# Stable isotope data as constraints on models for the origin of coralloid and massive speleothems: The interplay of substrate, water supply, degassing, and evaporation

Guglielmo A. Caddeo [a,*], L. Bruce Railsback [b], Jo De Waele [c], Franco Frau [a]

[a] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Via Trentino 51, 09127 Cagliari, Italy
[b] Department of Geology, University of Georgia, Athens, GA 30602-2501, USA
[c] Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Bologna, Via Zamboni 67, 40126 Bologna, Italy

## ABSTRACT

Many speleothems can be assigned to one of two morphological groups: massive speleothems, which consist of compact bulks of material, and coralloids, which are domal to digitate in form. Faster growth on protrusions of the substrate occurs in the typical growth layers of coralloids (where those layers are termed "coralloid accretions"), but it is not observed in the typical layers of massive speleothems, which in contrast tend to smoothen the speleothem surface (and can therefore be defined as "smoothing accretions"). The different growth rates on different areas of the substrate are explainable by various mechanisms of $CaCO_3$ deposition (e.g., differential aerosol deposition, differential $CO_2$ and/or $H_2O$ loss from a capillary film of solution, deposition in subaqueous environments). To identify the causes of formation of coralloids rather than massive speleothems, this article provides data about $\delta^{13}C$ and $\delta^{18}O$ at coeval points of both smoothing and coralloid accretions, examining the relationship between isotopic composition and the substrate morphology. In subaerial speleothems, data show enrichment in heavy isotopes both along the direction of water flow and toward the protrusions. The first effect is due to $H_2O$ evaporation and $CO_2$ degassing during a gravity-driven flow of water (gravity stage) and is observed in smoothing accretions; the second effect is due to evaporation and degassing during water movement by capillary action from recesses to prominences (capillary stage) and is observed in subaerial coralloids. Both effects coexist in smoothing accretions interspersed among coralloid ones (intermediate stage). Thus this study supports the origin of subaerial coralloids from dominantly capillary water and disproves their origin by deposition of aerosol from the cave air. On the other hand, subaqueous coralloids seem to form by a differential mass-transfer from a still bulk of water toward different zones of the substrate along diffusion flux vectors of nutrients perpendicular to the iso-depleted surfaces. Finally, this isotopic method has proved useful to investigate the controls on speleothem morphology and to obtain additional insights on the evolution of aqueous solutions inside caves.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Speleothems are mineral deposits that are chemically precipitated in caves, and they include flowstones, stalactites, stalagmites, and many other less familiar but diverse forms (Hill and Forti, 1997). Most speleothems consist of sequences of layers readily recognizable in sections perpendicular to their growth surface. Petrographic observations of these sections reveal two specific types of the growth surface progression through time, leading to two very different morphologies of the resulting speleothem. To distinguish between these two specific patterns of growth and their relationship with time, this paper will distinguish between smoothing and coralloid accretions. The word

"accretion" refers to the material deposited in a single speleothem during a fixed period of time, which can be a continuous or discontinuous layer, because it is defined as a temporally-bounded, rather than physically-bounded, entity. "Smoothing accretion" will refer to an accretion that is uniform or thinner on protrusions than in depressions of its substrate, tending to smooth any pre-existing topography and to form a compact bulk of material (Fig. 1a). On the other hand, "coralloid accretion" will refer to an accretion that thickens gradually from the depressions toward the protrusions of the substrate and thus imparts domal to digitate forms to the resulting speleothem (Fig. 1b).

Sequences of coralloid accretions are usually defined as coralloids (Figs. 1, 2) or by the colloquial name "popcorn" (Hill and Forti, 1997). On the other hand, sequences consisting mostly of smoothing accretions have been designated as massive speleothems (Alonso-Zarza et al., 2011) or bulk speleothems (White, 2012). These are further differentiated into various types, depending on their location and general

* Corresponding author.
E-mail addresses: mesucosta@alice.it (G.A. Caddeo), rlsbk@gly.uga.edu (L.B. Railsback), jo.dewaele@unibo.it (J. De Waele), frauf@unica.it (F. Frau).
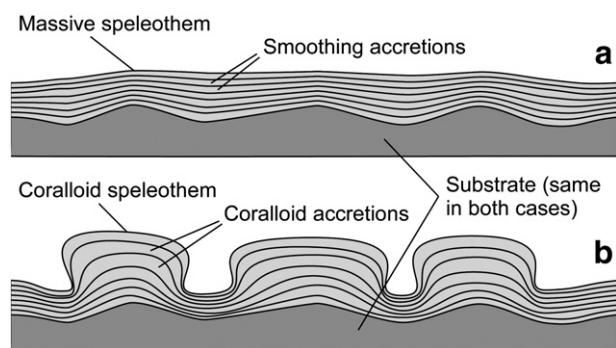
**Fig. 1.** Sketches illustrating a massive speleothem (a) and a speleothem consisting of corralloids (b). Both sketches show the accretions (material deposited in a single speleothem during a fixed period of time). Massive speleothems are sequences of typical smoothing accretions which do not grow faster on substrate protrusions than on substrate depressions (a). Corralloids are sequences of typical corralloid accretions growing faster on substrate protrusions than on substrate depressions (b).

morphology (e.g., flowstones, stalactites, stalagmites). Depending on the prevalent type of accretion, especially in the proximity of the speleothem surface, the resulting form of the speleothem can also be intermediate between a massive and a corralloid type (Stepanov, 1997). Many stalagmites or stalactites, including stalagmites used in paleoclimate research (Fairchild and Baker, 2012), are indeed intermediate forms, because they show a complete or partial corrugated surface and consist of assemblages of smoothing and corralloid accretions (Fig. 2e and f).

To explain the cause of the growth pattern of corralloids and its deviance from that observed in massive speleothems, various hypotheses have been advanced. Corralloids can form both subaerially and subaqueously and, in theory, by different mechanisms. Subaqueous deposition of corralloids seems comparatively straightforward, in that the source of constituents surrounds the growing speleothem. On the other hand, subaerial deposition of corralloids in the absence of standing or flowing water is more problematic and has been explained by two very different mechanisms. One is deposition from aerosols, either as solid material (Cser and Maucha, 1968; Klimchouk et al., 1995; Dublyansky and Pashenko, 1997) or as hydroaerosols from splashes (Perna, 1989), wherein the tips of corralloids grow faster because they are fed by aerosol particles coming from a wider angular range compared to the re-entrant parts of the corralloids' surface (Fig. 3a). The second is deposition from a thin capillary film of supersaturated solution (Şerban et al., 1961; Moroshkin, 1976; Maltsev, 1993, 1994, 1997; Stepanov, 1997, 1999; Self and Hill, 2003). This solution could have, in turn, various sources that include splash effects of dripping water (Balch, 1948), seepage through the cave bedrock, and condensation (Stepanov, 1999). The latter could result from cycles of condensation and evaporation (Istvan and Micle, 1994).

Dawkins (1874) already concluded that corralloids start to grow from a slight elevation of the substrate, probably because of greater evaporation of water there than from the surrounding recessive portions. Thrailkill (1965) attributed the origin of cave popcorn to the deposition of $CaCO_3$ mainly driven by $CO_2$ loss from a thin film of solution. Slyotov (1985) identified a geometric advantage for protruding regions to grow by mass-transfer with the medium. If, along the mass-transfer pathway between a point on a growth surface and the air, there is another growth surface which can lose $H_2O$ or $CO_2$ molecules from its capillary film, the two surfaces exchange an amount of these molecules and thereby inhibit each other's growth by increasing the concentration of $H_2O$ or $CO_2$ molecules in the intervening space. This effect, of course, should be greater as the two branches of corralloids approach each other. According to Slyotov (1985), this is why a gap is sustained between the two surfaces, rather than a joining of the two (Fig. 3b).

In light of the apparent importance of solute supply and substrate control to the hypothesized origins of the various kinds of speleothems, this

paper reports measurements of $\delta^{13}C$ and $\delta^{18}O$ from samples positioned sequentially along growth layers (accretions) in various speleothems. These measurements allow estimation of the varying extent of degassing and evaporation from water moving across the speleothems, and thus allow evaluation of the hypothesized origins of these varied speleothems, and especially of corralloids.

## 2. Speleothems studied

To compare isotopic characteristics of corralloid and smoothing accretions, we analyzed subaerial corralloids, subaqueous corralloids, a stalactite on which corralloids have formed, a flowstone, and a stalagmite with corralloids on its flanks. With the exception of the last one, these speleothems come from Is Zuddas Cave in Sulcis, the southwestern region of the Mediterranean island of Sardinia, the more northwestern of Italy's two large islands. The cave lies in dolomitized carbonate rocks of the Lower Cambrian Gonnesa Group (Bechstadt and Boni, 1996). This cave is about 1500 m long and is characterized by a succession of rooms connected by narrow natural tunnels. In this cave a wide variety of speleothem types has been identified, including flowstones, stalactites, stalagmites, subaerial and subaqueous corralloids, pool spar, frostworks, helictites and many others (Caddeo et al., 2008a, 2008b). Designations of these speleothems all begin with "IZ" for "Is Zuddas".

The stalagmite with corralloids on its flanks, which comes from the collection of Prof. George A. Brook of the University of Georgia (U.S.A.), was collected from Drotsky's Cave, located in the Gcwihaba Hills of the Ngamiland District of northwestern Botswana, within the Kalahari Desert (Africa). Drotsky's Cave is a little over 400 m long and lies in dolomitic marble of the upper Proterozoic Otavi Group or Damara Sequence (Railsback et al., 1994). Speleothems observed in this cave are most commonly stalactites and stalagmites, and the stalagmites like the one studied here have locally been coated with subaerial corralloids. The designation for this stalagmite begins with "DR" for "Drotsky's".

## 3. Methods and materials

Powders were drilled from sequential locations along the stratification of the layers in 6 speleothems. Layers were selected for (i) homogeneity, with no variation in mineralogy along the layer; (ii) sufficient distinction to allow clear identification; and (iii) sufficient thickness for extraction of samples. The latter is problematic because layers in corralloids are commonly very thin in the re-entrants between projections. Powders for X-ray diffraction (XRD) and isotopic analyses were sampled using a dental drill. Cutting of the speleothems, preparation of thin sections, and optical studies by conventional petrographic microscope were performed both at the Department of Chemical and Geological Sciences of the University of Cagliari (Sardinia, Italy) and at the Department of Geology of the University of Georgia (Athens, Georgia, USA). The mineral phases were also determined (Table 1) at both departments, respectively using an X-ray diffractometer Panalytical X'Pert Pro, operating at 40 mA and 40 kV with monochromatic CuKα radiation, and a Scintag X-ray diffractometer operating at 40 mA and 40 kV with monochromatic CoKα radiation.

Carbon and oxygen stable isotope analyses were performed at the Department of Geology of the University of Georgia (Athens, USA) by a method modified from McCrea (1950). About 5 mg of powder for each analysis point was reacted under vacuum in 100% phosphoric acid at 50 °C. The resulting $CO_2$ was extracted on a conventional vacuum line and analyzed on Finnigan MAT Delta E and MAT 252 mass spectrometers. Laboratory standards were prepared and analyzed with each batch of samples. Standards have been calibrated to NBS-19 ($\delta^{13}C = +1.95$, $\delta^{18}O = -2.2‰$ relative to VPDB) and NBS-18 ($\delta^{13}C = -5.0$ and $\delta^{18}O = -23.0‰$ relative to VPDB). Isotopic results are normalized to the lab standards using a two-point scale, so that all $\delta^{13}C$ and $\delta^{18}O$ values herein are reported relative to VPDB. The 2-sigma error of the combined extraction and analysis is 0.04‰ for $\delta^{13}C$ and 0.05‰ for $\delta^{18}O$.