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Kevin Moore

Susan White

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Cover photo : Keir Vaughan-Taylor on Lake 2, Koonalda Cave, Nullarbor Plain. (Photo by Kevin Moore)

Back Cover : The Khan and Beagum in Kubla Khan Cave Tasmania (Photo by Garry K. Smith)

Secondary minerals from halite caves in the Atacama Desert (Chile)

De Waele Jo[1], Carbone Cristina[2], Sanna Laura[3], Vattano Marco[4], Galli Ermanno[5], Forti Paolo[1]

Affiliation: [1] *BiGeA, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Alma Mater Studiorum - University of Bologna, Italy. E-mail:* jo.dewaele@unibo.it; paolo.forti@unibo.it
[2] *DISTAV, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, University of Genova, Corso Europa 26, 16132 Genova, Italy. E-mail:* carbone@dipteris.unige.it
[3] *IBIMET-CNR, Institute for Biometeorology, Traversa La Crucca 3, 07100 Sassari, Italy. E-mail:* speleokikers@tiscali.it
[4] *Department of Earth and Sea Sciences, University of Palermo, Via Archirafi 22, 90123 Palermo, Italy. E-mail:* marco.vattano@unipa.it
[5] *Dipartimento di Scienze Chimiche e Geologiche - University of Modena and Reggio Emilia. Largo S. Eufemia 19, 41121, Modena, Italy. E-mail:* ermanno.galli@unimore.it

Abstract

In the past 15 years several expeditions by French, American and especially Italian cavers have surveyed over 15 km of salt cave passages in the Cordillera de la Sal, close to San Pedro de Atacama village (Atacama Desert, Northern Chile). Over 50 caves have been explored up to now at an elevation around 2,500 m asl. These karst systems are characterized by in-cave temperature of around 17 °C and a relative humidity always very low, with a maximum of 15%. This extreme aridity is due to the severe conditions of the area with only a couple millimeters annual rainfall and several years without rain. Currently the rare precipitation events are enough to allow the dissolution of the salt rock and crusts, and the deepening of underground meandering river passages. Moreover, after the sporadic rain events, the water penetrating the cave's host rock along fractures and bedding plains leads to the dissolution of primary minerals and allows the formation of seeping brines with dissolved salts. Both these processes selectively add solutes to the incoming undersaturated rainwater. The evaporation of these resulting salt-rich fluids at the cave atmosphere interface causes secondary minerals to precipitate.

Mineral samples have been collected in eight caves, and include stalactites, flowstones, precipitates that form crusts in the streambeds and at the groundwater seeps, parietal coatings, earthy masses from the cave floors and efflorescence salts on ceiling rock outcrops. Most secondary deposits are composed of halite, but also other halides, carbonates, sulphates, nitrates, phosphates, and silicates have been discovered. Among the sixteen observed minerals, antarcticite, leonite, darapskite, blödite, atacamite and anhydrite are worth mentioning. The peculiar climate (extremely arid) and the very special environment dominated by NaCl and $CaSO_4$, allow the crystallization primarily of halite. Atacamite was found where local enrichment in Cu (of hydrothermal origin) occurs, and antarcticite precipitates by the final evaporation of SO_4-depleted brine (after early precipitation of anhydrite). Among sulphates, the metals necessary for the formation of these mineral species (magnesium, potassium, sulphate) derive from the cave sediments while nitrates are supplied by bird guano. Salt mineral precipitation is controlled by the temperature dependence solubility of the species in saline water, so that different secondary minerals were observed.

Keywords: salt karst, sulphates, halides, speleothems, minerogenesis

1. Introduction

Few regions worldwide characterized by an extremely arid climate, host salt caves in which halite survives over time. Among hypersaline desert areas, the central Atacama is one of the driest (Houston and Hartley 2003). Despite the scarcity of rainfall in this area, there are several solution caves in the Oligocene-Miocene evaporites of the Cordillera de la Sal, close to San Pedro de Atacama. Following the first cave exploration of the early 1990s (Salomon 1995), in this area almost 50 caves have been discovered, explored and surveyed for a total development of over 15 km (Fryer 1995; Sesiano 1998, 2006, 2007, 2009; Padovan 2015). Only recently the evaporite karst of Atacama has been the subject of scientific research (De Waele *et al.* 2009a, b, c, d; De Waele & Forti 2010; De Waele *et al.* 2017) describing eight cave minerals in the previously explored caves whereas the last sampling campaign in November 2015 enabled to investigate newly discovered caves on the higher part of the Cordillera (Padovan 2015). In this paper we refer to the sixteen known cave minerals from the Atacama region and the very special conditions that allowed their formation, following the recently published more detailed report of these mineralogical studies (De Waele *et al.* 2017).

2. Caves in the Cordillera de la Sal

The Cordillera de la Sal is a NE-SW elongated fold- and thrust belt a couple of km wide and over 100 km long, located near the San Pedro de Atacama village (2,446 m a.s.l.) in the Pre-Andean depression at about 150 km east from the Pacific coast of South America (Fig. 1).

From a geological point of view the Cordillera is composed of an over 1,800-m thick sequence of Tertiary continental sediments of the Paciencia Group, a package of alluvial conglomerates. These sediments interfinger with the San Pedro Formation, a series of fine-grained clastic sediments including some 20 to 60 m thick interbedded salt units (Wilkes and Görler 1994) where more than 50 caves are known, several of which are over 2 km long.

Cave microclimate conditions are characterized by in-cave temperatures ranging between 15-18 °C, depending on

Figure 1. The Cordillera de la Sal anticline and the investigated caves: 1. Chulacao Cave; 2. Lechuza del Campanario Cave; 3. Parede de Vidrios Cave; 4. Zorro Andina Cave; 5. Vicuña Seca Cave; 6. Arco de la Paciencia Cave; 7. Ventanas Cave; 8. Cressi Cave system.

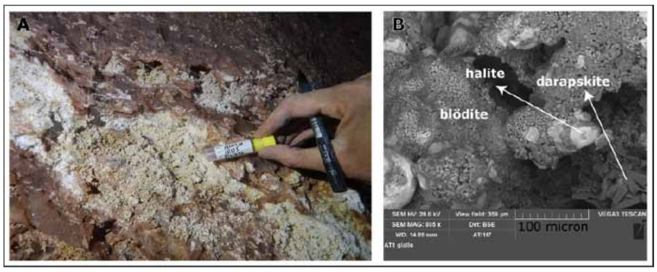

Figure 2. Sulphates of Atacama halite caves: A. Anhydrite powders in a pocket in Arco de la Paciencia Cave (photo Marco Vattano, La Venta Esplorazioni Geografiche); B. The association darapskite, blödite, and halite from the Cressi cave system (SEM photo, Genova University).

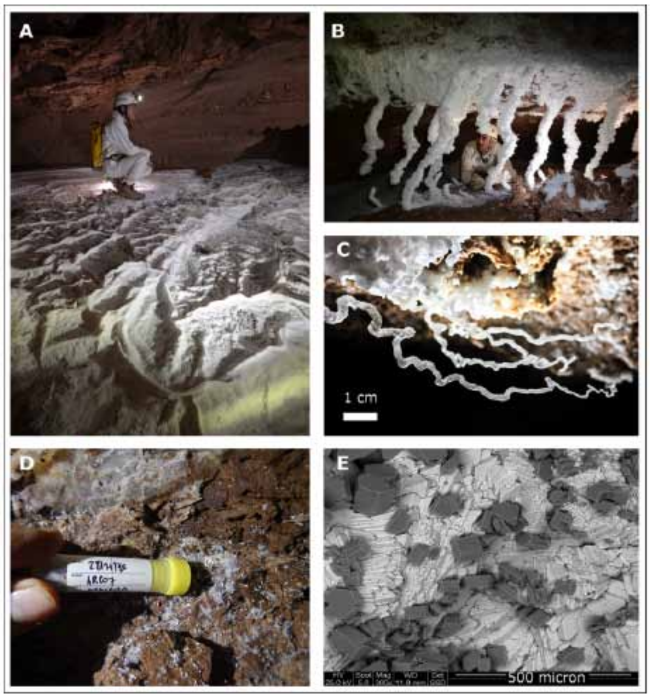

Figure 3. Halogenides of the Atacama desert caves: A. The typical white halite crust covering the cave river floors (Cressi Cave system) (photo Marco Vattano, La Venta Esplorazioni Geografiche); B. Bend halite columns in Cressi Cave system (photo Marco Vattano, La Venta Esplorazioni Geografiche); C. A 20 cm long halite helictite (Arco de la Paciencia Cave (photo Riccardo De Luca, La Venta Esplorazioni Geografiche); D. Antarcticite needles on the marly interbed in Arco de la Paciencia Cave (photo Marco Vattano, La Venta Esplorazioni Geografiche); E. Atacamite crystals on aragonite, Chulacao Cave (Sem image, Modena and Reggio Emilia University).

altitude, cave depth below the surface, and size/number of their openings. Cave relative humidity is always very low (between 10-15%) enforced by the constant airflow through the entire cave length. The long periods of extreme dryness favours evaporation on cave walls, except during rare rain events. Sometimes decades can pass between one rain event and another. Secondary minerals and speleothems have been sampled in eight caves (Fig. 1).

3. Methods

Secondary minerals sampled for this study include stalactites, flowstones, precipitates that form crusts in the streambeds and at the groundwater seeps, coatings along the cave walls, earthy masses from the cave floors and efflorescence salts on ceiling rock outcrops. Cave mineral and speleothem samples were collected during two expeditions (2009 and 2015) with a knife or a geological hammer using small plastic containers or sampling bags. Mineral phases were determined by combining X-ray diffraction data with semi-quantitative chemical analyses. Details on the methods used can be found in De Waele *et al.* (2017).

4. Cave minerals

Mineralogical analyses have revealed a great variety of secondary deposits for the Atacama salt caves, much more than in any other salt karst area of the World (Hill and Forti 1997; Filippi *et al.* 2011). Sixteen mineral species have been identified (Table 1, Fig. 2-3), six of which are quite rare for cave environments (antarcticite being a new cave mineral). Most secondary mineral phases are composed of halite but other minerals have been observed occasionally, such as other halides, sulphates, phosphates, nitrates, carbonates, and silicates.

Most of the secondary minerals found in the salt caves of Atacama are derived from the evaporation of brines (i.e, halite, gypsum, antarcticite, darapskite, blödite, leonite), or from the dehydration of gypsum (bassanite, anhydrite) induced by the hot, arid climate of the area. Halite occurs as crusts (Fig. 3A), white stalactites in euhedral cubic crystals, poorly crystalline trays, bent columns (Fig. 3B), rims, blisters, helictites (Fig. 3C) and cottonballs (Filippi *et al.* 2011). In few spots, also the very rare cave minerals atacamite and antarcticite (Fig. 3D) have been found. In a sample collected close to the southern entrance of Mina de Chulacao Cave, atacamite has been detected as rounded aggregates of emerald to dark green crystals and crystalline crusts on the cave walls, associated with small, thin, white to pale-green aragonite crusts (Fig. 3E). In the Arco de la Paciencia Cave, antarcticite, occurs as efflorescences of acicular crystal aggregates protruding outward from a marly interbedded layer on the cave walls (Fig. 3D). The genetic mechanism that has allowed the formation of this mineral in the karst environment, such as Atacama, is far more complex than the extreme evaporation of the hypersaline lakes of the other locations known in the world. In fact, in this cave antarcticite has not crystallised in evaporated pools, but on a dry cave wall. The mineral seems to have formed starting from capillary water seeping out from the fine-grained sediments, probably following exceptional rain and/or snow events that occurred some months before its discovery.

Gypsum, bassanite and anhydrite have commonly been found in the caves and at the surface (De Waele and Forti 2010). Anhydrite forms relatively pure white, fine powders filling fractures and dissolution pockets far from the entrance in the Arco de la Paciencia (Fig. 2A), Vicuña Seca and Ventanas caves. Leonite occurs together with antarcticite in Arco de la Paciencia Cave, but also in the yellowish crusts over dry lakes in the Cressi Cave system, together with other sulphates (blödite and darapskite) and halite (Fig. 2B). This is the third leonite occurrence in a cave, after Tausoare Cave in Romania (Onac *et al.* 2001) and Wooltana Cave in Australia (Snow *et al.* 2014). The leonite-blödite-darapskite paragenesis has been identified in the Cressi Cave system, upstream of a large salt lake; blödite and leonite probably precipitate during dehydration of lake water from a magnesium and potassium sulphate mixture, whereas the formation of darapskite is controlled by nitrogen that in Atacama it is supplied by urine and guano or recycled from cement in the sediments.

In the Parede de Vidrios Cave, biphosphammite, a very soluble mineral, has been preserved together with guanine, another rare cave mineral formed during the early stages of the mineralization of guano and/or bird droppings, already reported from desert caves in Chile, Western Australia and Mexico (Bridge 1974; Forti *et al.* 2004). Bird droppings and pellets can be seen close to the cave entrances, and these organic products have transformed into these crystalline species.. Moreover, Cl-apatite traces found in Arco de la Paciencia Cave are probably related to minor amounts of phosphates (bones) brought into the cave.

In a karst pocket close to the entrance of Chulacao Cave, authigenic Na-clinoptilolite has been found, which is a typical zeolite of alkaline saline lakes (Mason and Sand 1960; Gottardi and Galli 1985; Coombs *et al.* 1997). Clinoptilolite is probably

Table 1. Cave minerals identified in Atacama caves: Ch - Mina de Chulacao; Lec – Lechuza de Campanario; Pav – Parede de Vidrios; Zra – Zorro Andina; Arc – Arco de la Paciencia; Vs - Vicuña Seca; Vent – Ventanas; Cre – Cressi Cave system.

Cave	Mineral	Nominal chemical formula	Occurrence
All	Halite	$NaCl$	Ubiquitous as speleothem, sometimes present also as small euhedral ice-luster millimetric crystals
Arc	Antarcticite	$CaCl_2 \cdot 6H_2O$	White, ephemerous, millimeter-long curls on clay-marly substrate
Ch	Atacamite	$Cu_2Cl(OH)_3$	In globular aggregates of emerald green radial elongated crystals or, rarely, as millimetric veins of euhedral crystals
Ch	Aragonite	$CaCO_3$	Crusts up to 5 mm thick of vitreous luster transparent to pale-blue or light-green tabular prismatic crystals
Ch, Zra, Cre, Arc, Vent, Vs	Anhydrite	$CaSO_4$	Small lens-shaped aggregates of milky white fibres over euhedral partially corroded gypsum crystals, or white powders filling fractures or solution pockets.
Zra	Bassanite	$2CaSO_4 \cdot H_2O$	Rare very small fibres inside an earthy material in corrosion pockets on the surface of gypsum crystals
All	Gypsum	$CaSO_4 \cdot 2H_2O$	Transparent centimeter-sized, euhedral crystals, partially transformed into bassanite and anhydrite
Cre, Arc	Barite	$BaSO_4$	Small micrometric inclusions in halite, not visible with naked eye
Cre	Celestine	SrSO4	Small micrometric prismatic crystals in halite, not visible with naked eye
Cre	Blödite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	Granular material in the yellowish crusts on dried out cave pools
Arc, Cre	Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	Small amounts together with antarcticite, not visible with naked eye.
Cre	Darapskite	$Na_3(NO_3)(SO_4) \cdot H_2O$	Small submillimetric laminar crystals in yellowish crusts on dried out cave pools
Arc	Cl-Apatite	$Ca_5(PO_4)_3[Cl]$	Traces in some samples
Pav	Biphosphammite	$(NH_4, K)H_2PO_4$	Thin small pale yellow layered fibres
Pav	Guanine	$C_5H_3(NH_2)N_4O$	Earthy, silky-luster milky white to pale pink crusts
Ch	Clinoptilolite	$Na_4K_{1.5}Ca_{0.5}(Al_{6.5}Si_{29.5}O_{72}) \cdot 20H_2O$	Small whitish to pale-pink earthy grains with a few euhedral crystals always strongly associated with halite

a more common phase in evaporites, indicting greater aridity and reflecting the high level of Na in the saline brine.

5. Conclusions

A total of sixteen secondary minerals have been described as occurring in the salt caves of Atacama, including very rare minerals (atacamite, darapskite, blödite, and leonite) and the occurrence of antarcticite, a new cave mineral. An unknown calcium-strontium chloride mineral has also been found, but unfortunately its deliquescent behaviour and small quantity have not allowed for its detailed classification and description.

Most of the Atacama minerals are highly soluble in water. However, the extremely dry climate of the area permits the formation and permanence of these sometimes very rare mineral assemblages. Salt mineral precipitation is controlled by the temperature-dependent solubility of the species in saline water, so that different secondary minerals occur. Processes that drive the crystallization of these phases include the action of thermal fluid-rock interactions and the loss of water through evaporation. Atacamite and aragonite formed from slightly hydrothermal solutions rising along a fault plane in Chulacao Cave.

The other salt minerals in these caves precipitated by evaporative processes during the persistent dry conditions of the Atacama Desert. In fact, the water penetrating along fractures after sporadic rain events causes the dissolution of primary minerals in the host rock, and the slow evaporation of these salt-rich seeping fluids at the cave interface produces speleothems, salt efflorescences and crustal precipitation. Detailed conceptual models for the formation of some of these minerals (i.e. antarcticite, anhydrite, and the blödite-darapskite-leonite association) have been proposed recently (De Waele *et al.* 2017) for this extreme karst environment. It is worth emphasizing that the Atacama salt caves are potential analogues for the study of hygroscopic salts in the Martian subsurface.

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