INSIGHTS INTO SPELEOTHEMS FROM LAVA TUBES OF THE GALAPAGOS ISLANDS (ECUADOR): MINERALOGY AND BIOGENICITY

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Abstract

Different types of hard and soft speleothems (stalactites, stalagmites, columns, crusts, flowstones, micro-gours and botryoidal coralloids) have been observed throughout lava tubes in the Galapagos archipelago, Ecuador. Three lava tubes were studied in this work: Gallardo and Royal Palm volcanic caves (Santa Cruz Island) and Sucre Cave (Isabela Island). The studied speleothems were mainly formed by opal, calcite and clay minerals, including plagioclase and pyroxenes from the basaltic host rock. Rarely, iron oxides, gypsum were found in some speleothems, which were interpreted as alteration products of the primary volcanic materials. Field emission scanning electron microscopy revealed abundant filamentous

bacteria, and reticulated filaments similar to those recently observed in others lava tubes around the world. These filaments are associated with EPS and mineral deposits rich in Si, Ca or Fe. The identified minerals and the evidence of biosignatures suggest a biological contribution to speleothem development within Gallardo, Royal Palm and Sucre lava tubes.

Introduction

Lava tubes have been considered of little mineralogical interest until recently (Hill and Forti 1997; Forti 2005). However, studies on speleothems from volcanic caves are currently receiving more attention. Detailed mineralogical and geochemical analyses have been performed in lava tubes around the world over the last 20 years (Hill and Forti 1997; Forti 2005; Daza and Bustillo 2012, 2014; Miller et al. 2014a, 2015).

Volcanic caves host an especially interesting variety of mineral-utilizing microorganisms and mineralized microbial structures, which may be recognized as biosignatures (Miller et al. 2014a; Garcia-Sanchez et al. 2015). Many of these biosignatures have been found in speleothems of volcanic caves from Australia (Webb and Finlayson 1987), the Azores archipelago (Bustillo et al. 2010; De los Rios et al. 2011; Northup et al. 2011; Daza et al. 2014), United States (Boston et al. 2001; White et al. 2010; Northup et al. 2011), and Easter Island (Miller et al. 2014a, 2015), among others. Most of these authors report opal and ochre speleothems similar to those described in the present work.

In general, primary cave minerals are formed at the same time as lava tube formation and in the first stages of lava cooling (White, 2010). Secondary cave mineral deposits, or speleothems, may result from the leaching of materials by meteoric seepage water and mineralized with the aid of microbial activity (Northup et al. 2011). Studies on the mineralogy of lava tubes from Galapagos Islands are very scarce. Gallardo and Toulkeridis (2008) reported gypsum and calcite as the main minerals in speleothems from Gallardo Cave on Santa Cruz Island. Forti and Calaforra (2014) carried out a general description of Galapagos lava tubes in a sampling survey conducted during the 16th International Symposium of Vulcanospeleology, corroborating the previous results. An earlier study performed on the siliceous speleothems of Galapagos lava tubes revealed enigmatic reticulated filaments (mainly rich in Si) associated with other microbial cells and filamentous bacteria (Miller et al. 2014b).

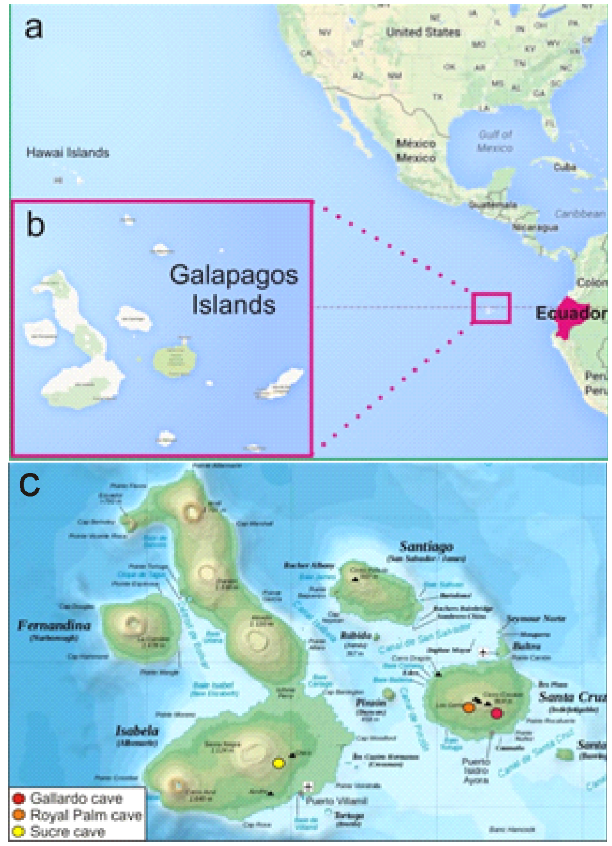

Figure 1.
a) Location of the Galapagos Islands, about 1000 km offshore from Ecuador; b) Detail of the Galapagos Archipelago. Google maps image. c) Location of the studied volcanic caves: Gallardo and Royal Palm lava tubes on Santa Cruz Island and Sucre lava tube on Isabela Island.

The aim of the present work is to advance in the mineralogy and microbe-mineral interactions of speleothems from lava tubes of the Galapagos Archipelago (Santa Cruz and Isabela Islands).

Geological Setting

The Galapagos Islands are situated within the equatorial zone, about 1000 km west from the Ecuador coast, in the eastern Pacific Ocean (Fig. 1a). The Galapagos microplate is at the junction of three oceanic plates: the Pacific, Cocos and Nazca plates, which are moving away from each other. Galapagos is located just east of the East Pacific Rise and south of the Galapagos Spreading Center (Gallardo and Toulkeridis 2008).

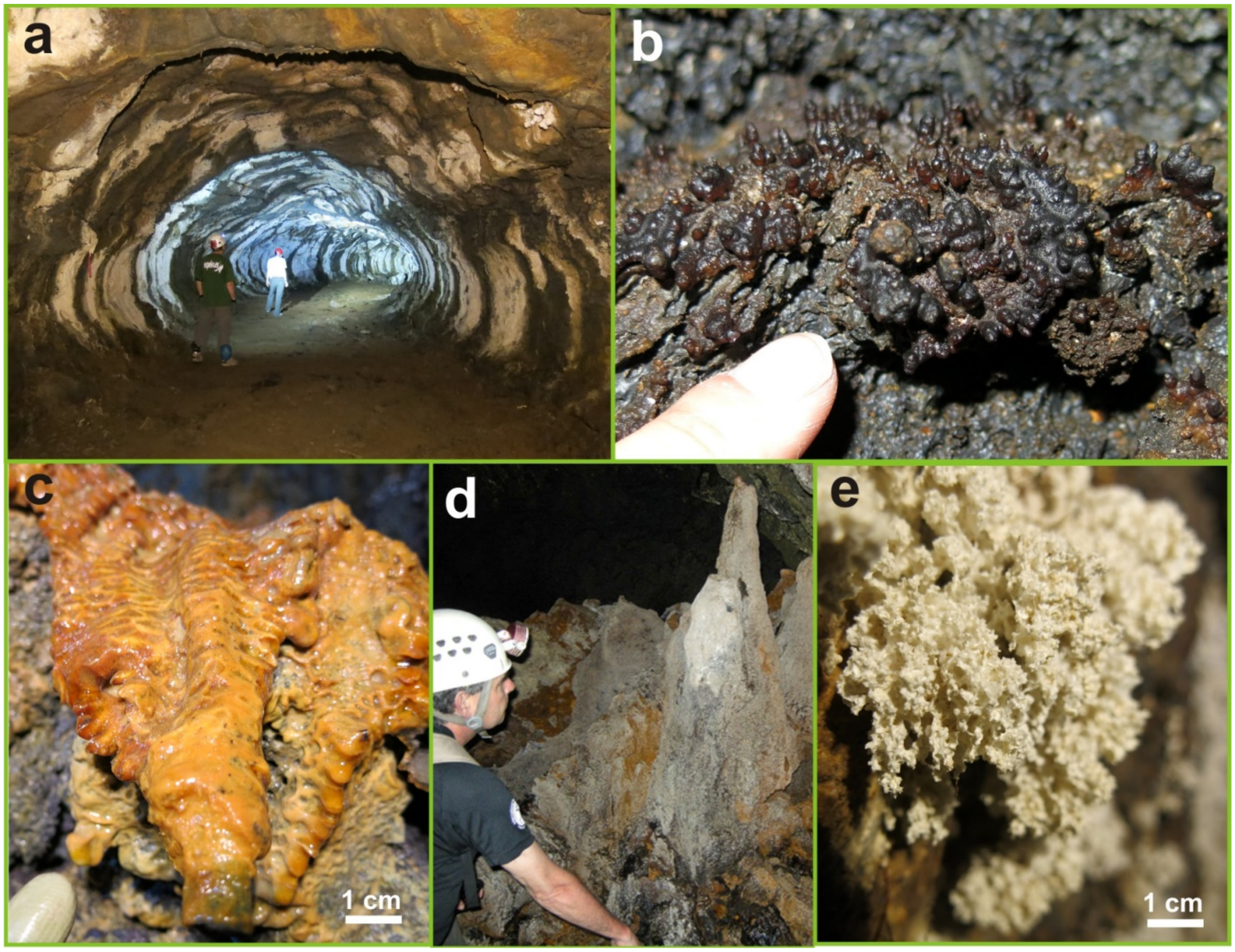

Figure 2.

Field images of speleothems from Galapagos lava tubes: a) General view of Bellavista lava tube (Gallardo Cave); b) Brownish small coralloids on the walls of Love tunnel (Gallardo Cave); c) Reddish stalactite on walls of Royal Palm lava tube; d) Big stalagmites near the entrance of Royal Palm Cave; e) Moonmilk on the walls of Bellavista lava tube (Gallardo Cave).

All islands of the Galapagos Archipelago are of volcanic origin: there are 7 islands with an area >100 km^2 (Isabela, Santa Cruz, Fernandina, Santiago, San Cristobal, Floreana and Marchena) (Fig. 1b), 12 islands (Pinta, Española, Baltra, Santa Fe, Pinzón, Genovesa, Rábida, Wolf, Darwin, Seymour North, Tortuga and Bartolomé) ranging from 60 to 1 km^2, as well as 42 small barren islands and 26 rocks, of only a few square meters (Gallardo and Toulkeridis 2008). All of these islands are still active, making it one of the most volcanically active places on earth (Gallardo and Toulkeridis 2008).

Three volcanic caves from Galapagos were sampled for this preliminary study, corresponding to two lava tubes (Gallardo and Royal Palm caves) on Santa Cruz Island, and one lava tube (Sucre Cave) from Isabela Island (Fig. 1c). All of them are hosted in basaltic lava flows (pahoehoe type) (Gallardo and Toulkeridis 2008).

Gallardo Cave is also known as “Bellavista Cave” and locally known as “Amor” or Love Tunnel depending on the cave section. It is located in the eastern part of the island, near Bellavista town and 6.8 km north of Puerto Ayora. The cave is a lava tube 2250 m long up to 9.8 m maximum height and 17.8 m maximum width. It is interrupted by six ceiling collapses and the first km is usually used as a tourist trail.

Royal Palm Cave is located in the western part of Santa Cruz Island, near Santa Rosa village and close to the Miconia Highland Forest, adjacent to the Galapagos National Park of Santa Cruz. This lava tube is 600 m long, with a mean of 5-15 m height and 2-10 m width. It is managed by the Royal Palm Hotel for touristic use.

Sucre lava tube is one of the longest tubes known on Isabela Island; the cave is also accessed by an ecotourism trail approximately 480 m long. It is located in an agricultural/forest zone, approximately 14 km from Puerto Villamil (Fig. 1c).

Different types of speleothems have been reported on the walls, ceilings and occasionally on the floor of these lava tubes (Fig. 2a). They comprise small coralloids (Fig. 2b), stalactites (Fig. 2c), stalagmites (Fig. 2d), columns, powdery crusts, botryoidal speleothems, flowstones, gours and moonmilk (Fig. 2e) with colorations from whitish and greyish to ochre, brownish and reddish. In many cases, the speleothems are still growing in response to specific physical and chemical processes within the cave, which are influenced by the extremely humid microclimate of the Galapagos Islands.

Materials and Methods

Different types of speleothems from the two parts of the Gallardo Cave (Santa Cruz Island) were studied: (i) fragments of coralloids, small powdery crusts and botryoidal speleothems from Love Tunnel, and (ii) white moonmilk and coralloids from the Bellavista lava tube. Ochre stalactites, stalagmites, columns, and beige and greyish small coralloids were collected in Royal Palm Cave (Santa Cruz Island). Small stalactites, thin powdery crust and coralloids from Sucre Cave (Isabela Island) were also selected for analysis.

The mineralogical characterization of the speleothems (19 samples) was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy and a Gandolfi camera.

XRD was carried out using a Philips PW1710 diffractometer with a Cu anode (CuKα, λ=0.154 nm). Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FTIR-ATR spectrometer in reflectance mode. Micro-Raman spectroscopy analyses were conducted using a Laser Research Electro-Optics (REO). The spectrometer used was a KOSI HoloSpec f/1.8i model made by Kaiser, covering a spectral range in Raman displacement of 0–3800 cm^{-1} and a spectral resolution of 5 cm^{-1}, and the CCD was a DV420A-OE-130 model from Andor (1024×256 pixels). Microanalyses up to 40 µm diameter spots were undertaken with a Nikon Eclipse E600 microscope using 50x magnification. Some speleothem samples were also analyzed using a Gandolfi camera (40 kV tube and 20 mA, radiation CuKa, λ = 1.5418 Å, with Ni filter). The internal structure and morphological characteristics of the speleothems were examined by scanning electron microscopy (SEM Philips XL40) coupled to an energy dispersive X-ray spectroscopy microprobe (EDS-EDAX 9900). Field Emission Scanning Electron Microscopy (FESEM) was also carried out using a Jeol JSM-7001F microscope equipped with an Oxford EDS detector.

Results and Discussion

Mineralogy

Powder XRD analyses of the speleothems from Gallardo lava tube showed patterns corresponding mainly to amorphous silicate, calcite and clay minerals (nontorsite, sepiolite, illite). XDR patterns were similar for speleothems from both sections of the cave (Love Tunnel and Bellavista lava tube). Noteworthy was the identification of iron oxides (hematite) in one stalactite from Love Tunnel.

The moonmilk deposits from Bellavista lava tube were mainly formed by calcite, with small amounts of montmorillonite, organic compounds and clay minerals as accessory minerals, as revealed by FTIR, micro-Raman and Gandolfi camera. However, the speleothems from Royal Palm Cave were mainly composed of iron oxides (including goethite and hematite), with some calcite, clay minerals and plagioclase; the latter are derived from the host basalts.

Speleothems from Sucre lava tube showed the same minerals as those found in samples from Gallardo Cave. Gypsum was also detected by XRD in a speleothem from this cave.

Hydroxyapatite was detected by all techniques in two speleothems from Royal Palm and Sucre caves. Their origin might be linked to the remains of bones of small dead animals (birds?).

Most samples comprised amorphous substances difficult to identify by XRD. For this reason, FTIR, Raman spectroscopy and Galdonfi camera were used. These analyses revealed that the amorphous silicate, mainly detected in speleothems from Love Tunnel, were composed of opal. Montmorillonite, organic compounds and amorphous carbon were detected by FTIR and micro-Raman in samples from Bellavista lava tube.

SEM Observations

FESEM images showed several inorganic and organic structures on the speleothem samples. Coralloid speleothems were generally of siliceous composition,

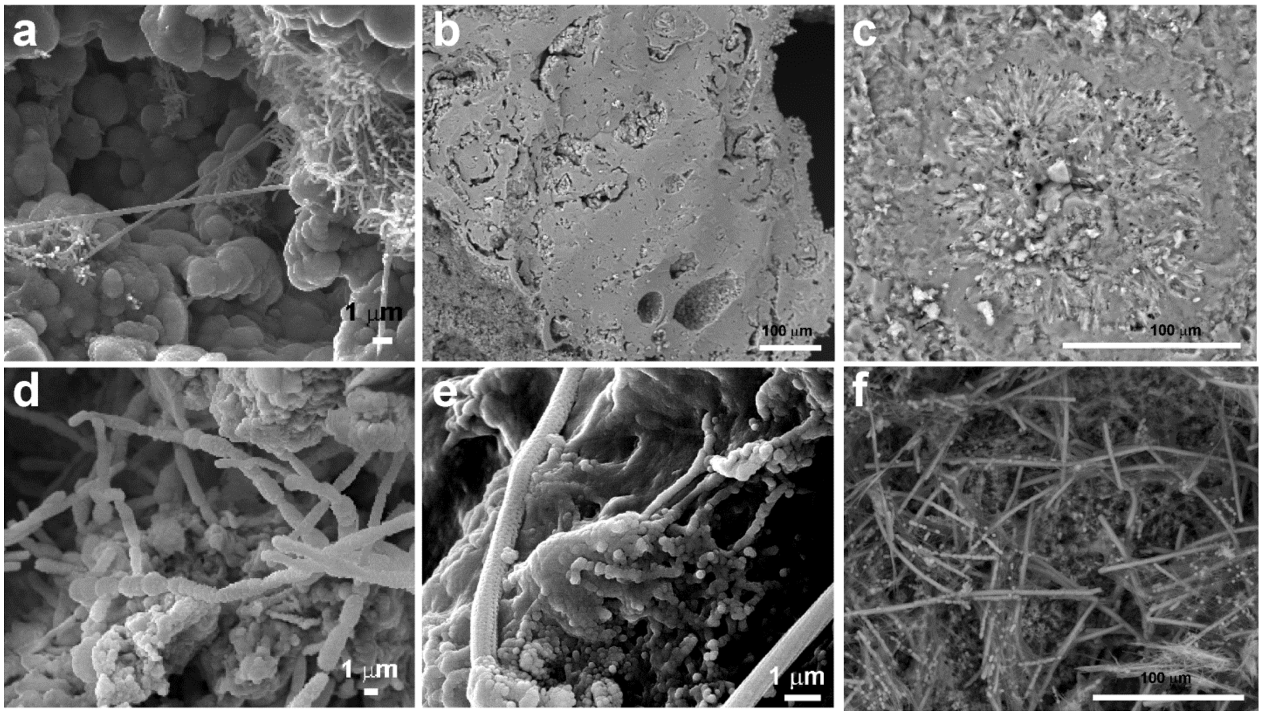

Figure 3.

FESEM images of speleothems from Galapagos lava tubes. a) Coralloid speleothems depicting opal microspheres from Royal Palm Cave. b) etch pits or microboring (arrows) produced by microbial cells on the mineral surfaces of coralloids from Love Tunnel (Gallardo Cave). c) Acicular calcite crystals in a coralloid; d) Actinobacteria-like structures from Love Tunnel (Gallardo Cave); e) Detail of a reticulated filament on a siliceous coralloid from Bellavista lava tube (Gallardo Cave); f) Large amounts of filamentous bacteria associated with EPS in moonmilk deposits from Royal Palm Cave.

depicting botryoidal aggregates formed by opal microspheres (Fig. 3a). Imprints and etch pits or microboring produced by bacteria were also observed on the mineral surfaces (Fig. 3b). In addition, filiform coralloids were sometimes found on siliceous coralloids with acicular structures formed by calcite crystals (Fig. 3c).

In general, the siliceous speleothems observed by FESEM showed abundant microbial structures, including actinobacteria-like cells (Fig. 3d), filamentous bacteria and reticulated filaments associated with extracellular polymeric substances (EPS) (Fig. 3e). These fibrous structures consist of long filaments with mineralized sheaths rich in Si, Ca, and Fe, as detected by EDS microanalyses (Fig. 3e).

Reticulated filaments similar to those observed in this study, have been also reported in speleothems collected from lava tubes in the Canary Islands (Spain), Easter Island (Chile) and Cape Verde Islands (Melim et al. 2008; Miller et al. 2014a,b), as well as in a granite springwater tunnel in Porto, Portugal (Miller et al. 2012) and limestone caves (Melim et al. 2008). Most of these reticulated filaments have been characterized as mineralized filaments with hexagonal and diamond-shaped chambers resembling honeycomb structures).

Occasionally, needle-shape calcite fibers associated with microbial cells were observed in Gallardo Cave samples (specifically on speleothems from Bellavista lava tube; Fig. 3f). These microbial cells were also found in close association with EPS, evidencing geomicrobiological interactions.

The formation of siliceous speleothems reported in many studies has been interpreted as having been mediated by microbes (Aubretch et al. 2008, 2012; Daza and Bustillo 2014; Forti 2005; Miller et al. 2014a; Urbani et al. 2005; Vidal Romaní et al. 2010; Willems et al. 2012). Their mineralogy has been mainly described as opal A, and the presence of microbial structures and EPS associated with opal microspheres indicating their biogenic origin (Aubretch et al. 2008; Miller et al. 2014a).

Conclusions

Several types of speleothems such as stalactites, stalagmites, columns, powder and crusts, botryoidal speleothems, flowstones, small coralloids and soft and hard micro-gours have been found in Gallardo, Royal Palm (Santa Cruz Island) and Sucre (Isabela Island) lava tubes. Most of these speleothems are composed of opal, calcite and clay minerals. Plagioclase and pyroxenes appear as secondary minerals of the host rock (basalt). Calcite is present in a small proportion of samples, and is interpreted as representing the most recent speleothemic stage in these caves. Gypsum was detected in a single sample, whereas iron oxides, including hematite and goethite were identified in several. These minerals are considered alteration products of the primary volcanic materials. Hydroxyapatite is the main mineral in two samples, whose origin might be linked to the decay of bones of small dead animals. Associated with this varied mineralogy, different filamentous bacteria were observed in almost all the studied speleothems, though reticulated filaments were found particularly on siliceous speleothems. The Galapagos Islands and their lava tubes seem to be a unique site for future geomicrobiological studies to gain a deeper and more accurate understanding of the biogenicity of these speleothems and the relationship between silica/opal/carbonate precipitation and microbial activity.

Acknowledgements

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