Exceptional silica speleothems in a volcanic cave: A unique example of silicification and sub-aquatic opaline stromatolite formation (Terceira, Azores)

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ABSTRACT
Silica stromatolites occur in a number of modern hydrothermal environments, but their formation in caves is very rare. The silica stromatolitic speleothems of the Branca Opala cave (Terceira Island, Azores), however, provide an excellent opportunity for their study. These formations may be analogous to ancient silica stromatolites seen around the world. Petrographic, mineralogical and geochemical analyses were undertaken on the silica speleothems of the above cave, and on the silica-tufa deposits outside it, with the aim of understanding their genesis. The possible hydrothermal origin of their silica is discussed. X-ray diffraction analyses showed opal-A to be the sole silica phase. Negligible ordering of this opal-A showed ageing to be insignificant, as expected for recent silica deposits. Most of the silica speleothems examined were definable as sub-aquatic opaline stromatolites that are not currently growing. Optical microscopy clearly revealed a lower microlaminated, an intermediate and an upper microlaminated zone within the stromatolites. Stromatolite types (I, II and III) were classified with respect to their internal structure and distribution throughout the cave. Scanning electron microscopy showed silicified bacterial filaments within the stromatolites, the silicified plant remains and the silica-tufa deposits. Bacteria therefore played a major role in the precipitation of the opal-A. Plasma emission/mass spectrometry showed major, minor and rare earth elements to be present in only small quantities. The rare earth elements were mainly hosted within volcanic grains. Rapid silica precipitation from highly super-saturated water would explain the intense silicification of the plant remains found inside and outside the cave. The opaline stromatolites, the silica-tufa deposits and the above-mentioned intense general silicification suggest a local hydrothermal source for the silica. Indeed, these deposits strongly resemble plant-rich silica sinter associated with low-temperature hot spring deposits that include bacterial filaments. However, no geochemical signals that might indicate a hydrothermal origin could be found.

Keywords Bacterial activity, geochemistry, opal, silica-tufa, stromatolitic speleothems.
INTRODUCTION

Silica speleothems are only rarely found in caves, although they do occur all over the world (Argentina, Australia, the Azores Islands, Spain, Sri Lanka, China, Italy, Kenya, Korea, Malaysia, New Zealand, the USA and Venezuela, among others; see references in Hill & Forti (1997)); they mainly occur in caves in siliceous material such as basalt (Webb & Finlayson, 1987), volcanic rock (Forti, 2005; Bustillo et al., 2010; Daza et al., 2012), granite (Webb & Finlayson, 1987; Willems et al., 2002; Vidal & Vaqueiro, 2007; Cioccale et al., 2008; Vidal et al., 2010), quartzite or sandstone (Wray, 1999, 2011, 2013; Aubrecht et al., 2008, 2012). Almost all silica speleothems are formed in tropical and/or humid warm climates, where silica-rich solutions arising from the alteration of silicates commonly form thin coralloidal or botryoidal coatings, and sometimes even stalactites, stalagmites or flowstones (Hill & Forti, 1997; Forti, 2005).

In the Azores Islands, stalactites, stalagmites, flowstones (Algar do Carvaõ cave, Terceira Island) and silica moonmilk vermiculations (Torres Cave, Pico Island; Forti, 2001, 2005) are found in lava tubes and magmatic chamber caves. Such speleothems are not found in the Branca Opala cave; dripping water or water flowing through cracks – a requirement for their genesis – is not present. Earlier studies performed on the siliceous speleothems at the Branca Opala cave entrance (photic zone), described their internal structure as an alternation of microlaminated compact zones with more porous zones. These speleothems were interpreted as microbial opaline stromatolites, as revealed by the presence of nanometric filamentous morphologies (Bustillo et al., 2010). A later study described large numbers of opaline stromatolites inside the cave, with different types distributed over the cave walls and ceiling (Daza et al., 2012). The existence of stromatolitic speleothems in carbonate settings is now largely accepted (Taborosi, 2006), but few references exist regarding silica speleothems. The predominantly microbial origin of some silica speleothems has been recognized by several authors (e.g. Forti, 1994; Léveillé et al., 2000; Willems et al., 2002; Aubrecht et al., 2008, 2012), with some noting the existence of filamentous bacteria, e.g. Willems et al. (2002) for the silica speleothems of Mezesse cave in southern Cameroon, and Aubrecht et al. (2008) for those of the Charles Brewer cave in Venezuela.

The opaline stromatolites of the Branca Opala cave are morphologically similar to speleothems known as ‘dolls’ and ‘champignons’ in the Charles Brewer cave (Aubrecht et al., 2008) and were also formed by several types of microbes. Nevertheless, neither the type of host rock (basalt) nor the internal structure of the opaline stromatolites of the Branca Opala cave resembles those of the Charles Brewer cave: indeed, they have rather more complex morphologies.

Siliceous stromatolites are rarely found in sedimentary environments and have mainly been related to hydrothermal environments such as geysers, hot springs and lakes/pools influenced by intermittent hydrothermal activity (Jones et al., 1997, 2005; Konhauser et al., 2001; Handley et al., 2005, 2008; Schinteie et al., 2007; Can- gemi et al., 2010; Pepe-Ranney et al., 2012). Some siliceous stromatolites show the signs of microbial activity, such as microbial mats, biofilms and mucus (exopolymers) (Jones et al., 2005; Handley et al., 2008), cyanobacteria (e.g. Pepe-Ranney et al., 2012), stromatolitic microfaccies colonized by bacilli, diatoms and coccolial algae (e.g. Schinteie et al., 2007), and bacterial filaments (e.g. Jones et al., 2005). Such stromatolites are found under water, emerging only at the water–air interface. Generally, siliceous stromatolites are thought to form only where there is sunshine, and where the depth of the water column, temperature and pH permit the growth of bacterial mats (e.g. Petryshyn & Corsetti, 2011).

The present work describes the opaline speleothems and associated siliceous deposits inside and outside the Branca Opala cave, with the aim of advancing current understanding of how silica stromatolitic speleothems form in subterranean environments, and of understanding their particular formation environment via comparison with other silica speleothems and deposits in the proximity of the cave. A possible hydrothermal source of the silica for these speleothems and surrounding deposits is discussed.

GEOLOGICAL SETTING

The Azores Islands lie in the North Atlantic Ocean about 1600 km west of Lisbon, Portugal. The archipelago comprises nine volcanic islands that fall into three main groups: the Flores and Corvo group to the west; the Graciosa, Terceira, São Jorge, Pico and Faial group in the centre; and São Miguel, Santa Maria and the Formigas Reef group to the east. These islands extend in a north-west/south-east direction for more than 600 km along the Azores-Gibraltar fault.
The islands were created by lava flows from the ocean floor at the conjunction of three tectonic plates (Navarro et al., 2009), i.e. the Eurasian plate to the north-east, the North American plate to north-west and the African plate to the south.

The Branca Opala cave, near Biscoitos, is located in the north-west of Terceira Island (Fig. 1B). Terceira comprises four polygenetic volcanic systems (Pico Alto, Santa Bárbara, Guilherme Moniz and Cinco Picos) and a Basaltic Fissural Zone that, over the last 50 000 years, was most active in the north-west (Nunes, 2000, 2004; França et al., 2003). The four volcanic systems developed along a prominent north-west/south-east oriented fissure zone that transects the island and is part of the expression of the Terceira Rift (Self & Gunn, 1976). Vogt & Jung (2004) argue that this rift is the world’s slowest spreading plate boundary. The exposed rocks on Terceira are all of Late Pleistocene and Holocene age (Calvert et al., 2006). The Branca Opala cave is located in the Basaltic Fissural Zone (Fig. 1B) in a basaltic flow of the eruptive episode of the Cavernicola Malha – Balcões – Chamusca System (~7130 years). The Basaltic Fissural Zone is home to the most recent activity on the island: the eruption of hawaiite lava in 1761 (Fig. 1B; Self & Gunn, 1976).

THE BRANCA OPALA CAVE AND ITS DEPOSITS

The Branca Opala cave, a lava tube some 99 m long, 0.7 to 5 m high and 1.6 to 10 m wide, is slightly inclined from the southern (5 m high, 10 m wide) towards the northern (<1 m high, 2 m wide) entrance, and has a skylight a few metres from the former (Fig. 2). Field observations showed three main types of siliceous deposit to be present (all inside the cave): opaline stromatolitic speleothems, deposits formed by plant remains mixed with volcaniclastic sediments and volcaniclastic sediments (Fig. 3A). Silica-tufa deposits are present outside the cave in an area known as the Ribeira da Biscoitos.

Opaline stromatolites

These deposits grew directly on the volcanic rock or other cave deposits, such as plant remains, collapse breccias (Fig. 3A) and volcaniclastic sediments. These sediments are beige and brown in colour, and their exterior morphology ranges from low-relief, cloud-like mounds to bulbous, botryoidal masses of linked domes (Fig. 3A to C); their interior shows accretionary laminated and layered structures. These stromatolites range from 1 to 12 cm in height, and have a diameter of 3 to 15 cm. The size of the stromatolites decreases from the cave centre towards the two entrances. Those with botryoidal morphologies are found mainly on the walls, but always beneath a horizontal line (a fossil water level; Figs 2, 3B and 3C). This water level can be followed throughout the cave (Figs 2, 3B and 3C). The botryoidal stromatolites are smaller just beneath the water mark, and increase in size downwards (Figs 2B.2, 2B.4 and 3C). Stromatolites with cloud/bulbous morphologies are seen mainly on the ceiling and on certain parts of the
Fig. 2. Topography of the Branca Opala cave and location of sampling points. Modified from ‘Os Montanheiros’ SBE: P. Borges, F. Pereira, A. Silva, O. Teixeira and J. Maria (15 March 1992): (A) Cave profile for when the cave was flooded and the northern entrance closed. (B) Current cave profile showing the distribution of the speleothems and siliceous deposits. (B.1) Relation between type III stromatolites (stromatolitic crust) and the fossil water mark. (B.2) Relation between the type I botryoidal stromatolites (found throughout the cave) and the fossil water mark. These stromatolites are smallest just beneath the water mark and increase in size downwards. (B.3) Distribution of cloud-like and botryoidal forms in a once totally flooded section. (B.4) The botryoidal stromatolites near the northern entrance are smaller just beneath the water level, and increase in size downwards.
walls. Specimens with botryoidal shapes and cloud-like morphologies sometimes co-occur (Fig. 2B.3). Thin stromatolitic crusts (1 to 2 cm) are seen at the southern entrance of the cave (Fig. 2B and B.1). Silicified plant remains are found between the stromatolites.

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Deposits formed by plant remains mixed with volcaniclastic sediments

More recent (non-silicified) and older (partially to totally silicified) accumulations of plant material can be seen in the cave. The latter are mainly found stuck to the walls, reaching up to 20 cm in depth (Figs 2B, 2B.2, 2B.3, 3B and 3D), but are also seen on wall projections and in some places on the cave ceiling; some have opaline stromatolitic coatings. The most common types of plant remains are fragments of leaves, wood from trunks, twigs and roots (Fig. 3D). Both the recent and older plant material was transported into the cave by flowing water.

Volcaniclastic rocks and sediments

These sediments consist of two types of deposit: (i) autochthonous breccias (coarse fraction >6.4 cm) from the collapse of the lava tube ceiling (Fig. 2B); and (ii) allochthonous volcaniclastic sediments of variable size (mud to gravel) transported into the cave by flowing water (the sediments of smallest size were probably deposited by settling; Fig. 3A). These are found throughout the cave, mainly on the floor. Large accumulations of breccias from the collapsed roof and coarse volcaniclastic fragments are found in two rooms within the cave (Fig. 3A and B); these formed before the silica speleothems. Very fine volcanic sediments cover much of the surface of the opaline stromatolites (Fig. 3B) and may also fill their interior porosity, as well as the porosity between volcanic blocks. In many cases, these fine sediments consist of a mixture of tiny volcanic rock fragments and opaline mud (here used as a descriptive term only with no genetic involvement implied, and referring to amorphous silica particles mainly <10 μm in diameter, plus their aggregates).

Silica-tufa deposits

These deposits, a mixture of silicified plant remains (trunks and twigs, roots, moss and lichens), volcanic clasts and iron oxides/hydroxides, are found in the surroundings of the cave in the Ribeira da Biscoitos area. Each of the above components is covered by compact or porous laminated silica coatings (Fig. 3E). The volcanic clasts (basalts) are of variable size; some show a reddish colouration, a consequence of alteration processes.

MATERIALS AND METHODS

Various types of opaline stromatolite, silicified plant remains, fine volcaniclastic sediments, volcanic host rock and silica-tufa from the Branca Opala cave, and nearby in the Ribeira da Biscoitos area, were sampled. Only a limited number of speleothem samples were collected to avoid excessive damage to the decoration of the cave.

The mineralogical composition of the samples was determined by standard optical microscopy and X-ray diffraction (XRD) analysis. Powder XRD patterns were obtained using pressed powder mounts employing a Philips semi-automatic PW 1710 diffractor producing monochromatized CuKα radiation (Panalytical, Almelo, Overijssel, The Netherlands). The oriented aggregates technique was used to study very fine sediments. Minus-2-micron fractions were mounted on glass microscope slides, saturated with glycol and heated to 450°C to generate diffraction data.

Transmitted-light microscopy was used for basic petrological analyses and microstructure description. Thin sections of representative parts of each sample were examined under polarized light. Some parts of the stromatolites were poorly lithified despite their silicification; thin sections were therefore taken from epoxy-impregnated samples.

Small fractured samples of the collected material were mounted on stubs and coated with a layer of gold for observation using a FEI INSPECT scanning electron microscope (SEM; FEI, Hillsboro, OR, USA) (30 kV, distance 10 mm, high vacuum) equipped with secondary electron and backscatter detectors and an Oxford ANALYTICAL-INCA X-ray energy dispersive system (EDX; Oxford Instruments, Abingdon, Oxfordshire, UK). Precise aluminium and silicon determinations were obtained by SEM using a FEI QUANTA 200 machine equipped with a wavelength dispersive spectrometer (WDS).

Geochemical analyses of whole-rock powder for major, minor and rare earth elements (REE) were performed at Acme Analytical Laboratories (Vancouver, Canada) using inductively coupled emission spectrometry (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Classical whole-rock analyses were performed using a lithium borate fusion and dilute acid digestion of 0.2 g samples. Loss on ignition (LOI) was determined by weight difference after ignition at 1000°C at the same laboratories. The analytical methods employed and their detection limits can be found at http://www.acmelab.com.
MINERALOGICAL AND BULK CHEMICAL COMPOSITIONS

X-ray diffraction

Powder XRD analysis of the silica deposits returned broad scattering with a prominent 15 to 30°2θ band, and a maximum centred around 22°2θ (ca 4 Å), corresponding to opal-A (SiO2-nH2O) (Jones & Segnit, 1971). Within this band, no peaks of around 4-04, 4-09 or 4-30 Α were observed; such peaks would have indicated the beginning of opal-C, opal-CT or quartz formation. The width of the 22°2θ band at half height (FWHM) determined the opal-A disorder (Herdianita et al., 2000). The opal-A of the lower zone of the stromatolites was more ordered (FWHM around 7-84°2θ) than that of the outer zone (FWHM around 8-00°2θ). Less ordered opal-A was found in the silica-tufa deposits from outside the cave (FWHM around 8-56°2θ).

Opaline stromatolites

Opal-A was found to be the dominant component (80 to 100%). Sporadically, feldspars and pyroxenes were found as accessories (5 to 10%). These minerals came from the fine volcanic grains trapped inside the stromatolites.

Deposits formed by plant remains mixed with volcaniclastic sediments

The proportion of opal-A and other minerals varied depending on the amount of silicified plant remains and the detritus content within the deposits. Opal-A values reached up to 70%; the rest was formed of feldspars (up to 20%) and pyroxenes (up to 10%).

Fine volcaniclastic sediments

These sediments consisted mainly of feldspars (30 to 80%) and pyroxenes (10 to 45%) mixed with opal-A (5 to 25%), and iron oxides/hydroxides (5%), such as hematite and goethite. Clays (kaolinite and illite), which are not generally observed in oriented aggregates, were found in two samples (5 to 10%). Material <15 μm was very rich in opal-A, mixed, in some cases with some allophone and/or amorphous iron oxides/hydroxides.

Silica-tufa deposits

The silica-tufa deposits consisted of opal-A (40 to 90%), feldspars (10 to 35%) and, in some samples, pyroxenes (5 to 25%).

Geochemistry

Major elements

The opaline stromatolites were rich in silica (87 to 89% SiO2) accompanied by variable proportions of Al2O3 (0-2 to 1-1%), Fe2O3 (0-1 to 0-5%), MgO (0-3 to 0-8%), CaO (0-2 to 0-4%), Na2O (≤0-2%), K2O (≤0-2%), TiO2 (≤0-1%), P2O5 (≤0-05%) and MnO (≤0-04%). The upper part of the stromatolites was slightly richer in silica (88-6 ± 0-40% compared with the lower part 87-39 ± 1-08%). Wavelength dispersive spectrometer (WDS) analysis of the stromatolite laminae revealed some Al in the opal-A structure (0-57 ± 0-20% atomic weight). Laminae with brown colouration showed higher aluminium concentrations (Si/Al atomic ratio 77-98 ± 22-48) than did beige laminae (Si/Al atomic ratio 100-36 ± 33-12). The remaining major elements (and some of the Al) detected in total whole-rock analysis must have come from mineralogical or biological impurities trapped inside the stromatolites.

The fine volcaniclastic sediments returned comparatively high values for all major elements: SiO2 39 to 49%, Al2O3 15 to 16%, Fe2O3 ~ 8%, MgO 1-2 to 1-4%, CaO 1-9 to 2-3%, Na2O 2-6 to 3-2%, K2O 1-6 to 1-9%, TiO2 1-2 to 1-5%, P2O5 0-6 to 0-8% and MnO 0-4 to 0-8%, a consequence of their high feldspar and pyroxene contents. The high iron content was also due to the presence of independent iron oxides/hydroxides.

The silica-tufa deposits returned highly variable amounts of silica (64 to 84%). The bulk composition depended on the degree of silicification of the plant remains and the quantity of intermixed volcaniclastic sediments.

Minor elements

For all of the samples studied, the minor element correlation matrix showed the majority of the elements analysed (Ba, Co, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, Zr and Y) to be strongly and positively correlated with Al2O3% (correlation coefficients >0-90), and negatively with SiO2% (<−0-84). Therefore, the minor elements detected mainly form part of the fine volcaniclastic deposits; the opal-A has only a slight influence on their content. The correlation matrix for the stromatolites showed strong correlations between the percentage of Al2O3 and all minor elements except for U (correlation coefficient ≤0-53), and Sn and W (below the detection limit).
Rare earth elements

The REE distribution patterns for the silica deposits were relatively flat and parallel (Fig. 4A and B). An influence of the volcaniclastic fragments on the REE concentrations was clearly observed. The percentage of $\text{Al}_2\text{O}_3$ and total REE ($\sum \text{REE}$) were positively and linearly correlated (correlation coefficient $+0.98$ for all the samples; $+0.97$ for the stromatolites, and $+0.99$ for the silica-tufa deposits). The correlation between percentage $\text{K}_2\text{O}$ and REE ($\sum \text{REE}$) was $+0.83$ for the stromatolites and $+0.98$ for the silica-tufa deposits. The correlation coefficients for percentage $\text{SiO}_2$ and REE ($\sum \text{REE}$) in the stromatolites and silica-tufa deposits were negative ($-0.81$ and $-0.95$, respectively). These correlations indicate that opal-A does not contribute to the REE content of the samples.

The enrichment of light elements compared to heavy elements was quantified by the $\text{La}_{(\text{N})}/\text{Yb}_{(\text{N})}$ ratio (Rollinson, 1993). The fine volcaniclastic deposits returned values of between 1/23 and 1/30, the silica-tufa deposits 1/01 to 1/33, the silicified plant remains and fine grain volcaniclastic sediments 1/10 to 1/24, and the stromatolites generally in the 1/03 to 1/73 range. The upper zone of the stromatolites returned higher values (1/42 to 1/73) than the lower zone (1/12 to 1/44). Europium and Cerium anomalies were quantified using the geometric mean recommended by Taylor & McLennan (1985) ($\text{Eu}/\text{Eu}^* = \text{Eu}_{(\text{N})}/[\text{Sm}_{(\text{N})}][\text{Gd}_{(\text{N})}]$) and ($\text{Ce}/\text{Ce}^* = \text{Ce}_{(\text{N})}/[\text{La}_{(\text{N})}][\text{Nd}_{(\text{N})}]$). The fine volcaniclastic sediments showed relatively flat distribution patterns with a positive anomaly for $\text{Ce}/\text{Ce}^*$, between 1/45 and 1/60. This positive anomaly was also recorded for the silica-tufa deposits ($\text{Ce}/\text{Ce}^*$, between 1/26 and 2/23; Fig. 4B), the stromatolites ($\text{Ce}/\text{Ce}^*$ between 1/0 and 2/41 (Fig. 4A), with lower values (1/00 to 1/34) in the upper zone than in the lower zone (1/46 to 2/40)], and in the deposits formed from plant remains and fine volcaniclastic sediments ($\text{Ce}/\text{Ce}^*$ 1/59 to 2/39). The stromatolites showed negative Eu anomalies ($\text{Eu}/\text{Eu}^* 0\text{-}71$ to 0/96; Fig. 4A). All other deposits showed positive Eu anomalies (Fig. 4B): the silica-tufa deposits showed the strongest ($\text{Eu}/\text{Eu}^* 1/42$ to 1/77), while those of the fine volcaniclastic sediments were insignificant ($\text{Eu}/\text{Eu}^* 1$ to 0/05).

STROMATOLITES: MORPHOLOGY AND STRUCTURE

Macroscale

The stromatolites are commonly covered by a hard, dark brown, exterior husk (EH) some 0.5 mm thick (Fig. 5A). When this EH is missing, the exterior surface is rough, with furrows and ridges. Fine volcaniclastic sediments cover this irregular surface. Completely silicified plant remains (frequently twigs) are commonly entombed within the stromatolites.

At first sight, three major growth layers can be differentiated in sections parallel to the maximum growth axis, perpendicular to the substrate (Fig. 5B); a lower microlaminated zone (LMZ; 0.5 to 1 cm thick) on the substrate, consisting of dense silica laminae (Fig. 5B); an un laminated intermediate zone (IZ; 1 to 10 cm thick) with spheroidal and fan-like structures and porosities [sometimes filled with fine volcaniclastic sediments (Fig. 5B)]; and an upper microlaminated...

Fig. 4. Distribution of the rare earth elements in the deposits: (A) Opaline stromatolites. (B) Other deposits: fine volcaniclastic sediments, silicified plant remains mixed with fine volcaniclastic sediments, and silica-tufa deposits. Normalized values versus NASC, data from Gromet et al. (1984).
Zone (UMZ; 0.5 to 1 cm thick) with compact microlaminations similar to those seen in the LMZ (Fig. 5B).

**Microscale**

In thin section, the opaline stromatolites consist of dense semi-opaque opaline silica (Figs 6, 7 and 8). Major growth layers show various contacts. The contact between the LMZ and the IZ is sharp (Figs 6A, 6B.5, 8A and 8B.1), whereas that between the IZ and UMZ is commonly gradational, with diffuse lamination and discontinuities between the top of the IZ and the lower part of the UMZ (Figs 6A, 6B.2, 8A, 8B.2 and 8B.3) where the discontinuities are less numerous and the lamination more clearly defined. Where the lamination is well-defined, the UMZ is clearly visible (Figs 6A and 8B.3).

Microlaminations of the LMZ and UMZ are very continuous (Figs 6B.5, 6B.6 and 8B.1), but those of the latter are always more diffuse (Fig. 6B.2) than those of the former. The first LMZ microlaminations mimic the relief of the volcanic host rock (Figs 6A, 6B.6, 7A, 7B, 8A and 8B.1) or the accumulations of small, lenticular, fine volcaniclastic sediments covering the host rock (Fig. 6A and 6B.6). The IZ shows globular, spheroidal, clotted and fan morphologies juxtaposed to build larger fans or arborescent growths (1 to 5 mm in height; Figs 6A, 6B.3, 7A and 7B). In the stromatolitic crusts in and around the southern entrance, the IZ is generally missing. The EH is formed by iron oxides/hydroxides (Figs 6B.1 and 8B.3), fine volcanic fragments and square-like opaque minerals (possibly pyrite sections) that appear locally at the base of this layer. Three general types of stromatolite (I to III) were defined according to variations in their thickness, internal structures, micromorphologies and distribution throughout the cave.

**Type I**

Found throughout the cave (Fig. 2B). The LMZ is 1 to 5 mm thick and shows very fine, flat-wavy, beige and dark brown laminae (Fig. 6A and 6B.6). The darker laminae may represent larger accumulations of opaline mud (Fig. 6B.6, black arrows). The flat-wavy lamination of the base progresses upwards to a pseudo-columnar or dome-shaped zone [following the terminology of Walter et al. (1976); Fig. 6A and 6B.5]. A microlaminated columnar zone (MCZ; 2 to 4 mm thick) is seen in the LMZ (Fig. 6A and 6B.4). In transverse sections, the MCZ shows spheroidal structures.

The intermediate zone (IZ; 1-5 to 2.5 cm thick) shows varying texture. The base (1 cm thick) has alveolar and arborescent morphologies and is partially porous (Fig. 6A and 6B.3). The porosity is partially or totally filled with a brown deposit formed by opaline mud. The top (1 to 0.5 cm thick) shows diffuse and discontinuous laminae (Fig. 6A and 6B.2).

The upper microlaminated zone (UMZ; 3 to 4 mm thick) shows parallel, diffuse and poorly defined, beige and dark brown opaline laminae (Fig. 6B.2). Two orders of stromatolitic growth patterns can be seen in the LMZ and UMZ: intermediate growth layers and minor growth
The intermediate growth layers consist of sets of opaline laminations. Each set is defined by a large accumulation of silica mud mixed with iron oxide, and occasionally with dispersed very fine volcaniclastic particles. The number of sets depends on the sample. Commonly, more sets are seen in the UMZ (two to seven sets of opaline laminations) than in the LMZ (one to four sets of opaline laminations). The last set of the LMZ has a domed pseudo-columnar shape, the consequence of the adaptation of the laminae to small silica mud accumulations at the lower boundary of the set.

Minor growth layers can be seen, commonly consisting of couplets of fine and continuous opaline microlaminations that form the sets previously described. Each couplet consists of a beige and dark brown opaline microlamination. Generally, the contact between these laminae is a gradual transition and the contact between couplets is clear-cut (although in some cases it can be diffuse). The couplets are 49 ± 10 μm thick in the LMZ and 107 ± 70 μm in the UMZ. The dark brown opaline microlaminas are commonly smaller than the beige opaline microlamina, and are located at the top of the cycle.

**Changes in the interior structure of type I stromatolites**

The stromatolites have complex three-dimensional structures, their interior structure varied in the thin sections taken perpendicular to the substrate. Four type I sub-types can be described:
(i) **subtype a**, which shows the four zones described above, i.e. a LMZ, a MCZ, an IZ with arborescent morphology and an UMZ (Fig. 7A); (ii) **subtype b**, which shows a thin LMZ, an IZ with cerebroid morphology and an UMZ (MCZ missing) (Fig. 7B); (iii) **subtype c**, which shows a sub-millimetric LMZ and an IZ grading from a clotted base to laminar columns at the top (UMZ missing; Fig. 7C); and (iv) **subtype d**, which possesses all zones, but with numerous intercalations of microlaminated layers and thin arborescent, cerebroidal and clotted layers (Fig. 7D).

**Type II**
This type is found only at the northern entrance below the fossil water mark (Fig. 8A). The LMZ is 1 to 2 mm thick at the base and shows very continuous, flat-wavy, beige and dark brown opaline laminations parallel to one another (Fig. 8A and 8B.1). At the top, irregular microlaminated dome morphologies are present (Fig. 8A).

The IZ (2 to 3 mm thick) is light-coloured, grows above the microlaminated irregular domes, and forms pseudocolumns at the base. This zone also shows lumpy masses of opal, along with diffuse and irregular laminae of small, closely linked hemispheroids that end as diffuse columns (Fig. 8A and 8B.1). At the top, irregular microlaminated dome morphologies are present (Fig. 8A).

In contrast to the LMZ, the UMZ has an interrupted microstructure with less diffuse intercalations of flat-wavy beige and dark brown opaline laminations. This zone shows two features: (i) domes of very variable size (1 to 3 cm thick) with parallel beige and dark brown microlaminations (Fig. 8A); and (ii) well-preserved columns (2 to 4 mm thick), formed by intercalations of beige and dark brown opaline microlaminations. These columns, which are rectangular at the top (Fig. 8A and 8B.3), show condensed laminae in the walls of the columns and in the depressed areas between them, and expanded laminae at the top. Darker, cyclical microlaminations can also be seen, indicating a probable accumulation of small amounts of opaline mud, very fine volcaniclastic sediments, and iron oxides (Fig. 8A).

In the direction of accretion, variations are observed in the thickness of the microlaminations that form the columns (Fig. 8B.3). Opaline mud, fine volcaniclastic sediments and iron oxides can be seen in the inter-columnar spaces. These deposits are episodically covered by new stromatolitic microlamination (Fig. 8B.3). Intermediate and minor growth layers also are observed in this type.

**Type III (stromatolitic crusts)**
This type — stromatolitic crusts — is found on the floor of the southern entrance (Fig. 9). These crusts are very thin (1 cm) compared to those of the other stromatolites found in the cave, and show no botryoidal shapes on the surface. The EH is lacking (Fig. 9A). The LMZ and UMZ can only be differentiated when a thin discontinuous IZ (<0.5 cm) interrupts the microlaminated growth with lenses of small, closely linked hemispheroids (Fig. 9B). The LMZ is 1 to 2 mm thick and the UMZ is 0.5 to 3 mm thick (Fig. 9B).
Scanning electron microscope observations

The stromatolites have a compact, dense UMZ and LMZ, both of which show many marks and moulds of bacterial filaments (diameters ca 0.5 μm) within dense opaline cement (Fig. 10A). The interior channel of some filaments can be clearly seen (Fig. 10B), along with pollen grains, fungi/algae and unidentified coccoid or elongated microorganisms (Fig. 11). Some zones show a microporous texture with rounded microcavities, possibly produced by microbial respiration producing microbubbles or possibly microspaces between opaline microspheres (Fig. 10B, black arrows). Perfectly spheroidal inorganic opal-A microspheres can be seen in some voids; their diameters reach 1.0 μm, but normally range between 0.3 μm and 0.5 μm (Fig. 10C). They may be interpreted as inorganic cements. Minor differences can be appreciated between the UMZ and LMZ; the UMZ has more pores than the LMZ and, in some cases, more visible granular opal masses and silicified bacterial filaments.

The components of the very porous IZ are more visible than in the laminated zone. Silica-coated filamentous bacterial-sheath frameworks (Fig. 10D) are sporadically mixed with fine volcaniclastic deposits, opaline microspheres, along with microorganisms such as diatoms, algae/fungi and unidentified others. The diameter of

Fig. 8. Thin section of a type II stromatolite. (A) Three parts can be observed: a lower microlaminated zone (LMZ); a clear intermediate zone (IZ) with diffuse columns; and an upper microlaminated zone (UMZ) with columns. The interdomal spaces and cracks/fissures are partially or totally filled with fine volcaniclastic sediments and silica mud (black arrows). (B) Thin section details: (B.1) columns of the UMZ covered by the EH formed by fine volcaniclastic sediments and iron oxides; (B.2) diffuse columns in the IZ; and (B.3) LMZ mimicking the volcanic host rock, showing spores and yellow mud.
the silica-coated filamentous bacterial sheaths ranges from 1.0 to 3.0 μm; the lengths were not accurately determined due to the entangled nature of the filament network, but reached up to at least 20 μm. Opaline microspheres form aggregates, cement pores or cover the bacterial filaments (Fig. 10D), increasing their thickness. The IZ comprises a fine matrix of opaline microspheres mixed with biofilms, filamentous shapes corresponding to silica-coated filamentous bacterial sheets, fine grains of volcanic rock, diatoms and spores, etc. (Fig. 10E).

The surface of the stromatolites is irregular and shows the presence of biofilms, filament nests/pompoms (Fig. 10F), patches of fine volcaniclastic sediments, scattered microorganisms (Fig. 11) such as diatoms, fungi and algae, unidentified testate amoeba [protistids; see similar protistids in Jones & Renaut (2007)] and pollen. The surfaces of some stromatolites show small mounds corresponding to the top of the columns, and accumulations of diatoms between them (Fig. 12A). Opal-A microspheres up to 500 nm in diameter (forming porous clotted aggregates and irregular clusters, chains and filamentous networks) were the first to precipitate on the basalt. Biofilm coatings (rich in C, detected by EDX) appear on the basalt surfaces (Fig. 12B). Locally, some aluminium phosphate (detected by EDX) appears on the basalt surface and on the stromatolitic crusts. The Si/Al atomic EDX ratio (ca 2.31%) of the fine, yellow sediments that fill the basal pores is much lower than that of the siliceous deposits (Si/Al atomic ratio 7 to 22%), indicating a mixture of allophane mixed with silica mud. Fine, orange sediments are mixed with iron oxides/oxyhydroxides (Si/Fe atomic ratio 1.23 to 2.72%).

**SILICEOUS DEPOSITS WITH SILICIFIED PLANT REMAINS (INSIDE AND OUTSIDE THE CAVE)**

The silica-tufa deposits outside the cave consist of silicified plant remains, such as well-preserved trunks, twigs, moss, leaves and roots, mixed with volcaniclastic sediments of variable size, silica mud and iron oxides/hydroxides. The silica-tufa deposits and those of plant remains mixed with fine volcaniclastic sediments inside the cave have similar components. The main differences are: (i) the volcanic fragments mixed in with the plant remains are smaller inside the cave than outside; (ii) the silica-tufa outside the cave contains more iron oxides/hydroxides than the deposits inside the cave; (iii) the plant remains in the silica-tufa deposits outside the cave are generally larger than any plant remains inside the cave; and (iv) the deposits inside the cave contain more silica mud (matrix) than the outside silica-tufa deposits.
Fig. 10. SEM photomicrographs of opaline stromatolites. (A) Moulds and marks left by bacterial filaments in the upper and lower microlaminated part of the stromatolite. (B) Microporous texture (black arrows) with very small, round cavities (<0.1 μm) and a mould of a silicified bacterial filament with an interior channel. (C) Inorganic opaline microspheres cementing a pore. (D) Filamentous bacteria covered by silica in the intermediate zone (porous part) of the stromatolite. (E) Fine volcaniclastic sediments mixed with opaline microspheres, biofilms, silicified bacteria sheaths and diatoms. (F) Silicified filaments nests/pompoms on the stromatolites.

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Fig. 11. SEM photomicrographs of various microorganisms in the opaline stromatolites: (A) silicified platelet microorganism and diatoms; (B) diatoms; (C) fungi and unidentified microorganisms; (D) coccoid morphologies inside a hole; (E) silicified spore with central pore; and (F) individual silicified platelet between silicified filamentous bacteria.

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Most of the clasts and silicified plant remains in both deposits are covered by an opaline stromatolitic crust (0 to 1 cm thick), similar to that seen in the LMZ, with very fine, flat-wavy laminations in the beige-dark brown laminae. The well-defined, laminated stromatolitic columns have round tops.

Scanning electron microscope observations

Fragments of silicified plant remains appear to be partially or totally cemented/replaced by microspheres of opal-A, sometimes with stromatolitic coatings, depending on their silicification stage (Fig. 13A). The stromatolitic coatings are compact and show signs of bacterial filaments. The silica-tufa deposits may be defined as stromatolitic tufas.

Well-preserved plant tissues and silica moulds of plant cells and their connections are visible under the SEM (Fig. 13B). Small amounts of silica microspheres cover the plant structures. Silicified bacterial filaments (Fig. 13C), diatoms and other organisms, mixed with inorganic silica microspheres, are found in pores in the interior of the plant structures.

Spiral tubes (10 to 30 μm in diameter and >2 mm in length), interpreted as silicified spirorgyra, all orientated in the same direction between the plant cells (Fig. 13D), cover and penetrate the plant remains. Dissolution processes, seen in both small superficial and deeper pores, reveal the internal spiral structure (Fig. 13D) of these algae. Silicified moss (Fig. 13E and F) with stromatolitic coatings appears in the silica-tufa deposits and in some deposits of plant remains inside the cave.

Opaline microspheres are visible all over the samples, forming a clotted silica matrix. Inorganic opaline microspheres appear in some pores; EDX analyses of these silica microspheres showed the inclusion of Ca, Al and Mg.

DISCUSSION

Opaline stromatolitic speleothems and silicified plant remains are the most significant features of the Branca Opala cave. Primary textures and structures can be observed in these stromatolites due to the lack of ageing; they are composed only of opal-A. No significant diagenesis due to ageing (Lynne et al., 2008) is visible; indeed, neither opal-CT nor quartz occur, and only in the LMZ is the opal-A slightly more ordered.

All of the opaline stromatolites occurred below a horizontal straight line interpreted as a fossil water level seen throughout the length of the cave (Fig. 2); they must therefore have formed beneath the surface of a standing body of water – a palaeolake in the lava tube. The horizontal straight line could be the record of the highest water level for this palaeolake. While the size of the stromatolitic botryoids varies randomly across the cave walls (type I stromatolites), they become smaller (type II stromatolites) just beneath of the fossil water level line. The thin type III stromatolites, which have

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Fig. 13. SEM photomicrographs of silicified plant remains. (A) Silicified twigs with a stromatolitic coating. (B) Well-preserved silicified moulds of plant cells and their connections. (C) Silicified bacterial filaments inside plant tissues. (D) Spiral tubes of spirogyra (10 to 30 μm in diameter and >2 mm long). (E) Silicified moss. (F) Detail of this silicified moss with bacterial filaments in the compact zone.

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only a UMZ and LMZ and are seen only at the southern entrance, are interpreted to have formed at the margin of the palaeolake. McInnish et al. (2002) suggest that stromatolites with flat laminated mats are typically restricted to shallow-water environments. The present stromatolites become larger, and their microlamination thicker, from the southern entrance towards the cave centre; they therefore appear to have become more complex where the water column was deeper. Nowadays, there is no lake in the cave; the current conditions are not the same as those that must have existed when the silica stromatolites formed. The dark EH is likely to be a response to more recent aerial conditions during which no growth occurred.

The stromatolites developed from a microlaminated continuous tabular biostroma (Preiss, 1976), growing into a zone with small accumulations of domes and columns, ending with another, new, tabular biostroma. Discontinuities between the zones are insignificant; no erosive surfaces were observed, suggesting continuous growth with no sub-aerial exposure. These observations suggest that a relatively closed system was maintained with stromatolites forming while constantly submerged. No mud-crack-like structures due to desiccation could be found.

The plant remains seen at different heights on the walls of the cave would have been floating on the surface of the palaeolake before adhering. Those plant remains mixed with volcaniclastic sediments on the floor of the cave may have accumulated by decantation before being silicified. Both types of plant remains were silicified under submerged conditions.

Currently, the cave has two entrances (northern and southern). On the walls of the northern entrance, the high water mark is clear, suggesting that this entrance did not exist during the period of stromatolite formation. The distribution of the stromatolites coincides with the submerged area within the cave (Fig. 2A). The northern entrance opened after the stromatolites had formed (Fig. 2A and B). The breakage/collapse of this end of the cave may have been the consequence of floods, seismic events, or even anthropic activity.

The fine volcaniclastic deposits inside the stromatolites, and covering their outsides, indicate them to have been, respectively, contemporaneous and subsequent to the formation of the stromatolites. These deposits are very atypical in other lava tubes on Terceira. Their accumulation in the Branca Opala cave may be a consequence of the northern entrance being closed for so long; even after its opening, its small size continued to act as a natural barrier to the deposition of fine volcaniclastic deposits.

Opaline stromatolites were found on some parts of the ceiling. Their cloud-like forms suggest that these parts of the cave were completely under water. In carbonate caves, cloud-like forms represent sub-aqueous carbonate coatings on larger bedrock projections produced beneath a body of water (Hill & Forti, 1997). The Lechugilla Cave in the Carlsbad Caverns National Park (New Mexico) and the Giusti Cave (Italy) both have cloud-like forms that were produced beneath a lake (Hill & Forti, 1997).

Filamentous structures were observed in all parts of all types of stromatolite. While the shape and size of these filaments are consistent with a bacterial origin (Jones et al., 2005), no bacteria could be identified from any of the fully silicified filament moulds and marks. Filamentous shapes were also found in the pores of basalt and other deposits in the cave, indicating that bacteria colonized the entire cave.

Bacteria provide reactive surface ligands that absorb silica from solution and, consequently, reduce the activation energy associated with opal nucleation (Konhauser, 2007). The opal microspheres precipitated on the filaments reproduce the morphology of the latter, thickening their diameter. The silicified filamentous bacteria form a substantial part of the different zones of the stromatolites. The opaline microspheres precipitated in the porous spaces between filaments have the same basic morphology as those that precipitated on the original filaments. Konhauser (2007) indicates that this occurs because silica precipitation continues auto-catalytically and abiotically for some time after bacterial death. During the experimental silification of Calothrix, Benning et al. (2004) confirmed the process to be initially governed by an increase in the thickness of the exopolymere polysaccharide sheath. In the present stromatolites, abiotic, inorganic silica precipitation occurred in a number of stromatolite pores. The best defined microspheres have surfaces that are less rough than those of the microspheres that cover the filaments (Fig. 10C).

The stromatolites grew perpendicularly to the walls and ceiling of the cave. Types I and II are located randomly across the walls to the level flooded by the palaeolake. Changes in the internal structure (major growth layers) of the stromatolites cannot be explained by variations in the energy of the water, fluctuations in the water...
level, or variations in light intensity, as proposed by Walter (1977) and Petryshyn & Corsetti (2011); the present stromatolites formed in a quiet, relatively closed palaeolake and in complete darkness (Fig. 2A).

The LMZ, IZ and UMZ were formed by distinct bacterial communities that produced different morphologies (microlaminated, arborescent, cerebroidal, etc). The microlaminated zones do not vary anywhere in the cave, indicating that the bacterial community was not influenced by the amount of light. However, the IZ only formed in deep parts of the palaeolake where there would have been no light; non-phototropic communities must therefore have been involved. Aubrecht et al. (2008) reported a fine-laminated morphology formed by silificed filamentous microbes, and a porous peloidal morphology (similar to the IZ studied) formed by Nostoc-type cyanobacteria. According to Cangemi et al. (2010), the alternation of the stromatolitic layers might respond to temporal or localized changes in environmental conditions that led to variations in the silica saturation of the palaeolake, inducing more or less abiotic/biotic silica accumulation.

The microlamination in the stromatolites (minor growth layers) may have a number of biological, geochemical, physical and sedimentological explanations, for example, alternating growth of the component organisms, periodic differences in the dominant bacteria, and periodic mineralization of the dominant bacteria, etc. (Monty, 1976). The microlamination in the LMZ and UMZ represents ancient silicified microbial mats, and would have required early lithification; without it, it is unlikely that a finely laminated microstructure could have been preserved (Reid et al., 2000; Berelson et al., 2011; among others). Reid et al. (2000) indicate that the recrystallization and/or rapid degradation of bacterial sheaths is not the only mechanism of lithification; the decomposition of an amorphous matrix of bacterial exopolymers can contribute towards it. Berelson et al. (2011) reported stromatolites that formed in hot springs to show submerged, finely laminated bodies with dark laminae composed of densely packed tubes orientated sub-parallel to the lamination, along with light laminae of greater porosity composed of sparsely packed tubes orientated sub-normally to the lamination. Mata et al. (2012) interpret this alternation as not attributable to a phototactic response, but rather to the alternation of laminae with filament bundles trapping oxygen-rich gas bubbles. In the present stromatolites, the interior microstructure of the laminae in the LMZ and UMZ are indistinguishable under the SEM, probably because subaqueous silification was very intense. Further, in addition to the replacement process associated with the microbial mats, intense silica cementation erased the microstructure.

The source of silica in the Branca Opala cave is unknown. The sub-aerial opaline stromatolitic speleothems of the Charles Brewer cave were formed by waters with silica concentrations of 16 p.p.m. (Aubrecht et al., 2012). The source of this silica is attributed to the dissolution of quartz from the sandstones that host the cave. A positive correlation between cave size and speleothem size has been reported, reflecting a relation between the total volume of SiO2 dissolved and re-precipitated (Aubrecht et al., 2008). In the Branca Opala cave, this correlation is absent because the opaline stromatolites are sub-aquatic and their distribution homogeneous.

Microbial catalysis can precipitate opal in the absence of very rich silica solutions, and probably contributed to the formation of the present opaline stromatolites. The intensely silicified, exceptionally well-preserved submerged wood and leaves observed in the cave indicate very rich silica solutions. The well-preserved silica-tufa deposits outside the cave indicate the same. Chen et al. (2009) argued that rapid precipitation in highly super-saturated silica conditions best preserves biological structures.

Silica-rich solutions can occur through the extensive weathering of volcanic rock and sediments, or they may originate in a local hydrothermal source. The basalt minerals in the walls and ceiling of the cave are not altered by weathering (Bustillo et al., 2010) and clay minerals rarely appear. While the composition of the amorphous matrix (major silica and minor iron oxides/hydroxides) of the fine volcaniclastic sediments might indicate strong leaching, the slight alteration of the detrital components does not support this. The simple leaching of meteoric water through volcanic rocks and sediments cannot, therefore, be the source of silica for the speleothems in the Branca Opala cave. However, CO2 accumulation via the decomposition of abundant organic matter (for example, in peat bogs) leads to strongly acidic soils; such pHs can lead to the strong alteration of soil silicates and volcanic rocks, the release of silica, and the formation of silica-rich groundwaters. Nonetheless, the formation of such a great quantity of opaline speleothems and silica-tufa deposits via such a silica source has never before been described.
Well-preserved siliceous stromatolites, silicified microbes and silicified plant remains are commonly formed in the presence of hydrothermal waters, for example, hot springs, geysers or hot water lakes. Such effluent solutions are highly super-saturated with respect to amorphous silica; examples include hot springs in Iceland (Konhauser et al., 2001, 2003) and those of Yellowstone National Park (Walter et al., 1972; Berelson et al., 2011; Pepe-Ranney et al., 2012), New Zealand (Jones, 2001; Jones et al., 2001, 2005; Handley et al., 2005, 2008; Schinteie et al., 2007) and Italy (Cangemi et al., 2010), among others.

The absence of speleothems of composition other than silica (for example, of ferrihydrite or allophane) in the Branca Opala cave, unlike in other caves of Terceira Island (Daza & Bustillo, 2013), might confirm the lack of any strong leaching of volcanic rocks or sediments, and may indirectly indicate a local source of hydrothermal water in the lava tube. Lynne (2012) reported sinter macrotextures over a range of temperatures. Those formed at low temperature (<35°C) showed plant material and bacterial filaments similar to those seen in the studied speleothems and silica-tufa deposits. The stromatolites and silica-tufa are rich in silica, but poor in the other elements hosted by volcaniclastic rock. Censi et al. (2013) used REE geochemical analysis to determine whether the hydrothermal fluids involved in the formation of siliceous stromatolites interacted with microbial mats during silica deposition. In the stromatolites of the Branca Opala cave, the linear correlation coefficient of Al2O3 and K2O with total REE reveals that the volcaniclastic grains hosted the REEs; the composition of these grains would distort any possible signs of hydrothermal water activity. Chemical rocks with bacterial contributions can be enriched in heavy REE (Takahashi et al., 2005, 2010), but no such enrichment was observed in the opaline stromatolites studied, probably because the volcaniclastic grains included in them distorted the REE signal. However, the stromatolite Eu anomalies were negative (Eu/Eu* 0-71 to 0-96), unlike those of the fine volcaniclastic sediments (Eu/Eu* 1 to 1-05), suggesting that this anomaly is not a legacy inherited from volcaniclastic sediment minerals, but the result of either bacterial activity (Censi et al., 2013) or local redox conditions (Calas et al., 2008). The positive Eu signature for the silica-tufa (Eu/Eu* 1-42 to 1-77) may be due to the REE composition of the volcanic clasts included in these deposits.

CONCLUSIONS

The silica speleothems (opaline stromatolites and silicified plant remains with stromatolitic coatings) of the Branca Opala Cave are formed only of opal-A; they show no important diagenetic modifications, facilitating the study of their genesis. Outside the cave, silica-tufa deposits show silicified plant remains with stromatolitic coatings of similar composition. The intense silicification that occurs in both environments can be explained by rapid silicification from highly super-saturated water.

These opaline stromatolites are recent, but currently inactive; a compact exterior husk marks the end of their growth; they were formed in submerged conditions in a palaeolake in the lava tube, below a well-defined and continuous, fossil high water level. During formation, the system was relatively closed; certainly, the northern entrance was not open. Internal growth patterns showing no important discontinuities indicate a tranquil formation environment.

The stromatolites extend no further than the perimeter of the palaeolake. The similar distribution of type I and II stromatolites along the walls of the cave indicates that the height of the column of water was more or less similar everywhere. The type III stromatolitic crusts found at the southern entrance indicate a shallower water column and the edge of the palaeolake. Some parts of the lava tube were flooded to the ceiling, as revealed by the cloud-like stromatolitic forms found there.

Different silicified filamentous bacterial frameworks were seen in the opaline stromatolites, in the silicified coating on plant remains, and in the cement in the pores of the volcanic host rock. Bacterial filaments therefore colonized the whole lava tube, along with small ponds outside. Distinct bacterial communities laid the major growth layers of the opaline stromatolites. Changes in bacterial communities cannot be explained by variations in the energy of the water, fluctuations in the water level, nor variations in the light intensity; the different major growth layers were formed in the same almost closed, dark and stable palaeolake.

The source of silica for the formation of the stromatolitic speleothems, and for the intense silicification that preserved plant remains both inside the cave and in the silica-tufa outside the cave, cannot be explained by the simple leaching of meteoric water through the volcanic rocks or sediments. Highly super-saturated silica waters and rapid silica precipitation suggest a
local hydrothermal source in the lava tube or nearby. However, analysis of the major, minor and rare earth elements of the opaline stromatolites and silica-tufa deposits could not confirm a hydrothermal origin; all elements, except for silica, were found in the volcanlastic grains included within them.

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