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

Running Head: Opaline stromatolites in a lava tube

RAQUEL DAZA BRUNET*and MARÍA ÁNGELES BUSTILLO REVUELTA†

**Departamento de Geología, Museo Nacional de Ciencias Naturales-CSIC-Madrid, 28006 Madrid (E-mail: raquel.daza@mncn.csic.es)*

†Departamento de Geología, Museo Nacional de Ciencias Naturales-CSIC-Madrid, 28006 Madrid. (abustillo@mncn.csic.es)

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 aging 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 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; Vidal & Vaquero, 2007; Cioccale *et al.*, 2008; Willems *et al.*, 2002; Vidal *et al.*, 2010), quartzite or sandstone (Aubrecht *et al.*, 2008, 2012; Wray, 1999, 2011, 2013). 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 Carvão 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. They 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 (Taboroši, 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; Lévillét *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 resemble 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; Cangemi *et*

1 *al.*, 2010; Pepe-Ranne *et al.*, 2012). Some siliceous stromatolites show the signs of
2 microbial activity, such as microbial mats, biofilms and mucus (exopolymers) (Jones *et*
3 *al.*, 2005; Handley *et al.*, 2008), cyanobacteria (e.g. Pepe-Ranne *et al.*, 2012),
4 stromatolitic microfacies colonized by bacilli, diatoms and coccoidal algae (e.g.
5 Schinteie *et al.*, 2007), and bacterial filaments (e.g. Jones *et al.*, 2005). Such
6 stromatolites are found under water, emerging only at the water-air interface. Generally,
7 siliceous stromatolites are thought to form only where there is sunshine, and where the
8 depth of the water column, temperature and pH permit the growth of bacterial mats (e.g.
9 Petryshyn&Corsetti, 2011).

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

18 **GEOLOGICAL SETTING**

19 The Azores Islands lie in the North Atlantic Ocean about 1600 km west of Lisbon,
20 Portugal. The archipelago comprises nine volcanic islands that fall into three main
21 groups; the Flores and Corvo group to the west, the Graciosa, Terceira, São Jorge, Pico,
22 and Faial group in the center, and São Miguel, Santa Maria and the Formigas Reef group
23 to the east. They extend in a northwest-southeast direction for more than 600 km along
24 the Azores-Gibraltar fault (Fig.1A). The islands were created by lava flows from the
25 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 northwest 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 northwest (Nunes, 2000, 2004; França *et al.*, 2003). The four volcanic systems developed along a prominent NW-SE 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 Cavernícola 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 meters 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 volcanoclastic sediments, and volcanoclastic sediments (Fig. 3A). Silica-tufa deposits are present outside the cave in an area known as the Ribeira da Biscoitos.

1 **a)Opaline stromatolites.** These deposits grew directly on the volcanic rock or other
2 cave deposits such as plants remains, collapse breccias (Fig. 3A) and volcanoclastic
3 sediments. These sediments are beige and brown in colour, and their exterior
4 morphology ranges from low-relief, cloud-like mounds to bulbous, botryoidal masses of
5 linked domes (Figs 3A to C). Their interior shows accretionary laminated and layered
6 structures. These stromatolites range from 1 to 12 cm in height, and have a diameter of 3
7 to 15 cm. Their size decreases from the cave center towards the two entrances. Those
8 with botryoidal morphologies are found mainly on the walls but always beneath a
9 horizontal line (a fossil water level; Figs 2 and 3B and C). This water level can be
10 followed throughout the cave (Figs 2 and 3B and C). The botryoidal stromatolites are
11 smaller just beneath the water mark, and increase in size downwards (Figs 2B.2 and B.4
12 and 3C). Stromatolites with cloud/bulbous morphologies are seen mainly on the ceiling
13 and on certain parts of the walls. Specimens with botryoidal shapes and cloud-like
14 morphologies sometimes co-occur (Fig. 2B.3). Thin stromatolitic crusts (1 to 2 cm) are
15 seen at the southern entrance of the cave (Fig. 2B and B.1). Silicified plant remains are
16 found between the stromatolites.

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

c) 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).

d) 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 CuK α 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 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; Hillsboro, OR, USA) (SEM) (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). Precise aluminum 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 centered around 22°2θ (~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 Å 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).

a) 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.

b) Deposits formed by plant remains mixed with volcanoclastic 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%).

c) Fine volcanoclastic 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.

d) 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% SiO_2) accompanied by variable proportions of Al_2O_3 (0.2 to 1.1%), Fe_2O_3 (0.1 to 0.5%), MgO (0.3 to 0.8%), CaO (0.2 to 0.4%), Na_2O ($\leq 0.2\%$), K_2O ($\leq 0.2\%$), TiO_2 ($\leq 0.1\%$), P_2O_5 ($\leq 0.05\%$) and MnO ($\leq 0.04\%$). The upper part of the stromatolites was slightly richer in silica (88.6 ± 0.40 compared to the lower part $87.39 \pm 1.08\%$). WDS analysis of the stromatolite laminae revealed some Al in the opal-A structure ($0.57 \pm 0.20\%$ atomic weight). Laminae with brown colouration showed higher aluminum 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 volcanoclastic sediments returned comparatively high values for all major elements: SiO_2 39 to 49%, Al_2O_3 15 to 16%, Fe_2O_3 ~ 8%, MgO 1.2 to 1.4%, CaO 1.9 to 2.3%, Na_2O 2.6 to 3.2%, K_2O 1.6 to 1.9%, TiO_2 1.2 to 1.5%, P_2O_5 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 volcanoclastic sediments.

Minor elements

For all the samples studied, the minor element correlation matrix showed the majority of the elements analyzed (Ba, Co, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, Zr, and Y) to be strongly and positively correlated with $\text{Al}_2\text{O}_3\%$ (correlation coefficients $>+0.90$), and negatively with $\text{SiO}_2\%$ (>-0.84). The minor elements detected therefore mainly form part of the fine volcanoclastic 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 Al_2O_3 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 volcanoclastic fragments on the REE concentrations was clearly observed. The percentage of Al_2O_3 and total REE (ΣREE) 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 K_2O and REE (ΣREE) was $+0.83$ for the stromatolites and $+0.98$ for the silica-tufa deposits. The correlation coefficients for percentage SiO_2 and REE (ΣREE) 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 $La_{(N)}/Yb_{(N)}$ ratio (Rollinson, 1993). The fine volcanoclastic deposits returned values of between 1.23 and 1.30, the silica-tufa deposits 1.01 to 1.33, the silicified plants remains and fine grain volcanoclastic 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). Eu and Ce anomalies were quantified using the geometric mean recommended by Taylor & McLennan (1985) ($Eu/Eu^* = Eu_{(N)}/\sqrt{[Sm_{(N)}] \cdot [Gd_{(N)}]}$) and ($Ce/Ce^* = Ce_{(N)}/\sqrt{[La_{(N)}] \cdot [Nd_{(N)}]}$). The fine volcanoclastic sediments showed relatively flat distribution patterns with a positive anomaly for Ce (Ce/Ce^* , between 1.45 and 1.60). This was also recorded for the silica-tufa deposits (Ce/Ce^* , between 1.26 and 2.23; Fig. 4B), the stromatolites [Ce/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 volcanoclastic sediments (Ce/Ce^* 1.59 to 2.39). The stromatolites showed negative Eu anomalies (Eu/Eu^* 0.71 to 0.96; Fig. 4A). All other deposits showed positive Eu anomalies (Fig. 4B): the silica-tufa deposits showed the strongest (Eu/Eu^* 1.42 to 1.77) while those of the fine volcanoclastic sediments were insignificant (Eu/Eu^* 1 to 1.05).

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,

1 with furrows and ridges. Fine volcanoclastic sediments cover this irregular surface.
2 Completely silicified plant remains (frequently twigs) are commonly entombed within
3 the stromatolites.

4 At first sight, three major growth layers can be differentiated in sections parallel to
5 the maximum growth axis, perpendicular to the substrate (Fig. 5B): a lower
6 microlaminated zone (LMZ; 0.5 to 1cm thick) on the substrate, consisting of dense silica
7 laminae (Fig. 5B); an unlaminated intermediate zone (IZ; 1 to 10 cm thick) with
8 spheroidal and fan-like structures and porosities[sometimes filled with fine
9 volcanoclastic sediments (Fig. 5B)]; and an upper microlaminated zone (UMZ; 0.5 to 1
10 cm thick) with compact microlaminations similar to those seen in the LMZ (Fig. 5B).

12 **Microscale**

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

20 Microlaminations of the LMZ and UMZ are very continuous (Figs 6B.5 and B.6 and
21 8B.1), but those of the latter are always more diffuse (Fig. 6B.2) than those of the
22 former. The first LMZ microlaminations mimic the relief of the volcanic host rock (Figs
23 6A and B.6, 7A and B and 8A and B.1) or the accumulations of small, lenticular, fine
24 volcanoclastic sediments covering the host rock (Fig. 6A and B.6). The IZ shows
25 globular, spheroidal, clotted and fan morphologies juxtaposed to build larger fans or

1 arborescent growths (1 to 5 mm in height; Figs 6A and B.3 and 7A and B). In the
2 stromatolitic crusts in and around the southern entrance, the IZ is generally missing. The
3 EH is formed by iron oxides/hydroxides (Figs 6B.1 and 8B.3), fine volcanic fragments
4 and square-like opaque minerals (pyrite sections?) that appear locally at the base of this
5 layer.

6 Three general types of stromatolite (I to III) were defined according to variations in their
7 thickness, internal structures, micromorphologies and distribution throughout the cave.

8 9 *Type I*

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

17 The intermediate zone (IZ; 1.5 to 2.5 cm thick) shows varying texture. The base (1
18 cm thick) has alveolar and arborescent morphologies and is partially porous (Fig. 6A
19 and B.3). The porosity is partially or totally filled with a brown deposit formed by
20 opaline mud. The top (1 to 0.5 cm thick) shows diffuse and discontinuous laminae (Fig.
21 6A and B.2).

22 The upper microlaminated zone (UMZ; 3 to 4 mm thick) shows parallel, diffuse and
23 poorly-defined, beige and dark brown opaline laminae (Fig. 6B.2). Two orders of
24 stromatolitic growth patterns can be seen in the LMZ and UMZ: intermediate growth
25 layers and minor growth layers. The intermediate growth layers consist of sets of

1 opaline laminations. Each set is defined by a large accumulation of silica mud mixed
2 with iron oxide, and occasionally with dispersed very fine volcanoclastic particles. The
3 number of sets depends on the sample. Commonly, more sets are seen in the UMZ (2 to
4 7 sets of opaline laminations) than in the LMZ (1 to 4 sets of opaline laminations). The
5 last set of the LMZ has a domed pseudo-columnar shape, the consequence of the
6 adaptation of the laminae to small silica mud accumulations at the set's lower boundary.

7 Minor growth layers can be seen, commonly consisting of couplets of fine and
8 continuous opaline microlaminations that form the sets previously described. Each
9 couplet consists of a beige and dark brown opaline microlamination. Generally, the
10 contact between these laminae is a gradual transition and the contact between couplets is
11 clear-cut (although in some cases it can be diffuse). The couplets are $49 \pm 10 \mu\text{m}$ thick in
12 the LMZ and $107 \pm 70 \mu\text{m}$ in the UMZ. The dark brown opaline microlaminae are
13 commonly smaller than the beige opaline microlamina, and are located at the top of the
14 cycle.

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

17 The stromatolites have complex three-dimensional structures, their interior structure
18 varied in the thin sections taken perpendicular to the substrate. Four type I sub-types can
19 be described: (i) *subtype a*, which shows the four zones described above, i.e., an LMZ,
20 an MCZ, an IZ with arborescent morphology, and a UMZ (Fig. 7A); (ii) *subtype b*, which
21 shows a thin LMZ, an IZ with cerebroid morphology, and a UMZ (MCZ missing) (Fig.
22 7B); (iii) *subtype c*, which shows a sub-millimetric LMZ and an IZ grading from a
23 clotted base to laminar columns at the top (UMZ missing; Fig. 7C); and (iv) *subtype d*,
24 which possesses all zones, but with numerous intercalations of microlaminated layers
25 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 B.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 B.2).

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 B.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 volcanoclastic 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 volcanoclastic 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. An 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 0.5 to 3 mm thick (Fig. 9B).

SEM observations

The stromatolites have a compact, dense UMZ and LMZ, both of which show many marks and molds of bacterial filaments (diameters $\sim 0.5 \mu\text{m}$) 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 cocoid 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 $1.0 \mu\text{m}$ but normally range between 0.3 and $0.5 \mu\text{m}$ (Fig. 10C). They may be interpreted as inorganic cements. Minor differences can be appreciated between the UMZ and LMZ; the UMZ have 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 volcanoclastic deposits, opaline microspheres, along with microorganisms such

as diatoms, algae/fungi and others unidentified. The diameter of 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 volcanoclastic sediments, scattered microorganisms (Fig. 11) such as diatoms, fungi and algae, unidentified testate amoeba [protistids; see similar protistids in Jones & Renault (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 aluminum phosphate (detected by EDX) appears on the basalt surface and on the stromatolitic crusts. The Si/Al atomic EDX ratio ($\sim 2.31\%$) of the fine, yellow sediments that fill the basalt 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 volcanoclastic sediments of variable size, silica mud and iron oxides/hydroxides. The silica-tufa deposits and those of plant remains mixed with fine volcanoclastic 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.

Most of the clasts and silicified plant remains in both deposits are covered by an opaline stromatolitic crust (0.1 to 1.0 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.

SEM observations

Fragments of silicified plant remains appear 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 molds of plant cells and their connections are visible under the SEM (Fig. 13B). Small amounts of silica microspheres cover the plant

1 structures. Silicified bacterial filaments (Fig. 13C), diatoms and other organisms, mixed
2 with inorganic silica microspheres, are found in pores in the interior of the plant
3 structures.

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

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

14 DISCUSSION

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

20 All the opaline stromatolites occurred below a horizontal straight line interpreted as a
21 fossil water level seen throughout the length of the cave (Fig. 2). They must therefore
22 have formed beneath the surface of a standing body of water - a paleolake in the lava
23 tube. The horizontal straight line could be the record of the highest water level for this
24 paleolake. While the size of the stromatolitic botryoides varies randomly across the cave
25 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 only an UMZ and LMZ and are seen only at the southern entrance, are interpreted as having formed at the margin of the paleolake. McInnis *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 center. 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 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 paleolake before adhering. Those plant remains mixed with volcanoclastic 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 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 volcanoclastic 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 volcanoclastic deposits.

Opaline stromatolites were found on some parts of the ceiling. Their cloud-like forms suggest 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 Lechuguilla 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 is consistent with a bacterial origin (Jones *et al.*, 2005), no bacteria could be identified from any of the fully silicified filament molds 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 latter's morphology, 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 this to occur because silica precipitation continues auto-catalytically and abiogenically for some time after bacterial death. During the experimental silicification of *Calothrix*, Benning *et al.* (2004) confirmed the process to be initially governed by an increase in the thickness of the exopolymeric polysaccharide sheath. In the present stromatolites, abiogenic, 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 paleolake. 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 paleolake 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 paleolake 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 silicified 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 paleolake's silica saturation, 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, e.g., 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 sub-aqueous silicification 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 ppm (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 relationship between the total volume of SiO₂ dissolved and re-precipitated (Aubrecht *et al.*, 2008). In the Branca Opala cave, this correlation is absent since the opaline stromatolites are sub-aquatic and their distribution homogeneous.

Microbial catalysis can precipitate opal in the absence of very rich silica solutions, and likely 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 volcanoclastic 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 (e.g., 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, e.g., hot springs, geysers or hot water lakes. Such effluent solutions are highly super-saturated with respect to amorphous silica; examples include Iceland's hot springs (Konhauser *et al.*, 2001, 2003), and those of Yellowstone National Park (Walter, *et al.*, 1972; Berelson *et al.*, 2011; Pepe-Rannek *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 (e.g. 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 volcanoclastic 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 volcanoclastic sediments (Eu/Eu^* 1 to 1.05), suggesting that this anomaly is not a legacy inherited from volcanoclastic sediment minerals but the result of either bacterial activity (Censi *et al.*, 2013) or local redox conditions (Calaset *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 EH marks the end of their growth. They were formed in submerged conditions in a paleolake 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 paleolake. The similar distribution of type I and II 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 less deep water column and the edge of the paleolake. 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 paleolake.

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 volcanoclastic grains included within them.

ACKNOWLEDGEMENTS

This research was funded by the Spanish Ministry of Economy and Competitiveness; project CGL2011-27826-CO2-02. Raquel Daza is supported by a CSIC JAE-Predocctoral grant co-financed by the European Social Fund (ESF). The authors are grateful to Fernando Pereira of the *Associação Os Montanheiros* for local logistic support, to Maria Rosario Carvalho of the University of Lisbon, and Joao Carlos

Nunes of the University of the Azores for scientific support, and to Laura Tormo, Marta Furió and Alberto Jorge García of the Non-destructive Analytical Techniques Laboratory, *Museo Nacional de Ciencias Naturales* (CSIC) Madrid, for assistance with SEM-EDS-WDS. We would like to thank reviewers unidentified, Drs. Paolo Forti and Tracy Frank for their detailed review of the manuscript. We also wish to thank Bernhard Riegl for helpful editorial comments. We thank James Cerne and Adrian Burton for assistance with our English.

REFERENCES

- Aubrecht, R., Barrio-Amoros, C.L., Breure, A.S.H., Brewer-Carías, C., Derka, T., O.A, F.-R., Gregor, M., Kodada, J., Kováčik, L., Lánzos, T., Lee, N.M., Liščák, P., Schlögl, J., Šmída, B. and Vlček, L. (2012) *Venezuelan tepuis: their caves and biota*. Acta Geol. Slovaca, Bratislava, 168 pp.
- Aubrecht, R., Brewer-Carías, C., Šmída, B., Audy, M. and Kováčik, L. (2008) Anatomy of biologically mediated opal speleothems in the World's largest sandstone cave: Cueva Charles Brewer, Chimantá Plateau, Venezuela. *Sed. Geol.* **203**, 181-195.
- Benning, L.G., Phoenix, V.R., Yee, N. and Konhauser, K.O. (2004) The dynamics of cyanobacterial silicification: an infrared micro-spectroscopic investigation. *Geochim. Cosmochim. Acta*, **68**, 743-757.
- Berelson, W.M., Corsetti, F.A., Pepe-Ranne, C., Hammond, D.E., Beaumont, W. and Spear, J.R. (2011) Hot spring siliceous stromatolites from Yellowstone National Park: assessing growth rate and laminae formation. *Geobiology*, **9**, 411-424.

- 1 **Bustillo, M., Aparicio, A. and Carvalho, M.** (2010) Estromatolitos silíceos en
2 Espeleotemas de la Cueva de Branca Opala (Isla Terceira, Azores). *Macla*,**13**, 51-
3 52.
- 4 **Calas, G., Agrinier, P., Allard, T. and Ildefonse, P.** (2008) Alteration geochemistry of
5 the Nopal I uranium deposit (Sierra Peña Blanca, Mexico), a natural analogue for a
6 radioactive waste repository in volcanic silica-silica-tufa. *Terra Nova*, **20**, 206-212.
- 7 **Calvert, A.T., Moore, R.B., McGeehin, J.P. and Rodrigues da Silva, A.M.** (2006)
8 Volcanic history and $^{40}\text{Ar}/^{39}\text{Ar}$ and ^{14}C geochronology of Terceira Island, Azores,
9 Portugal. *J. Volcanol. Geoth. Res.*,**156**, 103-115.
- 10 **Cangemi, M., A., B., Borin, S., Hopkinson, L., Mapelli, F. and Neri, R.** (2010) The
11 genesis of actively growing siliceous stromatolites: Evidence from Lake Specchio di
12 Venere, Pantelleria Island, Italy. *Chem. Geol.*, **276**, 318.
- 13 **Censi, P., Cangemi, M., Madonia, P., Saiano, F., Brusca, L. and Zuddas, P.** (2013)
14 Discrimination between Effects Induced by Microbial Activity and Water-Rock
15 Interactions under Hydrothermal Conditions According to REE Behaviour. *Proced.*
16 *Earth Planet. Sci.*, **7**, 123-126.
- 17 **Cioccale, M.A., Pasquini, A.I. and Depetris, P.J.** (2008) Hallazgo de espeleotemas
18 silíceos en rocas graníticas del batolito de Achala, Sierras Pampeanas de
19 Córdoba. *Rev. Asoc. Geol. Argentina*,**63**, pp. 417-420.
- 20 **Chen, X., Wang, W., Shang, Q., Lou, Y., Liu, X., Cao, C. and Wang, Y.** (2009)
21 Experimental evidence for eukaryotic fossil preservation: Onion skin cells in silica
22 solution. *Precambrian Res.*, **170**, 223-230.
- 23 **Daza, R. and Bustillo, M.A.** (2013) Mineralogía de los bioespeleotemas de la “Galeria
24 da Queimada” (Terceira, Azores). *Macla*, **16**. 43-44.

- 1 **Daza, R., Bustillo, M.A., Carvalho, M.R., Nunes, J.C. and Pereira, F. (2012)**
2 Distribución, composición y génesis de depósitos silíceos en la cueva volcánica de
3 Branca Opala (Terceira, Islas Azores). *Geogaceta*, **52**, 37-40.
- 4 **Forti, P. (1994)** Los depósitos químicos de la Sima AondaSuperious y de otras cavidades
5 del Auyn-Tepui, Venezuela. *Bol. Vol. Venezolana. Espeleol*, 28, 1-4.
- 6 **Forti, P. (2001)** Biogenic speleothems: an overview. *Int. J. Spele.*, **30**, 39-56.
- 7 **Forti, P. (2005)** Genetic processes of cave minerals in volcanic environments: An
8 overview. *J. Cave. Karst. Stud.*, **67**, 3-13.
- 9 **França, Z., Cruz, J.V., Nunes, J.C. andForjaz, V.H. (2003)** Geologia dos Açores: uma
10 perspectiva actual. *Açoreana*, **10**, 11-140.
- 11 **Gromet, L.P., Haskin, L.A., Korotev, R.L. andDymek, R.F. (1984)** The “North
12 American shale composite”: Its compilation, major and trace element
13 characteristics. *Geochim.Cosmochim.Acta*, **48**, 2469-2482.
- 14 **Handley, K.M., Campbell, K.A., Mountain, B.W. and Browne, P.R.L. (2005)**
15 Abiotic–biotic controls on the origin and development of spicular sinter: in situ
16 growth experiments, Champagne Pool, Waiotapu, New Zealand. *Geobiology*, **3**, 93-
17 114.
- 18 **Handley, K.M., Turner, S.J., Campbell, K.A. and Mountain, B.W. (2008)** Silicifying
19 Biofilm Exopolymers on a Hot-Spring Microstromatolite: Templating Nanometer-
20 Thick Laminae. *Astrobiology*, **8**, 747-770.
- 21 **Herdianita, N.R., Browne, P.R.L. and Rodgers, K.A. (2000)** Mineralogical and
22 textural changes accompanying ageing of silica sinter. *Mineral.Deposita*, **35**, 48-62.
- 23 **Hill, C.A. andForti, P. (1997)** *Cave minerals of the world*.National Speleological
24 Society, Huntsville, Alabama, USA, 463 pp.

- 1 **Jones, B.** (2001) Microbial Activity in Caves-A Geological Perspective. *Geomicrobiol. J.*,
2 **18**, 345-357.
- 3 **Jones, B. and Renaut, R.W.** (2007) Selective mineralization of microbes in Fe-rich
4 precipitates (jarosite, hydrous ferric oxides) from acid hot springs in the Waiotapu
5 geothermal area, North Island, New Zealand. *Sedim. Geol.*, **194**, 77-98.
- 6 **Jones, B., Renaut, R. and Konhauser, K.** (2005) Genesis of large siliceous
7 stromatolites at Frying Pan Lake, Waimangu geothermal field, North Island, New
8 Zealand. *Sedimentology*, **52**, 1229-1252.
- 9 **Jones, B., Renaut, R.W. and Rosen, M.R.** (1997) Biogenicity of silica precipitation
10 around geysers and hot-spring vents, North Island, New Zealand. *J. Sed. Res.*, **67**,
11 88-104.
- 12 **Jones, B., Renaut, R.W. and Rosen, M.R.** (2001) Microbial Construction of Siliceous
13 Stalactites at Geysers and Hot Springs: Examples from the Whakarewarewa
14 Geothermal Area, North Island, New Zealand. *Palaios*, **16**, 73-94.
- 15 **Jones, J.B. and Segnit, E.R.** (1971) The nature of opal I. Nomenclature and constituent
16 phases. *J. Geol. Soc. Aust.*, **18**, 57-68.
- 17 **Konhauser, K.O.** (2007) *Introduction to geomicrobiology*. Blackwell Science Ltd,
18 Oxford, UK, 452 pp.
- 19 **Konhauser, K.O., Jones, B., Reysenbach, A.L. and Renaut, R.W.** (2003) Hot spring
20 sinters: keys to understanding Earth's earliest life forms. *Can. J. Earth Sci.*, **40**,
21 1713-1724.
- 22 **Konhauser, K.O., Phoenix, V.R., Bottrell, S.H., Adams, D.G. and Head, I.M.** (2001)
23 Microbial-silica interactions in Icelandic hot spring sinter: possible analogues for
24 some Precambrian siliceous stromatolites. *Sedimentology*, **48**, 415-433.

- 1 **Léveillé, R.J., Fyfe, W.S., Longstaffe, F.J.**(2000) Geomicrobiology of carbonate–
2 silicate microbialites from Hawaiian basaltic sea caves. *Chemical Geol.*, **169**, 339–
3 355.
- 4 **Lynne, B.Y., Campbell, K.A., Moore, J. and Browne, P.R.L.** (2008) Origin and
5 evolution of the Steamboat Springs siliceous sinter deposit, Nevada, U.S.A. *Sedim.*
6 *Geol.*, **210**, 11-131.
- 7 **Lynne, B.Y.** (2012) Mapping vent to distal-apron hot spring paleo-flow pathways using
8 siliceous sinter architecture. *Geothermics*, **43**, 3-24.
- 9 **Mata, S.A., Harwood, C.L., Corsetti, F.A., Stork, N.J., Eilers, K., Berelson, W.M.**
10 and **Spear, J.R.** (2012) Influence of gas production and filament orientation on
11 stromatolite microfabric. *Palaios*, **27**, 206-219.
- 12 **McInnish, M.B., Bartley, J.K. and Kah, L.** (2002) Environmental change recorded by
13 stromatolite morphology: quantitative approaches. In: *2002 Denver Annual Meeting*,
14 *Denver, CO, USA*.
- 15 **Monty, C.L.V.** (1976) The Origin and Development of Cryptalgal Fabrics. In:
16 *Developments in Sedimentology* (Ed M.R. Walter), **20**, pp. 193-249. Elsevier.
17 Amsterdam.
- 18 **Navarro, A., Lourenço, N., Chorowicz, J., Miranda, J.M. and Catalão, J.** (2009)
19 Analysis of geometry of volcanoes and faults in Terceira Island (Azores): Evidence
20 for reactivation tectonics at the EUR/AFR plate boundary in the Azores triple
21 junction. *Tectonophysics*, **465**, 98-113.
- 22 **Nunes, J.C.** (2000) Notas sobre a geologia da Ilha Terceira. *Açoreana*, **9**, 205-215.
- 23 **Nunes, J.C.** (2004) Atlas Básico dos Açores: Observatório Vulcanológico e Geotérmico
24 dos Açores, Ponta Delgada. OVGA-São Miguel, Azores. 60-62.

- 1 **Pepe-Ranney, C., Berelson, W.M., Corsetti, F.A., Treants, M. and Spear, J.R.** (2012)
2 Cyanobacterial construction of hot spring siliceous stromatolites in Yellowstone
3 National Park.*Environ. Microbiol.*,**14**, 1182-1197.
- 4 **Petryshyn, V.A. and Corsetti, F.A.** (2011) Analysis of growth directions of columnar
5 stromatolites from Walker Lake, western Nevada. *Geobiology*, **9**, 425-435.
- 6 **Preiss, W.V.** (1976) Basic Field and Laboratory Methods for the Study of Stromatolites.
7 In: *Developments in Sedimentology* (Ed M.R. Walter), **20**, pp. 5-13. Elsevier.
8 Amsterdam.
- 9 **Reid, R.P., Visscher, P., Decho, A., Stolz, J.F., Bebout, B., Dupraz, C., Macintyre, I.,**
10 **Paerl, H., Pinckney, J. and Prufert-Bebout, L.** (2000) The role of microbes in
11 accretion, lamination and early lithification of modern marine stromatolites. *Nature*,
12 **406**, 989-992.
- 13 **Rollinson, H.R.** (1993) *Using geochemical data: evaluation, presentation,*
14 *interpretation.* Longman Scientific & Technical, Essex, 352 pp.
- 15 **Schinteie, R., Campbell, K.A. and Browne, P.R.** (2007) Microfacies of stromatolitic
16 Sinter from acid-sulphate-chloride springs at Parariki stream, Rotokawa Geothermal
17 Field, New Zealand. *Palaeontol. Electron.*,**10**. 33pp.
- 18 **Self, S. and Gunn, B.** (1976) Petrology, volume and age relations of alkaline and
19 saturated peralkaline volcanics from Terceira, Azores. *Contrib. Mineral. Petrol.*, **54**,
20 293-313.
- 21 **Taboroši, D.** (2006) Biologically influenced carbonate speleothems. *Perspectives on Karst*
22 *Geomorphology, Hydrology, and Geochemistry—A tribute volume to Derek C. Ford*
23 *and William B. White. Geol. Soc. Am. Spec. Paper*, 2006, vol. 404, p. 307-317.

- 1 **Takahashi, Y., Châtellier, X., Hattori, K.H., Kato, K. and Fortin, D.** (2005)
- 2 Adsorption of rare earth elements onto bacterial cell walls and its implication for
- 3 REE sorption onto natural microbial mats. *Chem.Geol.*,**219**, 53-67.
- 4 **Takahashi, Y., Yamamoto, M., Yamamoto, Y. and Tanaka, K.** (2010) EXAFS study
- 5 on the cause of enrichment of heavy REEs on bacterial cell surfaces.
- 6 *Geochim.Cosmochim.Acta*, **74**, 5443.
- 7 **Taylor, S.R. and McLennan, S.M.** (1985) *The continental crust: Its composition and*
- 8 *evolution*. Blackwell Science Ltd, Oxford, UK, 328 pp.
- 9 **Vidal, J.R., Sanjurjo, J., Vaqueiro, M. and Fernández, D.** (2010) Speleothems of
- 10 Granite Caves. *Comun.Geol.*,**97**, 71-80.
- 11 **Vidal, J.R. and Vaqueiro, M.** (2007) Types of granite cavities and associated
- 12 speleothems: genesis and evolution. *Nature Conserv.*,**63**, 41-46.
- 13 **Vogt, P.R. and Jung, W.Y.** (2004) The Terceira Rift as hyper-slow, hotspot-dominated
- 14 oblique spreading axis: A comparison with other slow-spreading plate boundaries.
- 15 *Earth Planet. Sci. Lett.*, **218**, 77-90.
- 16 **Walter, M.R.** (1977) Interpreting Stromatolites: These fossils can tell us much about
- 17 past organisms and environments if we can learn to decode their message. *Am.*
- 18 *Scient.*, **65**, 563-571.
- 19 **Walter, M.R., Bauld, J. and Brock, T.D.** (1972) Siliceous algal and bacterial
- 20 stromatolites in hot spring and geyser effluents of yellowstone national park.
- 21 *Science*, **178**, 402-405.
- 22 **Walter, M.R., Bauld, J. and Brock, T.D.** (1976) Microbiology and Morphogenesis of
- 23 Columnar Stromatolites (Conophyton, Vacerrilla) from Hot Springs in Yellowstone
- 24 National Park. In: *Developments in Sedimentology* (Ed M.R. Walter), **20**, pp. 273-
- 25 310. Elsevier. Amsterdam.

- Webb, J.A. and Finlayson, B.L.** (1987) Incorporation of Al, Mg, and water in opal-A--evidence from speleothems secondary minerals found in caves. *Am. Mineral.*, **72**, 1204-10.
- Willems, L., Compère, P., Hatert, F., Pouclet, A., Vicat, J.P., Ek, C. and Boulvain, F.** (2002) Karst in granitic rocks, South Cameroon: cave genesis and silica and taranakite speleothems. *Terra Nova*, **14**, 355-362.
- Wray, R.A.L.** (1999) Opal and chalcedony speleothems on quartz sandstones in the Sydney region, southeastern Australia. *Aust. J. Earth Sci.*, **46**, 623-632.
- Wray, R.A.L.** (2011) Alunite formation within silica stalactites from the Sydney Region, South-eastern Australia. *Int. J. Speleol.*, **40**, 109-116.
- Wray, R.A.L.** (2013) Solutional Weathering and Karstic Landscapes on Quartz Sandstones and Quartzite. In: *Treatise on Geomorphology* (Ed J.F. Shroder), pp. 463-483. Academic Press, San Diego.

Figure Captions

Fig. 1. Location of the Branca Opala cave on Terceira Island (Azores). Modified from Nunes (2004).

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 (15th 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) Relationship between type III stromatolites (stromatolitic

1 crust) and the fossil water mark. (B.2) Relationship between the type I botryoidal
2 stromatolites (found throughout the cave) and the fossil water mark. These stromatolites
3 are smallest just beneath the water mark, and increase in size downwards. (B.3)
4 Distribution of cloud-like and botryoidal forms in a once totally flooded section. (B.4)
5 The botryoidal stromatolites near the northern entrance are smaller just beneath the
6 water level, and increase in size downwards.

8
9 **Fig. 3.** Field photographs of siliceous deposits inside and outside the cave. (A) General
10 view of a large room in the lava tube. Opaline stromatolites cover the walls. Debris of

volcaniclastic rocks mixed with plant remains and fine volcaniclastic sediments are found at the center. (B) Botryoidal and cloudy shaped stromatolites on the walls and ceiling of the cave. (C) Close-up of the botryoidal stromatolites, showing the horizontal water mark (black arrows). (D) Silicified leaves, twigs and botryoidal stromatolites stuck to the walls mixed with fine volcaniclastic sediments. (E) Silica-tufa deposits. Detail of silicified twigs with silica coatings in the Ribeira da Biscoitos area.

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 vs. NASC, data from Gromet *et al.* (1984).

Fig.5. Opaline stromatolites. (A) Field photograph showing the hard and dark brown exterior husk (EH). (B) Cross section perpendicular to the substrate showing the lower

microlaminated zone (LMZ), intermediate zone (IZ) and upper microlaminated zone (UMZ).

Fig. 6. Thin section of a type I stromatolite. (A) Four zones are observed: a lower microlaminated zone (LMZ) mimicking the substratum; a microlaminated columnar zone (MCZ); an intermediate zone (IZ) with alveolar structures, high porosity and diffuse laminae at the top; and an upper microlaminated zone (UMZ) showing diffuse microlamination. (B) Thin section details: (B.1) hard and dark brown exterior husk (EH) with iron oxides covering the stromatolite (black arrows); (B.2) diffuse laminae between the IZ and UMZ; (B.3) porous intermediate zone; (B.4) building-like columns with spheroidal structures (MCZ); (B.5) transition between the LMZ and MCZ; and (B.6) detail of the beige and dark brown laminae of the LMZ. The dark and irregular laminae show major accumulations of opaline mud (black arrows).

Fig. 7. Changes in the interior structure of a type I stromatolite. (A), (B), (C) and (D) show the four sub-types observed in thin sections (perpendicular to the substrate).

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 volcanoclastic sediments and silica

- 1 mud (black arrows). (B) Thin section details: (B.1) columns of the UMZ covered by the
2 EH formed by fine volcaniclastic sediments and iron oxides;(B.2) diffuse columns in the
3 IZ; and (B.3) LMZ mimicking the volcanic host rock, showing spores and yellow mud.

- 4
5 **Fig. 9.** A type III stromatolite (stromatolitic crust). (A) Field photograph showing a clear
6 stromatolite crust on the basalt. Botryoidal morphologies are absent. (B) Thin section
7 with a microlaminated zone (LMZ and UMZ) and a small intermediate zone (IZ).

8

Fig. 10. SEM photomicrographs of opaline stromatolites. (A) Molds 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 ($<0.1\mu\text{m}$), and a mold 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 volcanoclastic sediments mixed with opaline microspheres, biofilms, silicified bacteria sheaths, and diatoms. (F) Silicified filaments nests/pompoms on the stromatolites.

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

1 spore with central pore; and (F) individual silicified platelet between silicified

2 filamentous bacteria.

1 **Fig. 12.** SEM photomicrographs: (A) diatom accumulations between small mounds on
2 the stromatolitic surface; and (B) silicified biofilms on the basalt surface.

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