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**High-resolution synchrotron X-ray fluorescence investigation of calcite coralloid speleothems:
Elemental incorporation and their potential as environmental archives**

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ABSTRACT

Synchrotron high-resolution and micro-X-ray fluorescence elemental mapping of two coeval coralloid speleothems from Lamalunga Cave (Italy) are complemented with petrographic, morphological and microstratigraphic studies. The importance of these speleothems relies on their direct and indirect association with a complete Neanderthal skeleton ('Altamura Man') found inside the cave. The coralloids grew discontinuously between 64.6 ka and the Holocene and reveal exceptionally high concentrations of Mg, Sr and Si, particularly on convex surfaces, where evaporation is more intense. The incorporation of trace elements depends on several factors including location, shape and geometrical evolution during their growth, as well as climate and environmental parameters. This resulted in calcite precipitation with Sr compositions from 100 to 1200 ppm and an average concentration of 7000 ppm Mg. An unusually high Si content (up to 16%) is possibly derived from volcanic ash transported as particulate and in solution inside the cave. The most common fabrics observed consist of non-fluorescent elongated columnar calcite forming clean isopachous bands and fluorescent fibre-like crystals associated with laminated, lenticular bands high in Sr, Mg and Si. Variability in Sr, Mg and Si concentrations appears to induce fabric changes in the coralloids. Elongation and lattice distortion of the crystals was found to coincide with high Mg concentrations. The transition from compact elongated to open to fibre-like, is here interpreted as due to high concentrations of Si and Sr, which are preferentially incorporated in the speleothem at crystal boundaries and intra-laminae. It is here inferred that coralloid fabric changes and their elemental content potentially record local rainfall variations through time, with the clean compact calcite marking high infiltration and open fibre-like and micrite fabrics recording dry periods.

Keywords – Calcite fabric, coralloids, Lamalunga, magnesium, micro-XRF, silica, strontium, synchrotron.

INTRODUCTION

Speleothems are geologic climate archives that can be precisely dated by U-Th methods, providing that they have not undergone destructive diagenesis (Hellstrom, 2003; Richards and Dorale, 2003; Fairchild and Baker, 2012; Frisia, 2015; Bajo et al., 2016). Study of speleothems resulted in breakthroughs in understanding of causes of global, hemispheric and regional climate changes through their physical and chemical properties (Bar-Matthews et al., 1999; Frisia et al., 2000; Wang et al., 2001). Stalagmites are the most common speleothem type used for past climate reconstructions, and they frequently show an internal structure consisting of time-equivalent stacked layers, which, similarly to tree rings, may encode annual variability. The thickness of these layers ranges from a few micrometres ($<10\ \mu\text{m}$) up to millimetres ($<2\ \text{mm}$), permitting construction of high resolution time series (Fairchild and Baker, 2012).

By contrast, coralloid speleothems, due to their small dimensions (total length usually $<2\ \text{cm}$), are rarely considered appropriate for palaeoclimate reconstruction. However, in some cases, these are the most common speleothem type available, because they can also grow in semi-arid settings, when the water supply inside a cave is relatively low whereas other speleothems, like stalagmites, require an active drip. Coralloids are a type of speleothem characterized by botryoidal morphology and curved internal structure (Thrailkill, 1965; Hill and Forti, 1997; Vanghi et al., 2017). Their formation is linked to: (i) hydroaerosols (Gadoros and Cser, 1986; Dublyansky and Pashenko, 1997; Vanghi et al., 2017), originating from drip-water sprays via splash and drop fragmentation, which transport and distribute particulate and dissolved chemicals onto the coralloid surface; (ii) seeping water combined to capillary forces that move the film of water upward through intercrystalline porosity (Maltsev, 1996; Cuevas-González et al., 2010; Merino et al., 2014) or, externally, from the base towards the top of the coralloid (Caddeo et al., 2015); and (iii) enhanced evaporation on the curved surfaces of the coralloids, which increases the supersaturation with respect to calcite (SI_{cc}) of the solution and leads to CaCO_3 precipitation on the protruding surfaces (Caddeo et al., 2015; Vanghi et al., 2017). If strong evaporation controls coralloid growth (Caddeo et al., 2015; Vanghi et al., 2017) this might imply that their stable isotopic composition is kinetically modified compromising the use of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ as

climate proxies (Caddeo et al., 2015). Evaporation can also affect trace element incorporation by preferentially concentrating them on the speleothem tips.

Lamalunga Cave, which is the object of this study, is located in southern Italy (Puglia). The cave gained international recognition after the discovery of a complete Neanderthal skeleton lying in the depths of the cavern (Lari et al., 2015). Coralloid speleothems, suitable material for dating the skeleton and reconstructing the environmental conditions of the cave developed on the cave walls, floor and on the Neanderthal bones. By using a petrographic, microstratigraphic and geochemical approach on four coralloids both directly and indirectly associated with the Neanderthal remains, this study investigates the potential of coralloids as reliable palaeoclimate and palaeoenvironmental archives, comparable to stalagmites. Microscopy, complemented by synchrotron and conventional micro-X-ray fluorescence (micro-XRF) elemental concentrations maps, helped to characterize the nature of layering in two dimensions (2D), thus developing a new concept of speleothem petrography, which accounts for the distribution of both lattice-substituted and interstitial elements. When the chemical information is only available for one or two single transects, it can be more challenging to accurately reconstruct the transfer function from the climate proxy to the chemical datum, especially in heterogeneous media and at a small scale such as that of coralloid convex layers. By using micro-XRF geochemical maps, the current study aims to identify the relationships between trace elements incorporated in speleae calcite, examine how they affect the development of the crystalline fabric of calcitic layers and, finally, identify their sources.

GEOGRAPHIC AND CLIMATIC SETTING

Lamalunga Cave (40°51'51.9"N 16°34'31.3"E, entrance elevation 508 m a.s.l.) is located close to the town of Altamura in Southern Italy at 508 m a.s.l. and *ca* 50 km from the Adriatic Sea and *ca* 70 km from the Ionian Sea (Fig. 1). The climate in the region is Mediterranean with wet winters and autumns (the rainfall is mainly concentrated during October to December) and dry summers (with July as the driest month). The mean annual precipitation in the area near (<35 km) the cave, ranges between *ca* 500 to 800 mm (Brandimarte et al., 2011) with mean precipitation <30 mm from June to August (data

from S.I.M.N., Italian National Hydrographic and Mareographic Service, Bari compartment, Cassano delle Murge weather station over the period 1921 to 1990; Andriani and Walsh, 2009). This results in infiltration deficit and cessation of most of the dripping inside Lamalunga Cave during June to August. Modern (past 10 years) mean temperatures range between 30°C in summer and 5°C in winter (Gioia del Colle weather station).

Lamalunga Cave developed within the well-bedded shallow marine Calcare di Altamura limestone of Upper Cretaceous age (Zezza, 2000). The cavity is 5 to 30 m deep and developed during the Pliocene and Pleistocene in the uppermost vadose level of the karstic system, which consists of a single sub-horizontal gallery less than 100 m long (Agostini, 2011). In 1993, the members of the local speleological society (C.A.R.S. – *Centro Altamurano Ricerche Speleologiche*) artificially enlarged the natural opening of the cave and discovered a complete human skeleton embedded in calcite crusts, named afterwards the ‘Altamura Man’. Uranium-series dating on coralloid coatings served to provide a minimum age to the ‘Altamura Man’, which is definitely older than 55.9 ± 1.8 ka and possibly older than 130.1 ± 1.9 ka (Lari et al., 2015). The DNA extracted from the bones revealed that this human belonged to *Homo neanderthalensis* (Lari et al., 2015) and attracted the attention of both the scientific community and the general public. The actual access to the cave is a 10 m deep narrow vertical pit, whereas the original entrance was a larger vertical shaft now completely obstructed by debris and collapse deposits.

Microclimate measurements performed between October 2011 and December 2012 revealed an almost constant temperature throughout the year of $16.1 \pm 0.1^\circ\text{C}$ in the innermost southern end of the cave, whereas towards the northern end, where most of the coralloids developed, the air temperature fluctuated sinusoidally from 17.4°C recorded in mid-October to 14.6°C in early March (Arcadia Ricerche, 2013).

During a speleological survey in September 2015, relative humidity and cave air CO₂ were measured, using a Vaisala Meter GM70 equipped with GMP222 probe (Vaisala, Vantaa, Finland), in the same location of the main chamber every hour, for 48 hours. Cave air CO₂ ranged from 4500

ppmv to 1000 ppmv during short episodes of cave ventilation. The relative humidity, which is usually near saturation level (100%) in winter (Arcadia Ricerche, 2013), slightly decreased to $98.0 \pm 1.5\%$ during the end of the summer, when the survey was performed.

Active speleothem formation in Lamalunga Cave is mostly represented by straw stalactites and a few small stalagmites located almost exclusively in the northern part of the cave. Coralloid formations are more developed in the northern branches of the cave where more pronounced internal air temperature fluctuations were observed compared to other sectors of the cave (Fig. 1). Coralloid, which in Lamalunga cave form from hydroaerosols, have been found within the splash-distance, downwind to the direction of in-cave air flows. Coralloids represent the last phase of cave calcite deposition as they systematically coat flowstones, stalagmites and fossil animal bones that are scattered on the floor (Zezza, 2000; Agostini, 2011).

MATERIALS AND METHODS

Morphological and structural characteristics of the coralloids

Samples ABS5 and ABS6 were collected in February 2011 in the northeast branches of the cave from a broken stalagmite and a bedrock fragment, respectively (Fig. 2). Another coralloid sample, ABS3, was removed from a bone of the human skeleton to perform chronological analyses and the results are published in Lari et al. (2015). Sample ABS5 was collected based on the rationale that it could have been coeval to ABS3. Critically, ABS5, once dated by the U-Th method, revealed some growth phases that are time equivalent with ABS3 (Lari et al., 2015). Sample ABS6 is a multi-aggregate of digitate coralloids from which three sub-samples were cut; ABS6-A, ABS6-B and ABS6-C (Fig. 2). Whilst ABS6-A and ABS6-B were cut along parallel planes, ABS6-C cut was along a perpendicular plane to ABS6-A and ABS6-B. All the different coralloid samples consist of calcite (Vanghi et al., 2017) and they were selected in order to test the influence of different growth mechanisms on crystal fabrics and trace element incorporation. Two 30 μm thick thin sections were obtained from ABS5 and ABS6-A and the petrographic observations were carried out using a Leica MZ16A stereomicroscope (Leica, Wetzlar, Germany) and a Zeiss Axioplan microscope (Zeiss, Oberkochen, Germany).

Fluorescent light images of the thin sections, stimulated by blue (488 nm) and green (543 nm) wavelength lasers, were obtained using a Zeiss Axio Imager A1 fluorescence microscope with an LED Colibri controller (Zeiss, Oberkochen, Germany) at the University of Newcastle, Australia.

Greyscale profiles were generated from 16-bit micrographs using ImageJ software (Schneider et al., 2012) by averaging the pixel brightness intensity (on a greyscale from 0 to 255). The traverses used to generate greyscale values profiles for each sample, were identical for both fluorescence and thin section images.

Water analyses

Given the impossibility of sampling the film of water at the top of the coralloids; samples were collected in the northern branch of the cave during May 2008. The two samples, water dripping from a soda straw and water contained in a small pool, were collected in polypropylene vials, pre-cleaned with 5% HNO₃ and rinsed with MilliQ® water. Water temperature and electrical conductivity (corrected to 20°C) were carried out using a WTW TetraCon 325 dual probe (Xylem Analytics, Weilheim, Germany) at a resolution of $\pm 3 \mu\text{S cm}^{-1}$ and 0.01°C and an accuracy of $\pm 2 \mu\text{S cm}^{-1}$ and $\pm 0.2^\circ\text{C}$. The pH measurements were carried out using a WTW MultiLine P3 instrument (accuracy ± 0.2 pH units; Xylem Analytics, Weilheim, Germany). Bicarbonate concentration was determined by titration. The samples were analyzed at the Hydrochemistry Laboratory of Fondazione Edmund Mach, S. Michele all'Adige, Italy, following the analytical procedure described in Borsato et al. (2016). The major cations (sodium, potassium, calcium and magnesium) and anions (sulphate and chloride) were measured with a Dionex 320 ion chromatography instrument (Thermo Fisher Scientific, Waltham, MA, USA). Silica was measured on undiluted samples in a Varian-Cary 50 Bio UV-VIS spectrophotometer (Varian Inc., Palo Alto, CA, USA) and Sr was measured on a Perkin Elmer 3300DV ICP-OES (inductively coupled plasma – optical emission spectrometer; PerkinElmer Inc., Waltham, MA, USA) using yttrium as an internal standard. Analytical reproducibility, calculated as the differences between 10 repeated analyses of the same sample, was 2% for Ca, Mg and SO₄, and

5% for Na, K, Cl, SiO₂ and Sr. The saturation indices, defined as the logarithm of the ion activity product divided by the solubility product ($SI = \log IAP/KS$) were calculated with the program PHREEQC (Parkhurst and Appelo, 1999), by accounting for the pH and temperature measured at the time of sampling.

U-series dating

Three U-series analyses were performed on coralloid ABS6-A. The samples were drilled using a manually navigated dental drill along the growth axis of the coralloid and chemically processed for U-Th dating following the methods described in Hellstrom (2003): 15 to 30 mg of powder were dissolved in double-distilled nitric acid and then spiked using a mix of ²²⁹Th–²³³U–²³⁶U tracer solution. The U and Th were eluted in Eichrom TRU-spec selective ion exchange resin. Dried samples were then dissolved in diluted nitric acid. The measurements were performed using a Nu Plasma MC–ICP–MS (multi-collector – inductively-coupled plasma – mass spectrometer; Nu Instruments Limited, Wrexham, UK) at the University of Melbourne, Australia. An equilibrium reference material (HU-1) was used to correct for instrumental drift and an additional in-house speleothem standard of known age (YB-1) was used to check for the reproducibility of results. An initial ²³⁰Th/²³²Th ratio of 1.5 ± 1.5 was used to calculate corrected ages following Hellstrom et al. (2006).

Micro-X-ray fluorescence and synchrotron radiation (SR) micro-XRF

Synchrotron radiation micro-X-ray fluorescence (SR-micro-XRF) microscopy was performed at the X-ray fluorescence microscopy (XFM) beamline at the Australian Synchrotron (Melbourne, VIC, Australia; Paterson et al., 2011). The XFM beamline is equipped with a Maia 384 detector array which is mounted upstream, 10 mm away from the sample target. The beam passes through the detector with an annular configuration, which enables a large solid-angle without imposing severe restrictions on sample size or on the scale of scanning (Ryan et al., 2014). The beam spot size was 2 µm and the monochromatic incident energy was at 18.5 keV. Single element Mn, Fe and Pt foils (Micromatter Technologies Inc., Surrey, BC, Canada) were utilized as references to calibrate the final

elemental spectra. The dwell time of the beam on each pixel (2 μm x 2 μm) varied between 0.8 and 4 milliseconds. In this fast-acquisition configuration the detected elements were Ca, Mn, Fe, Br, Sr, Y and U, with typical detection limits of 220 ppm for Ca, 70 ppm for Mn and Fe, 7 ppm for Br, 5 ppm for Sr, 2 ppm for Y and 1 ppm for U. The attenuation depths for the 18.5 keV energy are as follow: Ca = 6 μm , Mn = 21 μm , Fe = 27 μm , Br = 150 μm , Sr = 240 μm , Y = 280 μm , U = 370 μm .

The Maia XFM spectral data were analyzed using the GeoPIXE software suite, which uses the dynamic analysis (DA) method for spectral deconvolution and exploration of the elemental image data (Ryan et al., 2014). Quantified concentrations of Sr and Ca were extracted for ABS5 and ABS6-A thin sections through rectangular transects (50 μm wide) along straight lines in the axial part of the coralloids avoiding porous parts and evident crystal defects. An 11-average points smoothing was applied to ABS5 and ABS6-A data to capture the most important patterns and reduce noise (Fig. 3).

The high excitation energy of the hard X-ray fluorescence (XRF) beamline is not suitable to detect low Z elements such as Mg, Si, S and P when their concentrations are <1000 ppm. For this reason, a Bruker M4 Tornado micro-XRF (Bruker, Billerica, MA, USA) was utilized to test a selected area on the polished slab of sample ABS6-C. The experimental conditions were as follow: vacuum = 2 mbar; tube voltage = 30 keV; current = 200 μA ; acquisition time = 45 ms; beam spot size = 20 μm ; pixel size = 20 μm . The resulting intensity maps are represented with different arbitrary colours for each element; the quantification of the intensity data was made by using internal standards and normalized to 100% by taking into account the stoichiometry for oxygen and carbon in the carbonate and oxide species. In order to minimize the signal to background ratio and to quantify more accurately the elemental distribution, five pixels selected along near-horizontal laminae were clustered together (Devès et al., 2012).

Given the high concentration in the samples of Si and Mg, elements that were not detected with SR-micro-XRF, the normalization of the elements to 100% by taking into account the stoichiometry for oxygen and carbon in the carbonate and oxide species was not a suitable approach. For this reason, and in order to compare the two analytical techniques, the current study converts both micro-XRF and

SR-micro-XRF to ppm concentrations. However, it has to be noted that XRF technique are sensitive to background fluctuation during the analyses and this affect particularly measurements near the detection limit. For this reason, the accuracy of both micro-XRF and SR-micro-XRF can be estimated in around $\pm 5\%$ at the best, but as low as $\pm 25\%$ when approaching the detection limit of each element.

RESULTS

Water analyses

Stalactite drip LL-w1 and pool water LL-w2 are characterized by a similar composition (Table 1). This composition reflects the direct dissolution of an almost pure limestone host rock as indicated by the low Mg/Ca ratio (0.13 and 0.11 mol/mol).

Uranium-series dating

Lari et al. (2015) published a series of four and three U-Th dates on ABS5 and ABS3 respectively that revealed that the oldest phase of Lamalunga coralloid formation dated between 130.1 ± 1.9 ka and 121.9 ± 2.2 ka. The results for ABS5 have been included in Table 2 in this present work. Three new U-Th analyses were performed on ABS6-A (Table 2). The results revealed that the age of the oldest phase analyzed in this coralloid is 50.4 ± 0.8 ka. The 36.9 ± 0.4 ka date was recorded in the translucent region of ABS6-A, between 5 and 6 mm from the base. This age corresponds to the phase at 36.9 ± 0.2 ka sampled in the translucent part of ABS5 just underneath the hiatus represented by a micritic layer (Fig. 4). The last phase of ABS6-A is dated at 8.9 ± 0.05 ka and it correlates to the Holocene phase at the top of ABS5 dated 7.6 ± 0.04 ka. The high $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in both ABS5 and ABS6-A indicate the absence of detrital contamination.

Petrography, internal structure and morphology of Lamalunga coralloids

Lamalunga samples have different external morphologies. ABS6 is an aggregate of coralloids characterized by a cusate cylindrical shape. This is the typical and more common morphology in Lamalunga coralloids. In some cases, the coralloids merge together (like ABS6-A), in others, they are separated by a gap (ABS6-B and ABS6-C).

The morphology of ABS5 is not cylindrical and only slightly cusate. The external surface is smoother and flatter compared to ABS6 and, accordingly to its morphological aspect, ABS5 is similar to a flowstone at a millimetre-scale and to an incipient coralloid.

In contrast to ABS6, ABS5 growth was probably mostly controlled by localized dripping water and not by hydroaerosol spray and less affected by evaporative phenomena (cf. Vanghi et al., 2017). Sample ABS5 was selected to verify the influence of evaporation on different coralloid morphologies.

Lamalunga coralloids consist of calcite as shown by Raman spectroscopy measurements and confirmed by petrographic observations (Vanghi et al., 2017), which did not reveal aragonite relics embedded in the calcite (cf. Frisia et al., 2002). Samples ABS5 and ABS6 are formed by elongated columnar (Ce) calcite fabric (Frisia, 2015) consisting of columnar crystals whose length to width ratio exceeds 6:1 (Fig. 3). Cerium fabric forms isopachous, compact and translucent bands. Compared to ABS5, which consists entirely of compact Ce, ABS6 also shows a sub-type of elongated columnar fabrics with very thin, highly elongated crystals (fibre-like) arranged in bundles with slightly diverging lattice orientation and undulatory extinction pattern. Fibre-like fabric is mostly present close to the central axis along the curved layers and it is associated with dark impurity-rich layers and high intercrystalline porosity. Towards the flanks of ABS6 coralloids, the fabric gradually passes to Ce compact type. Micrite (M) and micro-sparite (Ms), whose crystal sizes range from less than 2 μm to between 2 μm and 30 μm , respectively (Frisia, 2015), are also associated with dark horizons and to corrosion and dissolution features in both ABS5 and ABS6.

The internal structure of ABS6-A, ABS6-B and ABS6-C is finely laminated with alternating clear and dark micrometre-thick, curved layers grouped in millimetre-thick dark bands. Dark layers taper out towards the flanks of the coralloid and this imparts an overall lenticular shape to the dark bands. By contrast, clean compact calcite bands maintain the same width along most of the coralloids. Sample ABS6-C was cut along a plane almost orthogonal to ABS6-A and ABS6-B at the extremity of the ABS6 aggregate of coralloids (Fig. 2). For this reason, its internal structure, as shown by the SR-micro-XRF and Bruker micro-XRF generated maps, is slightly different from the other two samples; the curvature of the ABS6-C layers is very accentuated and they almost close up like rings near the base. The internal anatomy of ABS5 is mostly formed by clear isopachous bands of dense Ce calcite, the lamination is less profuse than in ABS6 coralloids and dark layers are not curved.

Dissolution and corrosion features mark the boundaries between clear and dark laminae and in most of the cases are associated with micrite, microsparite and organic material as indicated by fluorescence (Fig. 3). Some layers show evidence of dissolution and corrosion that can be followed along the entire fossil surface of the speleothem. These layers have been interpreted as hiatuses (Ht) in Vanghi et al., (2017). After performing petrographic observation of Lamalunga coralloids, several discontinuities have been recognized. In ABS6, coralloid erosion is mainly observed along dark laminae whereas in ABS5 it is especially evident on the three stacked dark layers at *ca* 4 mm from its top. For these three stacked dark layers, which interrupted ABS5 slow growth U-Th ages obtained just below and above them yielded, respectively, 36.9 ± 0.17 ka and 7.6 ± 0.04 ka (Ht C; Fig. 4). Between 36.9 ka and 64.4 ka and between 121.9 ka and 64.4 ka (Lari et al., 2015) hiatuses A and B (Fig. 4) are characterized by the presence of dark micritic layers. In ABS6-A, two layers, just above 36.8 ka, (Ht B and C; Fig. 5) have considerably serrated surfaces. Above 50.4 ka, hiatus A is characterized by an abrupt change in fabric and colour, while erosion features are less accentuated.

Speleothem porosity, impurity and organic matter content

Porosity and impurity content in speleothems changes the way light is transmitted through the sample which is reflected as changes in colours on polished surfaces of speleothems. A way of quantifying these chromatic changes is by using greyscale values. Greyscale values in ABS5 and ABS6-A vary between 25 (dark, impurity-rich) and 250 (translucent, impurity-free) (Fig. 3). On the other hand, when greyscale values are extracted from the thin sections under transmitted light, compact elongated columnar (white) has higher greyscale levels compared to the micrite or fibre-like columnar (dark) values. Stimulated fluorescence on ABS5 and ABS6-A thin sections was also measured using greyscale values. Greyscale values for the fluorescence range from 5 (no fluorescence) to 120 (high fluorescence) (Fig. 3). By using the same imaging settings, ABS6 fluorescence intensity seems to be twice that of ABS5. In both samples the mixed micrite and fibre-like layers show the highest fluorescence, while the compact columnar elongated fabric is characterized by less intense fluorescence. Low greyscale values commonly characterize bright fluorescent zones.

Distribution maps of trace elements: SR-micro-XRF and micro-XRF maps

Figures 4 to 7 show the SR-micro-XRF maps (Ca, Sr, Fe, Br, Y and U) for samples ABS5 and ABS6 (A, B and C) and Bruker micro-XRF maps (Ca, Si, Mg and Sr) for sample ABS6-C. The Ca concentration in the SR-micro-XRF maps highlights porous regions and crystal boundaries as well as areas where Ca is partially replaced by other elements. Elastic scattering maps provide information on porosity, crystal orientation, crystal defects and boundaries and illustrate the elongation of crystals in ABS5 columnar fabric (Fig. 4).

In ABS5, Sr is generally between 120 ppm and 180 ppm (Fig. 4) increasing up to 300 ppm in the dark micritic layers and up to 600 ppm corresponding to the three stacked discontinuities at *ca* 4 mm from the top (Ht C). Fe maximum values (5000 ppm) are reached at the base of the sample associated with the red micrite layer, which most likely contains iron oxyhydroxides. Similarly to Sr, Fe is also present along hiatus Ht C, marking crystals terminations at the top of the corroded layers.

In ABS6, Sr is especially concentrated on the cusped parts of the coralloids, where it reaches up to 2400 ppm (ABS6-A) and where Ca concentration records minimum values (Figs 5 to 7). Higher Sr concentrations are associated with fibre-like crystals, which are mostly observed on the convex parts of the coralloid (Figs 3 and 5). Toward the flanks, characterized by compact calcite, Sr concentration progressively decreases and so do the lenticular dark bands (Figs 5 and 6).

Br concentration is highest at the apex of the bands (50 ppm), and uranium concentration can reach up to 10 ppm on the lenticular bands. Y and Fe exhibit a considerable increase especially in the basal micritic layer where they reach maximum values of 200 ppm and 25,000 ppm, respectively.

Micro-XRF maps for Ca, Si, Sr and Mg (Fig. 7) were also produced for ABS6-C. Si is the element with the highest concentration after Ca and its distribution is opposite to Ca. Another set of maps (for Si, Mg and Ca) were acquired for a smaller area but with higher dwell time to better constrain the spatial distribution of the elements at single laminae level (Fig. 8). Silicon and Mg are anti-correlative to a minor extent with Ca, and are preferentially concentrated in the porous opaque bands.

Elemental quantifications for micro-XRF

Synchrotron radiation (SR) micro-XRF Ca and Sr line scans

In order to compare the elemental distributions in samples ABS5 and ABS6-A with their petrographic and microstratigraphic characteristics, elemental line scans were extracted in the axial region of their SR-micro-XRF maps (Figs 4 and 5A) by averaging 25 pixels for each point (50 µm wide box selection). The resulting concentrations of Sr and Ca are illustrated in Fig. 3 and then compared to the greyscale levels of the thin sections that describe the porosity of the calcite. Calcium and Sr show opposing trends and Ca is very similar to the greyscale values of the thin section (Fig. 3) In ABS5 the highest Sr concentrations from 400 to 600 ppm are observed in the micrite layers. In ABS6-A, the highest Sr concentration ranges from 2000 to 2250 ppm and coincides with dark, impurity-rich layers

in thin section. Strontium average values for fibre-like crystals in ABS6-A are high (1100 ppm) compared to ABS6-B (650 ppm) and ABS6-C (770 ppm). Strontium average values calculated for Ce fabric are lower compared to fibre-like fabric. Strontium average concentration in compact elongated fabric is 178 ppm for ABS5 and 520 ppm for ABS6-A. Fibre-like fabric is less dense than compact elongated columnar fabric as showed by ABS6-A Ca average concentrations of 280,000 ppm and 380,000 ppm, respectively. Similarly to ABS6-A, in ABS5 Ca average concentration for translucent calcite is *ca* 390,000 ppm.

Brucker micro-X-ray fluorescence

A portion of ABS-6C coralloid has been also analyzed with micro-XRF and its elemental concentrations have been compared with those obtained by SR-micro-XRF (Table 3) for the different fabrics. Strontium shows general lower values in micro-XRF compared to synchrotron radiation (Table 3). Sr-micro-XRF concentrations are *ca* 3 times lower than those obtained from SR-micro-XRF, in both compact and opaque calcite. Mg and Si, which have been only measured with micro-XRF, appear mostly concentrated in ABS6-C fibre-like fabric regions. Silicon has a very high mean concentration (84,600 ppm) in the opaque calcite whereas in translucent regions it is 4300 ppm. Magnesium values vary from 1000 to 30,000 ppm with mean values of 4800 ppm and 9100 ppm, respectively, in the translucent and opaque layers. Yttrium and U are present at trace levels and their mean concentrations appear to be higher in opaque parts compared to translucent parts. Figure 8A shows the element distribution maps obtained in a small region of ABS6-C (yellow insert in Fig. 7) and how Si tends to be concentrated in 100 μ m thick bands consisting of grains up to 100 μ m and spaced 100 to 150 μ m along the band. Figure 8B shows Ca, Si, Sr and Mg concentration profiles extracted from the map. The elemental profile shows a substantial agreement between Mg and Sr and an opposite trend between Si and Ca.

Element correlations

Linear correlation analyses for pairs of elements for the two different end-member fabrics (compact-translucent and porous-opaque) in ABS6-C are represented in Fig. 9. Calcium is anti-correlative with all the other elements and the correlation improves remarkably when the two end-member fabric are considered separately. The highest anti-correlation is between Si and Ca in the porous-opaque layers ($R^2 = 0.92$), whereas the anti-correlation between Ca and Mg, Sr is higher in the compact-translucent fabric ($R^2 = 0.98$ and 0.90 respectively). Magnesium and Sr are strongly correlated ($R^2 = 0.81$), whereas there is no significant correlation between Si and Mg, Sr ($R^2 < 0.17$).

DISCUSSION

The available U-series dating suggest that coralloids in Lamalunga, akin to speleothems from temperate regions, preferentially grow during mild climatic phases such as interglacials or interstadials. The phases of coralloid growth occurred during marine isotope stages (MIS) 1.0, 3.1, 5.1 and 5.5 (cf. Martinson et al., 1987), which coincides with speleothem growth phases documented in other Mediterranean caves (Bar-Matthews et al., 2003; Badertscher et al., 2011). Elemental incorporation in calcite coralloid speleothems is mainly influenced by the factors controlling their formation, one of the most important of which is evaporation (Vanghi et al., 2017), which is stronger in digitate coralloid and would explain non-Ca element concentration preferentially distributed along the lenticular layers. In the following sections the elemental distribution in the coralloids is analyzed in order to better understand the provenance and mechanisms of incorporation of the different elements.

Magnesium and Strontium incorporation in Lamalunga coralloids

Lamalunga Cave coralloids are characterized by very high Mg concentrations (mean 6900 ± 4700 ppm; see Table 3), compared to stalagmites from limestone caves in temperate climate settings where Mg content is usually less than 1000 ppm (Neuser & Richter, 2007; Richter et al., 2011; Frisia, 2015;

Belli et al., 2017). Magnesium incorporated in speleaeen calcite might derive from the dissolution of the bedrock (Fairchild et al., 2000; Sinclair, 2011; Sinclair et al., 2012) followed by transport into the cave in solution as a simple inorganic complex. Magnesium concentration in cave drip water is a function of the residence time of water in the aquifer and prior calcite precipitation (PCP) (Fairchild et al., 2000; Sinclair et al., 2012). Bands characterized by high Mg content in the coralloid could then be due to PCP and/or a prolonged water–bedrock interaction during particularly dry periods, which increases the Mg/Ca ratio of the parent solution. In this case, Mg could be considered as proxy for palaeo-aridity (Belli et al., 2017).

Modern drip water composition can be utilized to gain insight on the provenance and incorporation mechanisms of trace elements (Tremaine & Froelich, 2013; Rutledge et al., 2014). Modern Lamalunga Cave drip water analyses show low Mg content and a low Mg/Ca ratio ($\text{Mg}^{2+} = 6 \text{ mg/L}$; $\text{Mg/Ca} = 0.12 \text{ mol/mol}$; Table 1). By taking into account a conservative distribution coefficient D_{Mg} of 0.021 ± 0.002 (Fairchild & Baker, 2012), the expected Mg concentration in Lamalunga calcite precipitated in equilibrium with the parent water should be *ca* $600 \pm 100 \text{ ppm}$. Magnesium concentration in Lamalunga coralloid ABS6 is one order of magnitude higher, thus, bedrock dissolution alone is unlikely responsible for the coralloid high Mg content and other sources or mechanisms must have played an important role.

Common sources of Sr found in speleothems are host rock dissolution as well as allogenic input especially from aeolian dust (cf. Rutledge et al., 2014; Belli et al., 2017). Laboratory experiments conducted in the temperature and saturation range of a natural cave environment (Day & Henderson, 2013) demonstrated that there is no change in Sr partitioning (D_{Sr}) when temperature and growth rate varied. However, studies of stalagmites in caves suggest that Sr incorporation in speleothems is influenced by growth kinetics (Borsato, 2007; Fairchild & Baker, 2012, and references therein; Belli et al., 2017) and it is commonly also positively correlated with CaCO_3 supersaturation (Wasylenki et al., 2005).

Altamura coralloids show a high Sr content, especially in the opaque bands (Table 3). High Sr content can be an indicator of diagenesis as Sr is preferentially incorporated in aragonite rather than in calcite because its orthorhombic crystal structure accommodates larger ions than the rhombohedral calcite (Speer, 1990; Railsback, 2000; Ortega et al., 2005). However, Lamalunga coralloids consist of primary calcite, with no petrographic evidence of aragonite precursor (see Vanghi et al., 2017).

In view of the present-day drip water composition (Ca ~87 mg/L, Sr ~67 µg/L; Table 1) and a conservative distribution coefficient D_{Sr} of 0.044 ± 0.1 , which takes into account the very slow extension rate of the coralloids (<3 µm/year; cf. Belli et al., 2017), the expected Sr concentration in speleothem calcite should be around 13 ppm. This is almost 22 times less than the average Sr concentration in ABS5 and about 40 times less than the maximum concentration detected in ABS6. Therefore, as in the case of Mg, the dissolution of the bedrock cannot be regarded as the sole contributor to the Sr incorporated in the coralloids. The high concentration of strontium in Lamalunga coralloids, suggests that this element is incorporated outside the crystals lattice and, in fact, Sr distribution in fibre-like fabric (Fig. 5), is preferentially concentrated along linear crystal margins and in the voids between crystal bundles. On the other hand, Mg, which is smaller than Sr, may be accommodated in the lattice (Folk, 1974) both in compact or open fabrics.

Given the positive high linear correlation between Sr and Mg ($R^2 = 0.82$; cf. Fig. 9), it could be assumed that there is a common mechanism leading to their exceptional high concentration. Prior calcite precipitation (Fairchild et al., 2000) and evaporation at the coralloid surface (Vanghi et al., 2017), are the two common mechanisms leading to a strong positive linear correlation and higher-than-expected concentrations.

In order to test which of these two mechanisms is more relevant, the Mg and Sr concentrations as reported in Fig. 8B were plotted along with the theoretical Mg and Sr content of the calcite precipitated in equilibrium from the present-day cave water (Fig. 10). The coralloid Sr and Mg concentrations are then compared with the theoretical composition of the calcite precipitated in equilibrium with the present-day cave water after a PCP of 75% (calculated with distribution

coefficient D_{Mg} of 0.021 and $D_{Sr} = 0.044$), representing an extreme case of PCP where only the 25% of Ca remained in the solution. The plotted red dashed line is the idealized trajectory following the complete evaporation of the solution and the precipitation of all the minerals dissolved in the parent fluid ($D_{Mg} = D_{Sr} = 1$). In Fig. 10, it is evident that the PCP mechanism played a minor role, whereas most data align along a trajectory covering almost the entire range of the evaporative field. However, the present-day evaporative line can explain the entire range of Mg variability but is still inadequate to describe the whole range of Sr concentrations, and the slope of the regression line suggests a Sr excess in the initial solution. By modelling the hypothetical initial Sr composition in the precipitating solution, it was observed that most of the coralloid data fall in an area defined by initial solution with a Sr concentration from 2.5 to 7 times the present-day value. This suggests a substantial additional source of Sr possibly related to aeolian dust particles accumulated at the top of the soil as documented in other studies of Sr in stalagmites during glacial climate episodes (Goede et al., 1998; Belli et al., 2017).

Silica concentration in Lamalunga coralloids

Silica investigated in ABS6-C is preferentially present in the opaque bands characterized by high fluorescence. There is no significant correlation between Si and Sr, and Si and Mg (Fig. 9). Given the present-day moderate to low content of dissolved SiO_2 in the cave water (Table 1), it is unlikely that Si derived exclusively from dissolution of silicates in the soil and in the aquifer, and an additional source and/or concentration mechanism has to be invoked.

Increases in drip water Si/Ca might reflect arid climatic conditions, which results in less dilution of dissolved Si in the drip water, more prior calcite precipitation and enhanced weathering of silicate rocks (Hu et al., 2005). Hu et al. (2005) investigated the relationship between silica content in a speleothem and past rainfall in a stalagmite from Southern China. The authors demonstrated that high Si/Ca content in the stalagmite coincides with more positive $\delta^{18}O$ values and, thus, reduced rainfall amount. Furthermore, microbial mediation in silica precipitation cannot be entirely ruled out as amorphous silica was observed associated with micrite laminae in stalagmites from the Nullarbor

(Australia) showing strong fluorescence and associated with S and P (Frisia et al. 2012). Thus, presence of intercrystalline silica may indicate microbial colonization of coralloid surface, most likely when the surface of the speleothem was relatively dry. Enhanced dissolved Si in drip water can also be related to the weathering of wind-blown particles in the overlying soil (Belli et al., 2017). Wind-blown minerals deposits (loess) can be particularly significant during glacial periods (Pye, 1995; Újvári et al., 2016). However, the hypothesis of a silica source as wind-blown material, is contradicted by no correlation with Sr, whose high content in the coralloids has been related to aeolian input.

Another possible allogenic Si source can be discrete inputs associated with major volcanic eruptions. Given the location of Lamalunga in the Alte Murge plateau, where middle to late Pleistocene ash deposits from the Campanian volcanic province have been documented at the surface (Wulf et al., 2004) as well as in karstic depression and caves (Sauro, 1991), it is plausible that excess Si in coralloids could be indeed linked to volcanic eruptions, which have been very intense in southern Italy over the last 200 ka (Siani et al., 2004; Santacroce et al., 2008; Wagner et al., 2008). The products of explosive southern Italian volcanism is extensively recognized in Adriatic and Ionian sea cores (Siani et al., 2004; Sicre et al., 2013), terrestrial deposits (Bertagnini et al., 1998; de Vita et al., 1999; Zanchetta et al., 2000; Scarciglia et al., 2008) and lacustrine deposits (St Seymour et al., 2004; Wulf et al., 2004; Magny et al., 2006; Wagner et al., 2008). Tephra fallouts from Mount Etna or from the Neapolitan volcanoes are present more than 500 km from the source as in the case of Lake Ohrid in the Balkans (Wagner et al., 2008) or in the Philippi peat basin, in Northern Greece (St Seymour et al., 2004). Vingiani et al. (2014) recognized the occurrence of volcanic soils (andosols) in southern Italy in non-volcanic landscapes (Calabria) like the Altamura area and their presence have been mainly attributed to the Aeolian volcanic arc and, in a minor part, to Campanian volcanism. It seems reasonable to infer that the high Si concentration in Lamalunga coralloids is related to volcanic ash, which consists of small, reactive particulates. In this scenario, Si-rich dust deposited over the soil would be rapidly dissolved and transported into the cave by infiltrating waters or introduced as particles through large karstic fractures. A volcanic origin for Si in coralloids can also explain why

appearance and disappearance of Si does not match with that of climate sensitive elements such as Sr and Mg.

The micro-XRF map in Fig. 8 shows that the highest Si concentration occurs in grains up to 100 μm in diameter suggesting transport as particulate rather than precipitated from solution. Foreign particles deposited on the surface of the coralloid, fostered the formation of crystals growing with different orientations and separated by gaps (Frisia, 2015). Similarly, rounded areas characterized by low Sr and Ca are showed in Fig. 5B. This suggests that many of the low-Ca and Sr areas possibly host Si. Silica particulates could be related to dry-aerosols (Dredge et al. 2013) transporting dust from the overlying soil or from desiccated clay surfaces found inside the cave. An in-cave origin for the dry-aerosol is suggested by the location of ABS6, which grew at the base of a detrital cone formed by bedrock fragments partially covered by a thin layer of red-clay. Other localized clay deposits, up to few cm thick, are present in several locations inside the main gallery, whereas in the north-eastern branch of the cave, where ABS5 was collected, the walls and floor are almost completely coated by speleothems. However, dry-aerosols should also increase detrital Th in the calcite, which contradicts U-series analyses showing low ^{232}Th content (Table 2). One possible explanation of discrete Si grains in the coralloids, is related to strong evaporative processes, which force the precipitation of all the minerals phases in the solution. In fact, globular amorphous and crystalline silica nanoparticles, have been documented in the initial phases of calcite precipitation experiments (Frisia et al., 2018) and are usually expelled from the speleothem surface when the growth occurs in the presence of a thick film of fluid. However, in highly evaporative settings, silica nanoparticles are trapped at the surface and act as nuclei for the precipitation of Si-rich phases. Although the data available so far cannot discriminate between solute or detrital origin of silica aggregates, their origin from volcanic ash is the most plausible hypothesis.

Uranium, iron, yttrium and bromine concentrations

Uranium commonly occurs as a trace element in calcite and it is used in speleothem U-series chronology. Dissolved U in natural solutions can be present as hexavalent (U^{6+}) which is very soluble and can be incorporated in the calcite and divalent (U_2^{2+}) which is too large to enter in calcite lattice sites (Sturchio et al., 1998; Kelly et al., 2003). The U concentration in calcite is usually <10 ppm (Reeder et al., 2001), but in speleothem calcite it is typically around 0.2 ppm (Eggins et al., 2005) and rarely above 10 ppm (Reeder et al., 2001; Hellstrom, 2003). In the Lamalunga coralloids, U can reach values of up to 12 ppm with a distribution that closely resembles the Sr concentration map (Fig. 7) suggesting a similar evapo-concentration mechanism for both the elements. The high U concentration in coralloids facilitates the U-series dating of this speleothem morphology.

Iron is mostly concentrated in the micrite levels at the base of coralloids (Figs 4 to 7). Concentrations also correspond to the hiatus (Ht C) in ABS5 linking Fe to periods of interruption in calcite deposition.

Yttrium is commonly bound to organic substances mobilized during leaching from the soil and transported into the cave by infiltrating water (Borsato et al., 2007; Hartland et al., 2012). In ABS6-B coralloid Y shows a bimodal behaviour; similar to Fe, the high Y concentration is associated with the micrite layer at the base, whereas in the calcite-rich portion, Y distribution mimics Sr and U (Fig. 6) and is, therefore, associated with the opaque calcite layers (Fig. 3).

The only element that does not show preferential incorporation in relation to the observed different fabrics is Br (Figs 6 and 7). Bromine has been documented in stalagmites from Ernesto cave, a shallow cave in northern Italy in association with laminae rich in colloiddally bound metals and humic substances (Borsato et al. 2007). In the high-elevation Obir cave in Austria (Fairchild et al., 2010) Br and other halogens were detected in annually laminated stalagmites, and their concentration were correlated to changes in vegetation cover and productivity. The more plausible natural source of the halogen Br, providing 75 to 95% of CH_3Br and bromide salts (for example, sodium bromide, NaBr), is sea aerosol, whereas terrestrial environments are usually comparatively poor in Br (Ziegler

et al., 2008). Goede and Vogel (1991) and Goede et al. (1998) studied the origins of Sr and Br and their relationship in two Tasmanian speleothems. These authors concluded that Sr input probably represented an input from terrestrial dust and Br possibly derived from sea-salt aerosols which is common in speleothems from caves in coastal areas like Lamalunga Cave which is not far (<70 km) from the Adriatic coast. Because of the chemical behaviour of halogens that strongly partition into the fluid phase (Zhu, 1993; Wei, 2005), the distribution of Br can be linked to presences of open pores in the coralloids. However, the data available so far are not sufficient to confirm this hypothesis.

Incorporation and concentration of the elements

The unusually high concentrations of Mg, Sr and Si in Lamalunga coralloids, are primarily caused by evaporative processes that tend to concentrate the elements in areas more exposed to air currents and/or temperature changes. This explains why these elements are preferentially located in the lens-shape convex parts on the coralloid tips. This is also demonstrated by the mean Sr and Y concentrations in ABS6 that has a proper coralloid morphology (Vanghi et al., 2017), which is two and a half to four times higher with respect to the flowstone-like ABS5 in both Ce and fibre-like fabrics (Table 3).

The SR-micro-XRF maps and greyscale values reveal that Sr has higher concentrations in fibre-like elongated crystal fabric in ABS5 and ABS6 (Figs 3 to 7; Table 3). On the other hand, columnar elongated calcite shows the lowest Sr concentration, rarely exceeding 200 ppm in ABS5 and 500 ppm in ABS6 (Fig. 3).

In ABS6-C (Figs 7 and 8), Mg is associated with Sr, suggesting a similar origin although not necessarily a similar incorporation mechanism in the different calcite fabrics. Previous work demonstrated that Mg influences speleothem fabrics by poisoning calcite growth sites and favouring the development of elongated crystals with undulatory extinction (Kendall, 1973; Folk, 1974; Turgeon & Lundberg, 2001; Han & Aizenberg, 2003; Neuser & Richter, 2007; Frisia, 2015; Richter et

al., 2015) like the fibre-like fabric observed in ABS6-C, which is high in Mg (Fig. 8). However, fibre-like fabric is also intimately associated with Sr and Si (Fig. 8), suggesting that incorporation of Mg in the calcite lattice is not the sole cause of its development.

In Lamalunga coralloids, Si is the most abundant element after Ca and appears to be mainly accommodated within intercrystalline boundaries and, likely, as particulate. Solid particles at the surface of a speleothem could preclude the formation of compact calcite by preventing the coalescence of crystal boundaries. Thus, while Sr and Si caused the opening of the fabric, from compact columnar to fibre-like, Mg is responsible for the elongation of the crystals and the distortion of the lattice (Fig. 11).

In Fig. 3 it is possible to observe that Sr is higher in regions of ABS5 showing high fluorescence. Fluorescence intensity and Sr are especially high at the micritic levels that represent a reduction or cessation of coralloid growth during arid phases as demonstrated by the observed hiatuses. During dry episodes, speleothem surfaces are also more likely colonized by microbes as discussed by Frisia et al. (2012) and this could explain the apparent correlation between fluorescence and Sr content.

On the other hand in ABS6-A, there is no clear correlation between Sr and fluorescence. This is possibly related to different growth mechanisms; while ABS6 was mostly formed by hydroaerosols, the growth of flowstone-like morphology, as ABS5, required more effective infiltration and it was more sensitive to dry periods.

Environment and climate significance of element incorporation

Based on petrographic observations, geochemical maps of Lamalunga samples and the microclimate characteristics of the cave, three models are proposed here to explain the source, the transport and the incorporation of elements into the coralloids. Two of the models are linked to climatic variations and act on a long-term temporal scale. The third model does not reflect climatic changes but is connected to discrete short-term events like volcanism or increased aeolian transport.

Humid phase (climatic)

During humid climatic phases, infiltration inside Lamalunga Cave and, similarly, the spray and the hydroaerosol circulating through the galleries, would have intensified. Leached material from the soil zone most likely entered in solution, but weaker evaporative processes would not have been able to concentrate the elements at the speleothem's growth surface. This could explain the precipitation of clean compact elongated columnar (Ce) calcite which is commonly linked to humid conditions (Fig. 3; Frisia, 2015).

Dry phase (climatic)

When the local climatic conditions changed to relatively drier and the infiltration regime into the cave decreased, evaporative phenomena increased due to enhanced ventilation. Evaporation would have concentrated elements at the tips of the coralloids forming the lenticular opaque bands rich in non-Ca elements (Figs 4 to 7). Particulate would have then created an ideal medium for the formation of fibre-like crystals (Fig. 9). Sample ABS6 grew in a large chamber, closer to the entrance and thus more affected by air circulations and evaporation, leading to the formation of fibre-like crystals. Sample ABS5 instead, grew in a small chamber almost at the end of the gallery with limited evaporation and the thick film of fluid at the tip of the coralloid fostered the development of Ce fabric. Enhanced evaporation on ABS6 tips also explains why Sr and Y results here are two and a half to four times more concentrated than in ABS5. In addition, fluorescence in ABS6 is almost twice than in ABS5 possibly suggesting that bacteria, dwelling at the surface during relatively dry conditions (Banks et al., 2010) could have colonized the ABS6 surface.

Short-term non climatic events

Discrete events, like volcanic eruptions, are usually shorter term compared to climatic oscillations and can happen during dry or humid periods. Occasionally, allochthonous material like aeolian dust or volcanic ash, accumulated in the soil zone and, being extremely reactive to weathering it was readily

transported inside the cave is solution. As for the humid phases, these episodes are visible in the coralloids as dark opaque bands. The ABS6-C micro-XRF maps, have shown that Si incorporated in the calcite has a granular appearance. Silica is thus allogenic and has been transported inside the cave mostly as solid particulate.

CONCLUSIONS

This study demonstrates that synchrotron-radiation-based and micro-X-ray fluorescence high resolution mapping are powerful tools to investigate the pattern of distribution of chemical elements in extremely fine laminated speleothems, opening the possibility to use of cave coralloids as possible palaeo-archives. In Lamalunga Cave, coralloids are crucial in extracting palaeodata associated with palaeoanthropological remains. These speleothems, which do not form from waters dripping directly on the surface, but from combined hydroaerosols, strong evaporative processes and possible dry aerosol contribution are subject to trace element incorporation in their thin layers that depends on their location inside the cave, which controls evaporation and, hence, calcite growth. In parts of the cave more subjected to air currents and located near to the entrances, strong evaporative processes, organic binding and dry aerosol, concentrate trace elements in the axial parts of the coralloids in the form of biconvex lenses. In this case, coralloids cluster in complex aggregates with typical cylindrical digitate shape mostly formed by fibre-like fabric with finely laminated internal structure. In deeper parts of the cave and in areas characterized by more efficient infiltration, dry aerosol is absent or negligible, evaporative effects are less pronounced, and microbial and organic binding are limited to growth interruptions.

The elemental incorporation in coralloids appears to be strongly influenced also by the climatic context. During dry phases and in highly evaporative morphologies (ABS6), the elements are incorporated intra-laminae, mimicking the internal microstratigraphy, which implies that visual changes also reflect chemical changes. Silicon and Sr are preferentially distributed between fibre-like crystals in opaque and high-fluorescent layers that form lens-shaped dark bands, or in micritic layers

(Fig. 11). During wet phases and in less evaporative morphologies (ABS5), coralloids form isopachous bands of compact calcite, consisting of elongated columnar crystals, with weak fluorescence and lower content in trace elements.

However, in both cases, Lamalunga coralloids have unusually high trace element concentrations compared to stalactites, stalagmites and flowstones from similar environmental and climatic contexts. In particular, in high-evaporative ABS6 coralloids, Strontium and Y are more than three times more concentrated with respect to coeval layers in ABS5 (Table 3). This confirms that the position of the coralloid inside the cave as well as its geometrical evolution during its growth, strongly controlled the incorporation of elements although there may have been influences due to external climate conditions and environmental changes.

In Lamalunga coralloids, Si is the most abundant element after Ca and appears to be mainly accommodated within intercrystalline boundaries and, likely, as particulate (Figs 8 and 11). Solid particles at the surface of a speleothem could preclude the formation of compact calcite by preventing the coalescence of crystal boundaries. Thus, possibly, the highly open fibre-like columnar fabric develops in the presence of Si-rich particulate in this particular speleothem type.

In conclusion, climate, discrete environmental events as well as the hydro-physical characteristics of the cave environment that control the amount of evaporation and dry-aerosol incorporation, influence growth and elemental incorporation in Lamalunga coralloids. Commonly, in coralloid speleothems, both stable isotope fractionation and the incorporation of trace elements account for evaporation. All of these factors contribute to increase the complexity of the interpretation of their chemistry in terms of palaeo-data. If coralloids need to be used as a palaeo-data alternative to stalagmites and flowstones, this study recommends the use of data from at least two different samples whose internal stratigraphy and growth intervals can be compared. Petrological observations coupled with fluorescence and greyscale analyses are necessary complementary tools that allow for the interpretation of speleothem growth and, thus, chemical proxy data.

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FIGURE CAPTIONS

Fig. 1. (A) Map of Italy with the location of Lamalunga Cave near Altamura. (B) Plan of Lamalunga Cave and schematic cross-section of the northern end of the cave. The orange dotted line represents the plan of the cross-section. The locations of the samples here studied (ABS5 and ABS6) are also indicated. The ABS3 coralloid, studied in Lari et al. (2015), was sampled in the same chamber of the 'Altamura Man' skeleton. Coralloid speleothems are represented with small dots. A vertical shaft completely filled by limestone debris clogs the former opening. The current entrance to the cave was artificially enlarged. (C) View of the hill where the cave opens to the surface (black cross).

Fig. 2. Polished slabs of the investigated coralloid samples: (A) ABS6-A, ABS6-B and ABS6-C are part of the same multiaggregate of coralloids. The corresponding planes of cut are also shown (white rectangles). Notice the different plane of cut for ABS6-C that is orthogonal to the other two; (B) ABS5 polished slab. The sample was growing on a broken stalagmite.

Fig. 3. Samples ABS5 and ABS6-A; synchrotron elemental (Ca and Sr) concentrations are plotted against greyscale value intensities from the thin section, where they reflect the degree of calcite porosity and presence of impurities, and from the fluorescence map (using two wavelengths, blue and green, combined) indicating the presence/absence of intralaminar organic matter. The corresponding fluorescence and greyscale value line scans were carried out along the dashed vertical lines. Fabrics and major discontinuities in the thin sections are labelled as follows: Ce = columnar elongated; M = micrite; OM = organic-rich layer; MS = microsparite. To facilitate the correlation of greyscale values and fluorescence intensity, different fabrics have been highlighted by diverse coloured bands. Blue has two different shades, dark and light, which are intended to reflect higher (++) or lower (+) concentrations of organic material (OM) and higher (ff) or lower (f) fluorescence intensity respectively. The presence of clean, compact Ce calcite parts is illustrated as white bands.

Hiatuses (clearly recognizable gaps) are marked by solid blue lines. Note that the transmittance intensity and Ca scales are inverted.

Fig. 4. Synchrotron-radiation (SR) micro-X-ray fluorescence (XRF) maps (Ca, Sr, Fe and elastic signal) of ABS5 compared to the corresponding image of the polished slab (A) and the petrographic thin section under polarized light (B). Note that the thin section was made from a location 2 mm away from the slab plane and thus it shows a slightly different architecture. Strontium and Fe are preferentially concentrated along the dark micritic-rich bands in the thin section, and correspond to the opaque bands on the slab. These corroded surfaces represent episodes of no calcite deposition (hiatuses) indicated by Ht A, B and C. The ages (ka) published in Lari et al., 2015 are indicated in (A). Scale bar unit is in ppm for the elements maps and in percentages for the elastic scatter (ela) map.

Fig. 5. (A) Synchrotron distribution map (Ca and Sr) of thin section ABS6-A compared to the polished slab and the thin section under plane polarized light (PPL). Strontium concentrates preferentially in the axial part of lenticular-shaped bands that appear opaque on the slab and dark in thin section. The Sr-rich layers are also present above hiatuses (Ht A, B and C) identified by clear dissolution features (arrows). The three U-Th ages (expressed in ka) are also indicated. Elemental scale bar is in ppm. (B) Close-up of the region indicated by a white rectangle in (A). Plane polarized (PPL) and crossed polarized (XPL) micrographs compared to Ca and Sr SR-micro-XRF maps of the laminated part in ABS6-B. Dark regions in PPL corresponds to low values of Ca and high Sr concentrations. White band in the PPL image corresponds to clear translucent fabric with high Ca and low Sr values. White arrows identify small rounded or elongated areas (40 to 100 μm in width) with low Ca and Sr concentrations representing voids or high concentrations of other elements not detected by SR-micro XRF. Elemental scale bar in ppm.

Fig. 6. (A) Synchrotron-radiation micro-X-ray fluorescence elemental maps of ABS6-B compared to an image of the corresponding polished slab. Strontium, U and Y are more concentrated where Ca concentration is low, and preferentially occur in the fibre-like fabric where the laminae appear white

under natural light. The highest Sr concentration in lenticular shaped stacks of layers. Iron and Y are mostly concentrated in the micrite layers at the base of the coralloid. Uranium concentration pattern is similar to Sr distribution. The position of the three main hiatuses (Ht A, B and C) and the samples for U-Th dating (ages expressed in ka) are also indicated. Scale bar for the elastic scatter map is in percent. (B) Red–green–blue (RGB) image of (A); in order to compare elements with different concentration the values for Sr have been multiplied by 4 and the values for Fe by 10 times. The three inserts show in detail different portions with fibre-like fabric. In (1) the fibres are spaced between 10 μm and 25 μm . Scale bars in inserts '1' to '3' is 200 μm .

Fig. 7. Synchrotron elemental (Ca, Sr, U, Br, Fe and Mn) distribution maps of ABS6-C compared to an image of the polished slab (A) and to the micro-X-ray fluorescence (XRF) intensity images (square maps on the left side) (Ca, Si, P, Mg and Sr). The tracers mostly concentrate where Ca concentration is low and where the laminae show a white colouration on the slab. The black rectangle on the slab shows the position of the micro-XRF maps. The small yellow rectangle show the region from where elemental concentrations have been quantified. Principal hiatuses (Ht A, B and C), are marked by white arrows. Scale bar in ppm.

Fig. 8. (A) Element distribution maps obtained by micro- ray fluorescence (XRF) for Mg, Si and Ca in a small region of ABS6-C (yellow insert in Fig. 7). Si has an opposite pattern of distribution with respect to Ca. In the opaque bands, Si values are up to 16% and Mg values can reach up to 3%. In compact translucent bands, Si is very low (*ca* 0.1 %) whereas Mg is around 0.4%. (B) Line scans of Ca, Si, Sr and Mg extracted in the central part of the maps (black rectangle) by geometrically interpolating the pixel values. Strontium and Mg trends show a similar distribution pattern. Silicon seems mostly concentrated in grains with a 50 to 100 μm diameter.

Fig. 9. Linear correlations between Sr, Mg, Si and Ca in ABS6-C [micro- ray fluorescence (XRF) data in Fig. 8] from a selected region of interest. The correlation coefficients were calculated for the whole interval (upper row) and then separately (lower row) in green for the compact-translucent and in orange for the porous-opaque fabric end-members.

Fig. 10. Magnesium and Sr coralloid data from ABS6 as reported in Fig. 8B. The black square represents the theoretical Mg and Sr content of the calcite precipitated in equilibrium with present-day cave water (cf. Table 1) calculated with $D_{Mg} = 0.021$ and $D_{Sr} = 0.044$. The blue diamond represents the theoretical composition of the calcite precipitated in equilibrium with the present-day cave water after a PCP of 75% (25% of Ca left in the solution). The bold red dashed line is the idealized trajectory describing the complete evaporation of the solution (present-day initial Mg/Ca molar ratio of 0.12 and Sr/Ca molar ratio of $0.35 \cdot 10^{-3}$). The thin red dashed lines are the idealized trajectory following the complete evaporation of the solution with an initial water Sr/Ca molar ratio of $0.88 \cdot 10^{-3}$ and $2.46 \cdot 10^{-3}$ corresponding, respectively, to two and a half and seven times the present-day value. The secondary vertical axis illustrates the contribution of evaporation assuming an initial water Mg/Ca molar ratio of 0.12 (present-day water composition) and without contribution from PCP.

Fig. 11. Schematic diagram of all principal characteristics of Lamalunga coralloids.

Table 1. Hydrochemical characteristics of the cave waters (water dripping from a soda straw and water contained in a small pool) collected in Lamalunga Cave in May 2008. EC = electrical conductivity at 20°C; SI = saturation index.

Table 2. Results of Multi-collector – inductively-coupled plasma – Mass Spectrometry U/Th analyses on the coralloid ABS6-A and ABS5 (Lari et al. 2015). Activity ratios (AR) are determined after Hellstrom (2003). Ages are calculated using the decay constants of Cheng et al. (2013) and corrected

for an initial $[^{230}\text{Th}/^{232}\text{Th}]$ of 1.5 ± 1.5 . Initial $[^{234}\text{U}/^{238}\text{U}]$ is calculated using the corrected age. Errors are reported in brackets as $\pm 2\sigma$.

Table 3. Mean values in translucent (Trans) and opaque calcite fabric expressed in mg/g $\pm 1\sigma$ for selected intervals in coralloid samples ABS6-B, ABS6-B C (cf. Fig. 7) and ABS5 (cf. Fig. 4) measured in conventional micro-X-ray fluorescence (μXRF) and with synchrotron-radiation (SR) μXRF .

Point	Type	T(°C)	pH	EC ($\mu\text{S}/\text{cm}$)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	Cl ⁻ (mg/l)	SiO ₂ (mg/l)	Sr ²⁺ ($\mu\text{g}/\text{l}$)	Mg/Ca (mol/mol)	SI calcite	SI dolomite	SI CO ₂ (gas)	SI Quartz
LL-w1 drip		15.50	7.62	420.00	88.40	6.80	4.90	0.70	295	4.80	11.20	7.50	64.50	0.13	0.51	0.12	-2.15	-0.14
LL-w2 pool		15.30	7.57	409.00	86.50	5.80	5.50	0.65	289	6.20	10.30	10.30	68.90	0.11	0.44	0.13	-2.20	0.02

ABS6-A	Mass (g)	^{238}U (ppm)	$^{230}\text{Th}/^{238}\text{U}$ AR	$^{234}\text{U}/^{238}\text{U}$ AR	$^{230}\text{Th}/^{232}\text{Th}$ AR	Age corrected (ka)	Initial $^{234}\text{U}/^{238}\text{U}$ AR
1	0.025	1.13 (0.08)	0.3819 (0.0022)	1.0194 (0.0026)	88.7	50.425 (0.802)	1.0225 (0.0030)
2	0.027	1.37 (0.1)	0.2972 (0.0020)	1.0305 (0.0023)	290.1	36.873 (0.352)	1.0338 (0.0025)
3	0.024	4.57 (0.3)	0.0796 (0.0004)	1.0126 (0.0022)	803.7	8.910 (0.054)	1.0129 (0.0023)
ABS5 (*)	Mass (g)	^{238}U (ppm)	$^{230}\text{Th}/^{238}\text{U}$ AR	$^{234}\text{U}/^{238}\text{U}$ AR	$^{230}\text{Th}/^{232}\text{Th}$ AR	Age corrected (ka)	Initial $^{234}\text{U}/^{238}\text{U}$ AR
1	0.063	0.62 (0.04)	0.4858 (0.0015)	1.0799 (0.0021)	2015.2	64.654 (0.331)	1.0960 (0.0025)
2	0.035	0.48 (0.03)	0.2997 (0.0010)	1.0427 (0.0020)	2793.5	36.901 (0.172)	1.0474 (0.0022)
3	0.067	0.71 (0.05)	0.0737 (0.0004)	1.0979 (0.0022)	770.1	7.571 (0.045)	1.1000 (0.0022)
4	0.008	0.73 (0.05)	0.7002 (0.0034)	1.0290 (0.0039)	68	121.904 (2.220)	1.0409 (0.0054)

Element	ABS6-C		ABS6-B (SR)		ABS5 (SR)	
	Trans	Opaque	Trans	Opaque	Trans	Opaque
Ca	391.6 ± 5.4	353.6 ± 9.4	386.9 ± 3.5	304.4 ± 7.9	398.7 ± 3.2	327.8 ± 46.6
Si	4.3 ± 2.7	84.7 ± 23.6				
Mg	4.8 ± 3.9	9.1 ± 4.3				
Sr	0.213 ± 0.193	0.435 ± 0.296	0.386 ± 0.122	1.273 ± 0.165	0.101 ± 0.020	0.497 ± 0.994
Y			0.003 ± 0.002	0.021 ± 0.003	0.001 ± 0.001	0.006 ± 0.002
U			0.001 ± 0.001	0.005 ± 0.002	n.d.	0.001 ± 0.001