagenetic front and euhedral crystals within the aragonite core ceased the recrystallization process when drainage into the speleothem stopped ~2 ka ago. The dense packed calcite lamina likely prevented the percolation of drip waters, but we do not discard an earlier cessation of the drainage into the speleothem. Thus, we assume that the replacement of aragonite to calcite observed in EA5 stalagmite took place in a maximum period of 10 ka. The triggers for diagenesis of speleothems are related to climate changes in many cases (Cabrol and Coudray, 1982; Woo and Choi, 2006;

Scholz et al., 2014). We speculate that climate changes occurring soon after Younger Dryas could have decreased saturation indexes in Eagle Cave (e.g., by diluting the solution due to enhanced rainfall and/or reduction of cave ventilation), since also other speleothems from the same cave stopped precipitating at that time (Domínguez-Villar et al., 2013b).

Secondary calcite crystals often evolve from tiny calcite crystals attached to the surface of aragonite crystals (Frisia et al., 2002; Martín-García et al., 2009) although calcite nuclei are not essential (Carlson, 1983). Therefore, the recrystallization process starts from inside the speleothem despite the external source of water (Melim and Spilde, 2011). The aragonite core of EA5 is located slightly off the central axis of the speleothem and does not extend until the side of the stalagmite. This supports aragonite replacement from solutions reaching this location from the axial sector of the speleothem and in less extent from infiltrations parallel to the external surface of the stalagmite. Several euhedral secondary calcite crystals in different stratigraphical levels of the aragonite core suggest that recrystallization occurred at the same time at different distance from the base of the sample. Also, equant secondary calcite crystals with different orientation are often widely distributed along the speleothem supporting multiple sites of initial nucleation in different stratigraphical levels. Water flow is an important control in aragonite to calcite replacement (Tomiak et al., 2016), and the recrystallization process likely started in those regions with higher hydraulic conductivity. However, we already pointed out that large size variations in contiguous crystals occur along the speleothem, neatly following speleothem growth surfaces. This might be related to textural changes and/or to periods of aragonite precipitation on the surface of the speleothem and subsequent replacement by calcite. Therefore, we cannot

confirm that drip water remained constantly subsaturated in aragonite and supersaturated in calcite during the diagenetic evolution of EA5 speleothem. In other words, alternation of periods with secondary calcite replacing aragonite with periods when increase in saturation indexes again favoured the precipitation of aragonite at the top of the speleothem causing vertical accretion were possible. The alternation of consecutive periods of early diagenesis with periods of stalagmite growth implies that the replacement of lower stratigraphical levels in the stalagmite took place earlier in time. Thus, speleothems with subsequent stages of early recrystallization may record a coherent relationship between distance from the base and age resulting in consecutive dates being in stratigraphical order (i.e., younger dates at the top of the speleothem).

Compositional maps of EA5 stalagmite show differential concentrations of Mg and Sr controlled by mineralogy as shown by secondary calcite crystals with homogeneous distribution of elements (Fig. 6). However, other crystals show a zoned pattern (Figs. 7, 8 and 9). EBSD analyses confirmed that the cause of this zoned pattern is not related to aragonite relics within secondary calcite crystals, supporting a variable composition of the parental solution as origin of the zoned patterns. The solution for all secondary crystals is the same: drip water. Nevertheless, in those portions of the speleothem with important hydraulic conductivity, the chemical composition of the solution will be controlled by the advection transport mechanism. On the other hand, the transport of elements and chemical species in the sectors of the speleothem with low hydraulic conductivity will be dominated by diffusion. Although diffusion is the only mechanism expected in thin films due to capillary forces preventing water flow (Pingitore, 1976; Carlson, 1983), advection in the proximity of the diagenetic front will dominate the hydrochemistry of the recrystallization. We consider that zoned patterns were closer to

preferential water flows that favoured diffusion of intra-annual Mg/Ca and Sr/Ca variations. These oscillations were smoothed in locations away from preferential flow, causing homogenization of the solution. Mg/Ca of several drip sites in Eagle Cave has a seasonal pattern (Domínguez-Villar et al., 2012). Therefore, we interpret the variable Mg composition of the zoned pattern as seasonal cycles of calcite precipitation. Thus, the thickness of compositional bands in zoned pattern crystals provides an estimate of the rate of recrystallization. Thickness of Mg compositional bands measured in four different sites of EA5 stalagmite varies between 5 and 170 μm ($n=40$) with an average thickness ($\pm 1\sigma$) of $50 \pm 45 \mu\text{m}$. With an average advance of diagenetic fronts at a rate of 50 $\mu\text{m}/\text{yr}$, a stalagmite having multitude of initial nucleation sites will complete the aragonite to secondary calcite recrystallization within few centuries. Frisia et al. (2002) found that diagenesis of one of their aragonite speleothems could have taken place within 1 ka. Lachniet et al. (2012) also found an aragonite speleothem that was recrystallized to calcite within centuries. Additionally, cave pearls precipitated on artificial substrates in a mine were found to be recrystallized (calcite to calcite) one order of magnitude faster (Melim and Spilde, 2011). Although rates of recrystallization in speleothems might vary over orders of magnitude, these data support that recrystallization of an aragonite speleothem with secondary calcite may start as early as days or months after its primary deposition and be completed within some hundreds of years.

During the recrystallization process, the geochemistry of EA5 stalagmite has been clearly modified for Mg and Sr as well as for oxygen and carbon isotope ratios. Thus, the secondary calcite crystals record the composition of the parental solution affected by the partitioning coefficient/fractionation factor between water and calcite. Stable isotope

profiles along the stalagmite show variability of $\sim 1\text{‰}$ in $\delta^{18}\text{O}$ and $\sim 3\text{‰}$ in $\delta^{13}\text{C}$ (Fig. 11A). The range of variability in these signals is in agreement with those recorded in other Eagle Cave speleothems since the Younger Dryas (Domínguez-Villar et al., 2013b). However, parallel stable isotope profiles in EA5 stalagmite along calcite and aragonite sectors of the speleothem show that the structure of the primary isotope signals was completely lost during diagenesis. A different response has been described by other researchers who record similar structure between parallel isotope records in secondary calcite and aragonite samples (Zhang et al., 2014; Lachniet, 2015). This could be related either to geochemical inheritance of the precursor mineral (more likely in the $\delta^{13}\text{C}$ than in the $\delta^{18}\text{O}$ signal), or due to early diagenesis, where the composition of the fluid responsible for the recrystallization has changed as much as the fractionation factor between both minerals. Early diagenesis in open system conditions may have preserved the structure of near-primary records, but the absolute values will differ due to different fractionation factors/coefficient partitions between aragonite and calcite. The lapse time between aragonite and secondary calcite precipitation is also critical for U-series geochemistry (Scholz et al., 2014). Early diagenesis will have a limited impact on ages calculated from U-series data (Frisia et al., 2002; Spötl, et al., 2002; Scholz et al., 2014). Thus, Lachniet et al. (2012) found that secondary calcites provided dates between 300 and 600 yr older than those from aragonite in same stratigraphical levels, confirming a limited impact of diagenesis in the accuracy of speleothem chronology. Although older ages are expected due to U leaching in the system during open system conditions, the opposite can also occur (Ortega et al., 2005; Wassenburg et al., 2012; Scholz et al., 2014).

Seasonal changes in saturation index are common in cave waters due to cave ventilation, prior calcite precipitation, or other factors (Railsback et al., 1994; Fairchild et al., 2000; Spötl et al., 2005). Inter-annual oscillations due to changes in climate or other environmental controls of the carbon system can also impact variability of saturation indexes (Scholz et al., 2014). These mechanisms can be responsible for early diagenesis at seasonal or inter-annual timescales that could explain the partial preservation of geochemical signatures after aragonite to calcite transformation. In these scenarios vertical accretion of the speleothem alternates with periods of replacement of aragonite by secondary calcite. However, in the case of EA5 stalagmite, U-Th dating of the aragonite core shows that the recrystallization process started at least 1 ka after the aragonite started its precipitation. At the base of the sample, where the aragonite core is preserved, the recrystallization did not follow any stratigraphical order, since secondary calcite crystals started their nucleation in different stratigraphical levels at the same time. Therefore, no relationship between distance from the base and age in the secondary calcite crystals is expected. However, we can not confirm that the full speleothem was precipitated as aragonite (except the topmost primary calcite lamina) before the recrystallization started, since alternating periods of drip water subsaturated and supersaturated in aragonite were plausible. So, the preservation of paleoclimatological/paleoenvironmental signatures in secondary calcite sectors of the sample at scales <1ka are not completely spoiled for the middle and upper sectors of this speleothem. Thus, secondary calcite of speleothems formed after alternating periods with aragonite precipitation and calcite recrystallization, may preserve certain distance from the base-age relationship. The resolution of the record in these speleothems depends on the frequency of such alternation and the rate of advance of diagenetic fronts.

5. CONCLUSIONS

In EA5 stalagmite, aragonite was replaced by secondary calcite as a consequence of a change in drip hydrochemistry, where the solution became subsaturated in aragonite but still was supersaturated in calcite. Permeability of the aragonite speleothem favoured the drip water to infiltrate into the speleothem enabling multiple nucleation sites at different stratigraphical levels. Despite the porosity reorganization resulting from the recrystallization process, the original growing bands of the speleothem are clearly preserved. The speleothem records sharp changes in secondary calcite crystal size following growing bands of the former aragonite speleothem in the middle and upper sectors of the speleothem. These variations could respond to textural changes in the precursor mineral, or to successive periods of recrystallization. A solution being alternatively subsaturated and supersaturated in aragonite could have caused periods of recrystallization, where secondary calcite replaced previous aragonite crystals, with periods of aragonite precipitation causing speleothem accretion. The top millimetre of the speleothem records a primary calcite lamina that represents drastic changes in the drip hydrochemistry, likely the result of modifications of the drip hydrology dynamics.

Composition of Mg and Sr, as well as carbon and oxygen isotope ratios of aragonite are not inherited in secondary calcite crystals from same stratigraphical levels. Open system conditions in relation to these elements caused the secondary calcites to record the composition of the solution at the time of recrystallization, affected by calcite partition coefficients/fractionation factors. The structures of parallel isotope records from the base of the stalagmite, collected along the growth direction of the speleothem in

aragonite and calcite sectors, do not resemble to each other. This is expected because recrystallization took place: (1) at least 1 ka after primary mineral deposition, and (2) under open system conditions with multiple nucleation sites distributed across different stratigraphical levels favoured by preferential flow paths. However, if the textural changes in secondary calcite recorded in the middle and upper sectors of the speleothem are the result of alternating periods of aragonite precipitation and recrystallization, secondary calcites might record some distance from the base-age relationship. On the other hand, the recrystallization occurred in a semi-closed system in relation to larger chemical species such as those formed by U and Th. Due to the larger volume of their chemical species and their specific solubility their effective diffusion transport requires larger periods of water-rock interaction and/or larger amount of water passing through the speleothem. Thus, dates calculated from U-series geochemical data support a semi-closed system. Parallel analysis in aragonite and calcite samples from the base of the stalagmite show that the accuracy of calculated ages differ notably depending on particular samples, suggesting significant variability in the diagenetic conditions within the speleothem. U concentration and $\delta^{234}\text{U}$ values were not diagnostic criteria for identifying inaccurate dates due to large variability of these parameters in aragonite samples.

Most of the primary geochemical record of EA5 stalagmite was lost during the recrystallization process. However, the study of diagenetically affected speleothems provides valuable information about the timing and geochemical composition of fluids that caused their diagenesis. The hydrochemical changes that triggered EA5 stalagmite recrystallization were likely related to climate changes at the onset of the Holocene. Paleoclimate and paleoenvironmental records can be obtained from former aragonite

speleothems recrystallized to calcite when diagenesis takes place in an early stage (e.g., speleothems formed from alternating drip waters being subsaturated and supersaturated in aragonite at seasonal or inter-annual timescales). Under these early diagenesis conditions U-Th dates are more accurate than in other semi-closed system scenarios (Scholz et al., 2014), and the speleothem has distance from base-age relationship with a precision depending on the thickness of every new event of aragonite precipitation. In any case, even these speleothems are subject to variability between open and semi-closed system conditions in relation to different elements, depending on local hydrological and hydrochemical conditions. This research has shown that speleothems affected by aragonite to calcite recrystallization record valuable paleoenvironmental information, although even in the best scenarios, their geochemical signature is likely to be partially affected by factors other than the original hydrochemistry of the parental solution. Therefore, though speleothems affected by diagenesis should be taken with caution, they still can record good paleoclimate records (Lachniet, 2015).

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FIGURE CAPTIONS

Fig. 1. Scanned section of EA5 stalagmite. The white-coloured sector at the base of the stalagmite is composed of aragonite whereas the rest of the sample is dominated by secondary calcite. The last millimetre of the stalagmite is composed of primary calcite. Several euhedral secondary calcite crystals within the aragonite core suggest that diagenesis progressed from multiple nucleation sites at different stratigraphical levels rather than from a unique diagenetic front. Notice the neat preservation of growth bands in the middle and upper sectors of the speleothem.

Fig. 2. Proportion of aragonite in secondary calcite crystal samples obtained by X-ray diffraction analyses along the growth direction of EA5 stalagmite.

Fig. 3. Secondary electron microscopy images of EA5 stalagmite. (A) Texture of aragonite fibres, from thick section. (B) Euhedral secondary calcite crystal enclosed in aragonite crystals, from thick section. (C) Texture of aragonite fibres, from fresh cut in hand specimen. (D) Straight diagenetic front, from fresh cut in hand specimen. Aragonite is in the lower side and secondary calcite in the upper side of the image. (E) Irregular diagenetic front, from fresh cut in hand specimen. Aragonite is in the upper side and secondary calcite in the lower side of the image. Notice the textural and mineralogical relics within the secondary calcite. (F) Detail of an irregular diagenetic front showing aragonite needles partially dissolved, from fresh cut in hand specimen.

Fig. 4. Optical microscope images of EA5 stalagmite using plane (pp) or crossed polarized (cp) light. (A) Mosaic of secondary calcite crystals with relics of aragonite fibres (pp). (B) Columnar secondary calcite crystals replacing former fans of aragonite in the centre of the speleothem (pp). Notice that the vertical oriented c- axis of the columnar crystals has fewer relics compared to off the axis positions, where former fibres diverged from vertical orientation. (C) Columnar and equant secondary calcite crystals of different sizes with variable proportion of relics (cp). (D) Detail of non-coalescent equant secondary calcite crystals showing higher density of relics in the core of the crystals (cp). (E) Euhedral calcite crystal showing variable density of relics during different periods of crystal growth (pp). Notice that the c-axis of this secondary calcite crystal is oriented oblique in relation to the vertically oriented c-axis of aragonite fibres. (F) Set of columnar crystals with divergent orientations (cp).

Fig. 5. Images of mineral phases obtained by electron backscatter diffraction (EBSD) analyses. Forward scatter electron (FSE) images for the same sectors are provided first to identify rock textures. cc: secondary calcite, ar: aragonite. EBSD images show calcite (blue), aragonite (red) and cells with poor data acquisition (black) due to pores, cracks or poor polishing of the surface. (A-B) FSE and EBSD images of euhedral crystal of secondary calcite enclosed by aragonite. (C-D) FSE and EBSD images of secondary calcite crystals with mineral relics of aragonite. (E-F) FSE and EBSD images of a diagenetic front with secondary calcites having compositional zoned pattern (see Fig. 9). Previous particle-induced X-ray emission (PIXE) analyses in the same area prevented a better polishing of the surface, increasing the number of cells without information. However, the image clearly shows a limited number of aragonite relics that do not concentrate preferentially along isochronous areas of crystal growth.

Fig. 6. Compositional distribution of elements calculated after particle-induced X-ray emission (PIXE) analyses from a diagenetic front of EA5 stalagmite. cc secondary calcite, ar: aragonite. (A) Ca compositional map is provided to visualize the texture of the analysis area. (B) Mg compositional map. Average Mg content of aragonite is 15200 ± 207 ppm and calcite 18000 ± 173 ppm. (C) Sr compositional map. Average Sr content of aragonite is 117 ± 2 ppm and calcite 48.3 ± 1 ppm.

Fig. 7. Distribution of Mg obtained with electron probe microanalysis (EPMA) from a sector of EA5 stalagmite where secondary calcite crystals enclose aragonite relics. (A) Back scatter (BS) image of the extended selected area. Light grey areas are aragonite relics. The white square frames the area of compositional mapping. (B) Mg compositional map showing zoned pattern in the secondary calcite crystals. White arrows indicate aragonite relics with lower Mg content.

Fig. 8. Compositional maps of two areas from the diagenetic front of EA5 stalagmite obtained with electron probe microanalysis (EPMA). cc secondary calcite, ar: aragonite. Back scatter (BS) image is provided to identify rock textures and Ca distribution maps to show cells with low counts due to porosity. The white arrows in BS images point towards the direction of aragonite speleothem growth (up). Images E and F show Mg compositional maps in both areas. (A-C-E) Three different secondary calcite crystals showing zoned compositional pattern. Continuity of compositional banding between crystals indicates that they grew simultaneously. (B-D-F) Secondary calcite crystal at the diagenetic front with zoned compositional patterns. Notice the different morphology of the crystal termination during its evolution depending on the

Mg content. Dominant growth direction of secondary calcite crystals in these two particular examples is nearly opposite to that of the aragonite speleothem. Although other secondary crystals often have different preferential growth directions, these examples illustrate how the distance from the base-age relationship is impacted in recrystallized speleothems.

Fig. 9. Compositional distribution of elements calculated from particle-induced X-ray emission (PIXE) analyses from a sector of the diagenetic front in EA5 stalagmite where secondary calcite crystals have a zoned compositional pattern. cc secondary calcite, ar: aragonite. (A) Ca compositional map is provided to visualize the texture of the analysis area. Notice that a fracture extends along the diagenetic front at this particular site. (B) Mg compositional map. Average Mg content of aragonite is <450 ppm. Mg content in secondary calcites alternates between 1100-3300 and <850 ppm. (C) Sr compositional map. Average Sr content of aragonite is 272 ± 5 ppm. Sr content in secondary calcites alternates between 80-105 and 100-170 ppm.

Fig. 10. Optical microscope image and Sr compositional map from a sector of euhedral crystal calculated from particle-induced X-ray emission (PIXE) analyses. Black square in the upper image indicates the area of analysis. Porosity between crystals has dark blue colour in the compositional map. Mg analyses were below detection limits due to large Ca tail in the spectrum. Distribution of Sr varies significantly along isochronous areas of the crystal, likely related to local permeability of the sample impacted by the orientation of aragonite crystals. The Sr content in the whole area with zoned pattern is 250 ± 1 ppm, whereas Sr content in the homogeneous area is 147 ± 1 ppm.

Fig. 11. Oxygen and carbon stable isotope records of EA5 stalagmite. (A) Isotope records of secondary calcites along the central axis of the speleothem. The grey shaded area shows the base of the stalagmite shown in B. (B) Isotope records of two parallel profiles from the base of the stalagmite collected along the speleothem growth direction in the aragonite (triangles) and secondary calcite sectors (circles). (C) Three isotope profiles (black, grey and white symbols) along speleothem growth bands. Two of the profiles cross the diagenetic front between aragonite (triangles) and secondary calcite (circles). The average compositional shift between aragonite and calcite in these two profiles is in agreement with the mean shift recorded along the growth direction of the speleothem.

Fig. 12. Calculated age and U-series geochemistry plots. Colour of symbols is related to the mineralogy of the samples: aragonite (grey) and calcite (black). (A) Graph showing the relationship between age and distance from the base. Notice that the age axis is cut to facilitate visualization. Arrows indicate samples that are clearly out of stratigraphical order. (B) Graph showing the relationship between U content and measured $\delta^{234}\text{U}$. Arrows point to the same two samples selected in graph A. Notice that neither U content nor $\delta^{234}\text{U}$ values differ significantly from primary aragonite samples, preventing their use as indicators of open system conditions during secondary calcite precipitation.

Table 1. U-series geochemistry and calculated age.

Sample (1)	DFB [mm] (2)	^{238}U [ppb]	^{232}Th [ppt]	$^{230}\text{Th}/^{232}\text{Th}$ [Act.]	$^{230}\text{Th}/^{238}\text{U}$ [Act.]	$\delta^{234}\text{U}_m$ (3)	Calculated age [ka BP]
EA5-7cc	161	38.1 ± 0.0	47.0 ± 1.3	61.0 ± 4.0	0.02464 ± 0.00145	101.7 ± 1.4	2.375 ± 0.148
EA5-3cc	148	931.1 ± 2.3	1.0 ± 5.8	3.7×10^5 $\pm 2.2 \times 10^6$	0.12361 ± 0.00080	147.7 ± 2.8	12.340 ± 0.091
EA5-2cc	82	1859.9 ± 5.7	1.7 ± 3.4	4.2×10^5 $\pm 8.7 \times 10^5$	0.12209 ± 0.00064	133.6 ± 2.8	12.341 ± 0.076
EA5-6cc	36	998.9 ± 3.1	569.1 ± 3.9	812.1 ± 7.1	0.15138 ± 0.00094	132.6 ± 2.8	15.531 ± 0.112
EA5-5cc	10	843.7 ± 2.4	16.5 ± 3.1	20216.9 ± 3766.3	0.12930 ± 0.00078	123.8 ± 3.1	13.162 ± 0.094
17ar	38	777.1 ± 0.7	95.3 ± 8.8	3036.5 ± 282.5	0.12188 ± 0.00087	130.9 ± 1.3	12.341 ± 0.095
EA5-4ar	37	1373.8 ± 3.4	1.3 ± 8.8	4.0×10^5 $\pm 2.7 \times 10^6$	0.12278 ± 0.00098	131.3 ± 2.9	12.444 ± 0.111
EA5-1ar	10	1046.1 ± 2.9	0.0 ± 6.1	3.8×10^6 $\pm 2.3 \times 10^{12}$	0.11793 ± 0.00085	123.8 ± 3.1	12.008 ± 0.098
18ar	7	1150.1 ± 1.5	0.9 ± 5.6	5.2×10^5 $\pm 3.3 \times 10^6$	0.12729 ± 0.00052	127.0 ± 1.6	12.977 ± 0.060
43ar	5	1426.5 ± 1.7	6.1 ± 4.1	90111.2 ± 59586.5	0.12767 ± 0.00039	128.7 ± 1.4	12.996 ± 0.046

(1) "cc" stands for calcite and "ar" for aragonite samples; (2) DFB stands for distance from base; (3) "m" stands for measured