Gypsum speleothems in lava tubes from Lanzarote (Canary Islands). Ion sources and pathways

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Abstract

Lava tubes from Lanzarote Island in the Canary Archipelago commonly show white speleothems that stand out from the black basaltic rock. Mineralogical analyses of the speleothems from El Covón and Chiflleta lava tubes show that gypsum is the dominant mineral with minor amounts of halite. Speleothems composed of microcrystalline gypsum (up to 150 μm long) are: coatings, globules, or extensive white powder accumulations covering the tube floor. Those composed of macrocrystalline gypsum with millimeter-size tabular and lenticular crystals are: crusts and stalactites. Uranium series dating of speleothems show ages ranging from 6217 ± 1644 yr to 40,039 ± 4748 yr. δ34S and δ18O of gypsum speleothems (δ34S is 20.97‰, V-CDT and δ18O is 9.78‰, V-CDT) is similar to that of sulphate dissolved in seawater. δ34S and δ18O from speleothems (0.708655−0.708976) suggest that the main source of Ca is seawater, but additional Ca contributions from aeolian dust have reduced the Sr isotope values. These data support the idea that gypsum precipitates in the lava tube by evaporation of marine spray or solutions derived from marine spray. Two probable vias for ions input into the lava tube are considered: 1) sea spray circulating through the lava tube; 2) low-frequency rain infiltration leaching the marine spray salts precipitated at the surface. The constant supply of ions from sea spray, air currents in the cave, and the fast, but partial, evaporation due to the high relative humidity in the lava tube favours accumulation of major amounts of gypsum and subordinately halite. Scarcity of precipitation in the western Canary Islands prevents dissolution of gypsum speleothems.

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1. Introduction

Gypsum, identified in numerous caves around the world (Hill and Forti, 1997), is considered the second most abundant cave mineral after calcite (Onac, 2012). Gypsum speleothems are predominant in gypsum karstic caves in arid climates (Calaforra et al., 2008), where they form by evaporation (Gázquez et al., 2011). In limestone caves SO4 2− is supplied by the oxidation of pyrite or other sulphides, oxidation of H2S or by dissolution of interbedded evaporites in the limestone (Hill and Forti, 1997). Gypsum deposits replacing calcite in limestone caves constitute one of the main features of sulphuric acid speleogenesis (Galdenzi and Menichetti, 1995; Poljak and Provencio, 2001; Palmer, 2013). In volcanic caves such as lava tubes, gypsum is also considered one of the most abundant minerals (Forte, 2005) but very few studies provide detailed description of gypsum speleothems in these settings (Jakobsson et al., 1992; White, 2010), particularly regarding their geochemistry (Dillon et al., 2009; LaPointe et al., 2013).

There are few processes involving sulphate precipitation in volcanic settings (Hill and Forti, 1997; Onac and Forti, 2011): 1) processes related to high temperatures during early stages of lava tube formation, such as sublimation from fumarole gases or solubilization of previously formed minerals interacting with water; 2) low temperature processes like bat guano alteration or infiltration of sulphate-enriched meteoric waters.

The study of sulphur isotopes (δ34S) and 87Sr/86Sr ratios have been used to identify the ion sources for gypsum in caves in different settings around the world, such as the quartz-sandstone caves in the Gran Sabana region, Venezuela (Sauro et al., 2014), the deep caves of Nullarbor Plain, Australia (Lipar et al., in press), caves from Cerna Valley in Romania, coastal caves of the Bahamas (Bottrell et al., 1993; Onac et al., 2009) and lava tubes of New Mexico (Dillon et al., 2009; LaPointe et al., 2013).

An important number of lava tubes in the Lanzarote Island (i.e. Covón/Chiflleta, Esqueleto, Prendes, etc.) contain abundant gypsum speleothems covering walls and floors. This work aims to: 1) characterize
the mineralogy and petrography of all varieties of gypsum speleothems; 2) identify calcium and sulphate sources and pathways and 3) understand the processes of speleothem formation. This study contributes to the understanding of the formation and preservation processes that have favored the decimetric accumulations of gypsum. While these speleothems are rather common in other lava tubes, they have not been widely described in the literature.

2. Geological settings

Lanzarote, the northern and easternmost island of the volcanic Canary Archipelago, about 100 km from the African coast (Fig. 1), is considered, along with Fuerteventura, as the oldest and lowest relief islands of the Canaries. Volcanic eruptions in the last 300 years in Lanzarote are Timanfaya, 1730–1736 and Tinguatón and Chinero, 1824 (Carracedo et al., 1992; Criado et al., 2013). Rocks in Lanzarote are mainly composed of basalts, although aeolian sediments and elevated marine deposits appear also close to the coast (Zazo et al., 2002). Lanzarote has a highly eroded landscape with deep-incised valleys and wide low-relief areas with major calcrete development (Alonso-Zarza and Silva, 2002; Alonso-Zarza et al., 2016).

Lanzarote preserves an important number of lava tubes formed during various eruptions. Some of them host gypsum speleothems (Smith, 2015). One of the most famous is the Corona volcano lava tube (7.6 km long), which can be visited at the Cueva de los Verdes in the north eastern part of the island (Carracedo et al., 2003). Others occur in Middle Pleistocene lavas from the western part of Lanzarote, like the Covón and Chifletera lava tubes, as well as those identified in the 1730–1736 lavas (Gómez-Ortiz et al., 2014). Covón and Chifletera are the names of two lava tubes located in the same sector (Fig. 1). In this study we used the names given by the personnel of the National Park to avoid confusion with different names and locations indicated in different publications (Serantes Vergara and Pena Muiño, 2013b, a; Stenhouse, 2015). The entrance of Covón (Coordinates UTM 28N, E: 613893; Y: 3208135) (also called Pardelas), is located 40 m from the shore at the top of a 30 m high cliff, and Chifletera (Coordinates UTM 28N, E: 614241; Y: 3207920) has its entrance 400 m inland at 50 m above sea level. Its sea entrance (Coordinates UTM 28N, E: 614241; Y: 3207920) was opened at 15 m in a 25 m high cliff which limits tourist visits, favouring their protection.

Climate in Lanzarote is dominated by the scarcity of rainfall (105 mm of mean annual) and warm temperatures that range from 17°C to 25°C as mean minimum and maximum, respectively. Marine trade winds influence the Canary islands during most of the year, although the low relief of Lanzarote and Fuerteventura do not exert any orographic effect. Rainfall is very scarce in comparison with islands of higher relief. Canary Islands receive major amounts of Saharan dust (quartz, limestone fragments, etc.) (Coudé-Gaussen et al., 1987; Menéndez et al., 2007; Criado et al., 2012) brought by African winds related to the Saharan Air Layer (SAL) (Prospero and Lamb, 2003).

3. Methodology

Speleothem samples were collected from two lava tubes. 1) In Covón-Pardelas, samples and environmental parameters were obtained in the same area, about 60 m from the entrance. 2) In Chifletera, samples were recovered within the 200 m from the inland entrance of the lava tube. Environmental parameters were measured in the same area (Fig. 1).

Bulk mineralogy of 20 samples of speleothems was studied using X-ray diffraction (XRD). Patterns were obtained from powder mounts using a Philips semiautomatic PW 1710 diffractometer with monochromatized CuKα radiation. Semiquantitative analyses were performed using EVA software by Bruker (DIFFRAC“Diffractometer” 2006 version).

Conventional optical petrography was performed on thin sections. Due to the fragility, the speleothems were embedded in Epofer EX 401 and Epofer E 432 resin in a vacuum system before cutting and polishing.

X-ray fluorescence (XRF) analysis was conducted on 11 samples of various speleothems using the Ajos spectrometer from PANalyticalthe LTD, in the facilities of the Universidad Complutense de Madrid. Specimens were examined on a JEOL JSM-T100 scanning electron microscope (SEM) at the Institute of Palaeontology ZRC SAZU, Ljubljana and at the Museo de Ciencias Naturales de Madrid under a FEI INSPECT scanning electron microscope. Uncoated specimens were observed and photographed in low-vacuum mode (40 Pa) with an accelerating voltage of 15 kV, 20 kV, and 30 kV at a working distance of 9 to 11 mm. Photomicrographs were taken in shadow backscattered electron imaging mode (BSE). Qualitative and semi-quantitative Energy Dispersive X-ray Spectroscopy analysis (EDS) was performed under the same low-vacuum (LV) conditions.

The 34S/32S and 18O/16O ratios of gypsum sulphate (10 samples) were analysed at the Serveis Científicots de la Universitat de Barcelona. Samples were first dissolved with deionized water, then filtered and precipitated as BaSO4. Mass spectrometer SO2 analysis was carried out with a TC/EA DELTA PLUS XP THERMOFISHER mass spectrometer. Reproducibilities were calculated using international and internal laboratory standards systematically interspersed in the analytical batches: 0.2‰ for δ34S and 0.6‰ for δ18O.

Fig. 1. Map showing location of Lanzarote Island and lava tubes studied. a) General map. Numbers refer to: 1. El Hierro, 2. La Palma, 3. La Gomera, 4. Tenerife, 5. Gran Canaria, 6. Fuerteventura, 7 Lanzarote. b) Orthophoto indicating position, and approximate trace of Covón and Chifletera. White dashed line marks the boundary between 1730-1736 eruption lava flows and Pleistocene volcanics.
Relative humidity in Covón is about 50% probably thicker inland. The sections are about 7 m wide by 4 m high.

... is 2 m thick around the entrance, with multiple roof collapses and is a collapse that produces another opening close to the entrance. The roof fractures cut the lava tubes from base to top. The width of the fractures varies from millimeters to 3 cm. Most of them are dry and can be filled with gypsum. Temperature and relative humidity measured in Covón are more variable and more sensitive to external temperature changes than those measured in Chiflterera.

Covón (Pardelas) has a wide entrance at the top of a cliff with roof collapse that produces another opening close to the entrance. The roof is 2 m thick around the entrance, with multiple roof collapses and is probably thicker inland. The sections are about 7 m wide by 4 m high. Relative humidity in Covón is about 50%–70% and temperature varies from 16 °C to 19 °C.

4. Main characteristics of the lava tubes

Lava tubes are dry, without water ponds nor drops on the walls or roofs. The host rock is impervious basalt whose randomly oriented fractures cut the lava tubes from base to top. The width of the fractures varies from millimeters to 3 cm. Most of them are dry and can be filled with gypsum. Temperature and relative humidity measured in Covón are more variable and more sensitive to external temperature changes than those measured in Chiflterera.

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5. Characterization of speleothems

According to XRD and EDS analyses of individual crystals performed during SEM observation, all the speleothems from Covón and Chiflterera lava tubes are composed of gypsum and minor amounts of halite (Table 1).

Gypsum speleothems are of two types: microcrystalline, and macrocrystalline. Their detailed description follows, when possible, the terminology used by Hill and Forti (1997) (Fig. 2).

5.1. Microcrystalline gypsum

It is composed of euhedral crystals around 5 μm thick and up to 150 μm long which show flattened morphologies varying from bladed to platy habits. These crystals form loose aggregates and according to their occurrence in different parts of the lava tubes we have distinguished the following types.

5.1.1. Powder accumulations

These are fine white powder deposits that cover most parts of the floor and large areas of walls in both lava tubes, although they are especially abundant in Chiflterera. They can pile up to several cm, appearing as dust or snow accumulations. In areas of the lava tube close to entrances,
the white gypsum powder is covered by an orange dust mainly composed of quartz and phyllosilicates mixed with gypsum and halite.

On walls, powder accumulates in ledges forming layers up to 10 cm thick that cover areas from a few cm² up to a few dm² wide (Fig. 3a). On the floor, powder covers most of the surface and forms mounds of variable thickness, from just a few cm up to 60 cm (Fig. 3b). Sometimes, the surface of powder accumulations displays a white or orange crust usually <1 mm thick (Fig. 3b).

Powder is formed by a mass of randomly arranged crystals showing morphologies that vary from square platelets up to 100 μm size and 5 μm thick (Fig. 3c) to euhedral elongated bladed crystals 70 μm long, 15 μm wide and <5 μm in thickness. Most commonly, gypsum crystals appear either totally loose or weakly welded together. However, in some areas, they are cemented by halite (Fig. 3d–f). Gypsum powder can appear also inside fractures of the basalt host rock (Fig. 3d). These fractures are up to 3 cm wide. Powder can be present only in the most external part of the fracture (2–3 cm) (Fig. 3b, c), while in some cases it fills the fracture up to at least 60 cm. Powder mounds are located on the floor just below fractures filled with powder (Fig. 4a).

5.1.2. Coatings

In some of the vacuoles and fractures of volcanic host rock, and sometimes on the walls, transparent acicular or bladed gypsum crystals grow perpendicularly to the surface, coating the cavities (Fig. 5a). The crystals are very delicate and easily detach from the wall by gravity. Their size is very uniform, between 1 and 5 μm thick, around 10 μm wide and up to 150 μm long (Fig. 5b). They are euhedral and show no signs of dissolution. Some coatings cover recently exposed surfaces like a bird skull or a small area on the lava tube floor where powder was recently washed away by dripping water.

5.1.3. Globules

Globules (Fig. 6) are botryoidal speleothems ranging in size from few mm to several cm, generally occurring on the lava tube ceiling.
Fig. 3. Powder speleothems. a) Accumulation of powder on a ledge on the wall; b) mound of powder approximately 30 cm thick showing thin orange crusts over surface; c) SEM image of loose aggregates of gypsum crystals of heterogeneous size and shape, d) SEM image of elongated tabular gypsum crystals (g), some of them cemented by halite (h); e and f) SEM images of gypsum crystals cemented by halite (h) which form thin crusts over the powder accumulations.

Fig. 4. Fractures filled by powder speleothems. a) General view of the lava tube showing associated crystalline crusts and a mound of powder at tube floor below a fracture. b) Fracture completely filled by powder. c) Fracture partially filled by powder and crystal coatings inside.
They are formed by white microcrystalline aggregates that are either crumbly or compact. Some globules are white (Fig. 6c) whereas others have an external indurated orange crust (Fig. 6a and b).

In thin section, globules have the following textures: a) an external orange crust composed of lenticular crystals 0.4 mm long, arranged perpendicularly to the outer surface (Fig. 6d); b) internal crumbly aggregates composed of lenticular crystals 120 μm long and 40 μm wide contained in a mass of smaller fibrous crystals 50 to 70 μm (Fig. 6e); c) internal compact aggregates composed of randomly arranged masses of homogeneous fibrous crystals up to 120 μm (Fig. 6f).

5.2. Macrocry stalline gypsum

It constitutes compact speleothems composed of tabular or lenticular crystals reaching millimetric sizes. They can be classified as follows.

5.2.1. Crusts

Crusts (Fig. 7a–c) are compact beige, orange or yellow deposits, which appear mostly on the upper part of walls and ceilings of the lava tubes. They are up to 5 mm thick and occur scattered as patches that cover areas of some dm² (Fig. 7b). Crusts are composed of tabular or lenticular crystals, sometimes forming rosettes (Fig. 7c), and apparently they are not connected with any visible fracture or crack in the host rock. In thin section gypsum crystals show various morphologies, but they are usually elongated and form fans that cross each other in all directions. Their size ranges from 0.2 to 5 mm long and up to 1 mm wide (Fig. 7g and h).

5.2.2. Stalactites

Stalactites are relatively common in both lava tubes and appear along the whole tube without any particular distribution. They are orange and translucent and occur in groups on ceilings, protruding out of gypsum crusts (Fig. 7d). Gypsum stalactites are conical, up to 4 cm long and about 1–2 cm wide (Fig. 7e) and composed of lenticular and tabular crystals forming fans and rosettes, which results in an irregular outer texture. They lack an internal channel and at the moment of sampling were totally dry, we have not observed dripping on any of them. In thin section they show the same characteristics as crusts (Fig. 7g and h).

Between some crusts and the basaltic host-rock a botryoidal layer, less than 1 mm thick (Fig. 8), has been observed. Under the microscope it is reddish-brown with laminar or irregular shapes (Fig. 8a). Crystal morphology and EDS analyses performed in SEM (Si O and small amounts of Fe) (Fig. 8b–d) suggest that it is composed of opal.

5.2.3. Laminated crusts

Laminated crusts are up to 10 cm thick accumulations of compact gypsum observed only in Covón lava tube. They appear in the lower...
part of walls, over powder accumulations and below areas of the ceiling that have crusts or stalactites (Fig. 7f). This speleothem is similar to ceiling crusts, but in some areas has a faint internal lamination. They are often weathered, broken and/or covered with gypsum powder.

6. Geochemistry

6.1. X-ray fluorescence

XRF shows no differences in any element content among samples with different textures. Results reported below refer to all analysed samples excluding CHI-6, which is very different due to its higher Na and Cl content. All analyses display higher Ca than S contents.

Covón samples show the highest contents in Cl, Mg, Al, Ti and Fe. Speleothems of both lava tubes have similar Sr, Si, and K contents. Br appears sporadically and in very small amounts (Table 1).

Some pairs of elements display linear trends (Fig. 9), with high $r^2$ values, mainly in Covón. This is the case of the relationships between Si-Al, Fe-Al, and Fe-Si ($r^2 > 0.9$). Ca-Si, Mg and Al-Mg relationships show $r^2$ values between 0.5 and 0.9. In Chiflereita linear trends between elements have lower $r^2$ values than in Covón, being the highest, Fe-Al ($r^2 = 0.86$), Si-Al ($r^2 = 0.66$) and Fe-Si ($r^2 = 0.62$). However, the existence of outliers in such relationships (Fig. 9) together with the small amount of data, do not allow to consider any of them as correlated.

6.2. $\text{Sr}^{87}/\text{Sr}^{86}$

The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios for our gypsum speleothems range between 0.708665 and 0.708976 (Table 1). The lowest values correspond to Chiflereita, showing a difference of 0.0005 with respect to the present day marine value (0.7092), whereas those from Covón differ only by 0.0003 (Fig. 10). Obtained values are similar to those of the calcretes from Lanzarote and Fuerteventura developed on aeolian sandstones with marine bioclasts. These are the main source of marine-derived Ca (Huerta et al., 2015).

6.3. Stable isotopes and uranium series dating

Stable isotopic values of gypsum speleothems range from 20.7 to 21.7‰ (mean value of 20.97‰) V-CDT for $\delta^{34}S$, and from 9.12 to 10.43‰ (mean value of 9.78‰) V-SMOW for $\delta^{18}O$ (Fig. 11).

Analysed samples (Table 2) show ages that range from 40,039 ± 4748 yr to 6217 ± 1644 yr. Accordingly, gypsum from Covón, (PAR) and Chiflereita (CHI) precipitated from the Upper Pleistocene to Holocene, during Marine Isotope Stages (MIS) 3 to 1.
7. Discussion

7.1. \(SO_4^{2-}\) and Ca supply

Geochemical and isotopic analyses indicate that the origin of the sulphate and Ca forming the gypsum speleothems from Covón and Chifletera is seawater. The \(^{87}\text{Sr}/^{86}\text{Sr}\) values for gypsum are close to those of seawater (0.7092; see Whipkey et al., 2000), and thus the main source of Ca (Sr) should also be seawater. Slight differences between gypsum and seawater values are interpreted as indicating a secondary source of Sr, such as aeolian dust or volcanic rocks. However, the low content in Ti, Mn and Ni, and the low \(r^2\) values of the linear trends Si-Mg; Si-Fe; Si-Ca (typical elements in basalt minerals like olivine and plagioclase) observed in XRF and the major differences with Sr ratios from Lanzarote basalts (0.703317) indicate that the volcanic rock contribution is minor. The higher Ca content with respect to S, together the low \(r^2\) values between both elements suggest an additional mineral phase containing Ca supporting the idea of aeolian dust contribution in these lava tubes (Fig. 9). The contribution of aeolian dust coming from Sahara Desert and Sahel has been recognized in travertines from Gran Canaria (Rodríguez-Berriguete et al., 2018) and in Lanzarote calcretes (Huerta et al., 2015), but the latter show wider ranges of \(^{87}\text{Sr}/^{86}\text{Sr}\) than those of the gypsum from lava tubes. Probably this is a consequence of the variety of rocks (in composition and age) from which the aeolian dust is derived (Menéndez et al., 2007; Hefferan et al., 2014). However, calcretes developed on aeolian sands composed of marine bioclasts have Sr ratios similar to seawater (Fig. 10).

\(\delta^{34}\text{S}\) and \(\delta^{18}\text{O}\) values of gypsum from lava tubes of Lanzarote reflect those of the sulphate dissolved in modern seawater. Gypsum precipitated from seawater usually displays the same values than dissolved sulphate (\(\delta^{34}\text{S}\) of 20–21‰, V-CDT, and \(\delta^{18}\text{O}\) of about 9.5–9.6‰, V-SMOW) (Hoefs, 2008), or the gypsum isotopes are slightly enriched compared to those of dissolved sulphate by 1.65–1.7 and 3.5–3.6‰, in \(\delta^{34}\text{S}\) and \(\delta^{18}\text{O}\), respectively (Mayer, 2005; Warren, 2006). Differences between \(\delta^{34}\text{S}\) and \(\delta^{18}\text{O}\) values of marine dissolved sulphate and gypsum speleothems are lower than those reported by Warren (2006) and Mayer (2005) in marine evaporites, so fractionation and/or mixing processes for both isotopes are minor (Fig. 11).

7.2. Age of speleothems

Speleothems show a wide range of ages, from Upper Pleistocene to Holocene, and formed in warm and cold marine isotope stages. The wide range of the ages measured (Table 2), the different climatic conditions in which speleothems formed and the occurrence of crystal coatings developed on recent surfaces suggest that speleothems are still forming during the present day.

7.3. Solution pathways

Isotopic data show that seawater is the main source of ions for the formation of speleothems. Seawater can reach the lava tubes in a variety of ways (Fig. 12).

7.3.1. Pathway 1

Marine spray entering the lava tube is composed of micrometric seawater drops (Taylor and Wu, 1992), which can partially evaporate inside the cave, increasing their solute concentration and thus precipitating gypsum. During air circulation, micro drops evaporate only partially due to the high relative humidity in the coastal areas of Lanzarote (60–70%). Evaporation concentrates micro drops allowing gypsum precipitation, but halite oversaturation is rarely reached, as occurs in areas with relative humidity higher than 80% (Sonnenfeld, 1984). Sea spray is considered a common source of ions for formation of evaporative minerals in caves near the coast (Bottrell et al., 1993; Onac et al., 2009).

7.3.2. Pathway 2

Marine spray in the exterior of the cave causes precipitation of salts that are later dissolved during rain events, and transported inside the lava tubes. Here they affected by evaporation, thus becoming oversaturated with respect to gypsum. In Fuerteventura, airborne salts
from sea spray are carried by rainfall into groundwaters, increasing their salinity (Custodio, 1990; Herrera and Custodio, 2000).

7.4. Mechanisms of speleothems formation

Direct evaporation is the main process to concentrate the brine, and later oversaturate it with respect to gypsum. Morphological variations and textures of gypsum speleothems are influenced by the amount and pathway of water (infiltrated water vs. sea spray aerosols), the type of water flow (capillarity, drip), the temperature of the rock and the air, the relative humidity and the presence of air currents in the lava tube.

Microcrystalline gypsum crystals, such as those composing coatings and powder, are known to precipitate in conditions of high supersaturation usually caused by fast evaporation (Forti, 2017). The presence of an airflow can enhance evaporation (Calaforra and Forti, 1994; Buecher, 1999; Gázquez et al., 2011), of marine spray entering the tube, triggering precipitation of very small bladed or fibrous crystals. The droplets forming marine spray can deposit through several mechanisms, as for instance, interception or impaction with an obstacle and sedimentation, depositing by gravity when the airflow can no longer transport them (Dredge et al., 2013). When droplets impact the surface of the basalt on the tube walls, they evaporate and form coatings, when they deposit by gravity, powder forms on the floor. The presence of coatings on recently exposed surfaces indicates that some of these crystals are precipitating today, and this process is still taking place.

Powder accumulations probably result from the repetition through time of the previously described processes, when sea spray entering the cave evaporates precipitating microcrystalline gypsum directly in the air or on walls as coatings, which later falls and accumulates on the floor and wall ledges.

Similar accumulations, also called gypsum powder or gypsum snow, have been interpreted as disintegration of other fibrous speleothems (Hill and Forti, 1997), weathering products of crusts (James, 1991) or evaporation of capillary waters (Calaforra and Forti, 1994; Hill and Forti, 1997).

Fig. 9. Comparison between different element (expressed as oxides) obtained through XRF for Covón (blue rhombs) and Chiflentera (red squares) lava tubes. All data are referred in mol (%).
Gypsum powder filling fractures can form by direct precipitation from sea spray entering tubes and fractures. Alternatively, powder filling cracks could have precipitated from water coming from above, from outside the tube (Pathway 2). Rainwater would dissolve sea salts from the surface and enter the fractures. If the amount of water is small enough to form a capillary film highly supersaturated in gypsum, small bladed and platy crystals typical of gypsum powder can precipitate in the cracks (Fig. 4).

Macrocrystalline gypsum crystals, such as the ones forming crusts and stalactites, require low levels of supersaturation (Forti, 2017) and hence, reduced nucleation rates (Otalora and García-Ruiz, 2014). Such situations could be possibly due to: 1) direct precipitation in periods of rainfall when infiltrated water would dissolve airborne salts deposited outside the cave, reaching only smaller values of supersaturation when arriving inside the lava tube; 2) process of dissolution of microcrystalline gypsum and slow reprecipitation of larger crystals in the following two contexts: A) in stages of high rainfall, by infiltration of meteoric water undersaturated with respect to gypsum, B) Dissolution can be caused by condensation of water on the speleothems if humid air warmer than the speleothems surface enters the lava tube. Dissolution and reprecipitation of microcrystalline gypsum on the outer surface of globules can explain the presence of the outer crust composed of larger crystals, while the internal part of globules remains microcrystalline (Fig. 6a, b). Condensation water dissolving gypsum powder and slowly dripping along the wall, while slowly evaporating, would produce crusts and stalactites not connected to major fractures or cracks. Condensation is a relatively common phenomenon in caves, including those developed in semiarid climates (Gázquez et al., 2015), where recent stable isotope studies have highlighted its role in precipitation of gypsum speleothems (Gázquez et al., 2017).

Laminated crusts probably have also formed by processes of dissolution and re-precipitation of powder accumulations caused by water dripping, as suggested by their location below groups of stalactites. Lamination would form by alternation of dripping processes with gypsum dust deposition, similarly as it has been described in Cueva del León, Argentina, where so-called “gypsum dust flowstones” form by alternation of dry periods with very short wet periods, when dripping water partially dissolves and further cements gypsum powder, forming layers (Hill and Forti, 1997; Forti, 2017).

8. Conclusions

El Covón-Chifltera lava tubes located in Lanzarote (Canary Islands) contains microcrystalline gypsum speleothems such as: 1) powder accumulations, 2) coatings, 3) globules; and macro-crystalline speleothems such as: 4) crusts, 5) stalactites and 6) laminated crusts.
Gypsum speleothems, formed over the past 40,039 ± 4748 yr BP to 6217 ± 1644 yr BP (Upper Pleistocene-Holocene), and the process is still active. They formed probably under dominant evaporating conditions interrupted by episodic rainy periods.

Sea spray is the main source of ions in the formation of gypsum speleothems in lava tubes of Lanzarote as indicated by the δ34S, δ18O, and 87Sr/86Sr ratios of gypsum. Two pathways for ion input in the lava tube have been considered: 1) Sea spray circulating within the lava tube; 2) salt precipitation above the lava tube, followed by dissolution by scant rains and percolation underground.

Microcrystalline gypsum formed under high supersaturation conditions produced by the fast evaporation of marine spray due to the small size of spray particles. On the other hand, macrocrystalline gypsum speleothems formed under low supersaturation conditions favoured by infiltration of rainwaters that dissolved salts on the surface, and/or by dissolution-reprecipitation produced by undersaturated infiltration waters or by condensation processes on microcrystalline gypsum.

Large accumulations of gypsum are possible when precipitation is scarce because in rainy climates gypsum deposits are dissolved by rainfall. The constant input of sea spray into the cave, the presence of air currents and the partial but rapid evaporation of sea spray produce large amounts of gypsum precipitation.

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Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>238U (ng/g)</th>
<th>232Th (pg/g)</th>
<th>230Th/232Th</th>
<th>δ234Umeasured</th>
<th>δ234Uinitial</th>
<th>Uncorrected age (years BP)</th>
<th>Corrected age (years BP)</th>
<th>Speleothem (type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHI-15</td>
<td>129.8 ± 0.1</td>
<td>14,767 ± 32</td>
<td>2.29 ± 0.05</td>
<td>0.085 ± 0.002</td>
<td>21 ± 2</td>
<td>22 ± 2</td>
<td>9506 ± 203</td>
<td>6217 ± 1644</td>
</tr>
<tr>
<td>CHI-16</td>
<td>33.3 ± 0.1</td>
<td>13,446 ± 59</td>
<td>3.51 ± 0.03</td>
<td>0.390 ± 0.004</td>
<td>62 ± 3</td>
<td>69 ± 4</td>
<td>40,039 ± 4748</td>
<td>Powder</td>
</tr>
<tr>
<td>CHI-18</td>
<td>68.8 ± 0.1</td>
<td>23,351 ± 79</td>
<td>3.51 ± 0.03</td>
<td>0.390 ± 0.004</td>
<td>62 ± 3</td>
<td>69 ± 4</td>
<td>40,039 ± 4748</td>
<td>Powder</td>
</tr>
<tr>
<td>PAR-11</td>
<td>110.7 ± 0.3</td>
<td>26,342 ± 88</td>
<td>2.30 ± 0.05</td>
<td>0.304 ± 0.004</td>
<td>85 ± 6</td>
<td>92 ± 6</td>
<td>25,055 ± 3237</td>
<td>Stalactite</td>
</tr>
<tr>
<td>PAR-12</td>
<td>69.7 ± 0.1</td>
<td>13,309 ± 22</td>
<td>2.83 ± 0.03</td>
<td>0.176 ± 0.002</td>
<td>81 ± 3</td>
<td>84 ± 3</td>
<td>14,154 ± 2503</td>
<td>Crust</td>
</tr>
</tbody>
</table>

Fig. 12. Sketch showing different processes and pathways for ion input involved in the origin of gypsum speleothems. 1) Marine spray entering the lava tube; 2) airborne salts from surface are dissolved during rain event and infiltrated into the lava tube.

References


