New Insights into the Bioinduced Precipitation of Hydrated Sulfates in Hypersaline Microbialites

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INTRODUCTION

Saline playa-lakes from La Mancha region (Central Spain) bring the opportunity to study in situ mineral precipitation processes. They are one of the few modern magnesium sulfate lakes with abundant epsomite deposits described (Renaut, 1994). There is increasing evidence that in these systems the microbial communities thrive and play a role in mineral formation (Cabestrero and Sanz Montero 2016).

El Longar lake is the largest and the only permanent body of water of the three shallow basins located near Lillo (Toledo Lat: 39.701.965 Long: -3.322.196). The water on its surface comes mainly from precipitation while groundwater contribution is not significant (Sanz Montero et al. 2015). The variability of rocks in Longar watershed results in a Mg^{2+}-SO_4^{2-}–Cl^- brine composition which leads to the precipitation of diverse sulfate salts, dominantly gypsum. Due to the lack of water input during summer and autumn in the lake, the salinity levels in november 2016 were the maximum recorded since 2010. The abnormally high brine concentration (exceeding 400 g/L as documented by Cabestrero et al, this volume) led to the subaqueous crystallization of saline crusts. Despite the extreme hypersaline conditions, a layer of red-orange halophilic bacteria proliferated in the crust.

This work deals with mineralogical and textural features of the hypersaline crusts. Special attention is paid to the relations between minerals and the microbial mats that occurred associated with the evaporites.

MATHERIALS AND METHODS

During field work conducted in El Longar on 2/11/16, three samples of saline crusts were collected following atransect from the margin (LG -7) to the centre of the water body (LG -11 and LG-12). The samples were comprised of evaporites and microbial characterized by greenish and red colours. They were preserved in the fridge until their mineralogical and petrographical characterization by using LEICA loupe, optical microscopy (Olympus BX51), environmental electron microscopy (SEM FEI INSPECT) and x-ray diffraction (XPERT-PRO).

Previous to the petrographic observations, in order to preserve the textural features, the samples were placed in a freeze drying chamber operating at 0,059 mBar and-49,3 ºC, during 47h 12min.

Later, on the purpose of consolidating the saline crusts, these were impregnated in resin (CaldoFix – 2Kit Struers) under vacuum conditions (-1kg/cm²). Finally, samples were introduced into a high-pressure device (4 bar) during 24 hours to enable the resin solidification without any bubbles. Once saline crusts were embedded in solid resin, they could be studied under loupe.

Thin sections were elaborated using ethanol (96%) instead of water to prevent mineral dissolution.

To minimize the risk of dehydration of the minerals during the mineralogical analysis by X-ray diffraction, the samples were slightly powdered and introduced in silicon capsules covered with kapton. Five repeated scans were performed per sample to control possible phase variations during the diffraction procedure. Difractograms were interpreted with X´Pert High Score Plus software.

RESULTS

The up to 0,5 cm thick, crystalline crusts show a biolaminated structure formed by microbial mats and authigenic evaporites that grow within the purple-red, green and black layers of the mats (Fig 1). The paragenesis of the minerals embedded by the organic matrix invariably includes bloedite, epsomite, gypsum and mirabilite (Table 1).

Petrographic observations show the close relation between the evaporites and the microbial communities embedding them (fig 1, 2). The framework of the crust is formed by coalescent bloedite crystals. Alotriomorphous crystals of bloedite (2 mm) show a greenish color due to the inclusion of the organic components (fig 2A). Furthermore, bloedite include formerly precipitated epsomite and gypsum crystals (fig 2B).

Whilst, idiomorphic crystals of epsomite, up to 3 mm in size, crystalized displacively in the matrix and even destroy lamination. They occur isolated or forming horizontally layered clusters associated with organic slimes (fig 2A).

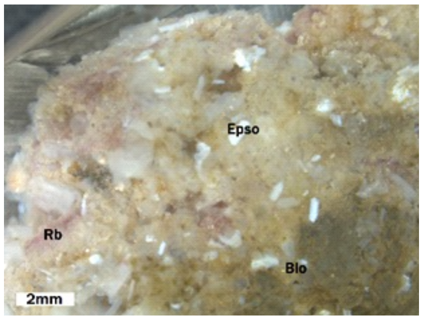

Fig 1. *Loupe picture of the crusts. Epsomite (Epso) and bloedite (Blo) grow inside microbial mat, whith prevalent green and red bacteria (Rb).*

Transparent crystals of mirabilite form continuous layers following the discontinuities and porosity of the crust. The up to 4 mm-long mirabilite crystals are subidiomorphic and occur as mosaics as well as fibrous or radiating aggregates (fig 2B). Red microorganisms seem to be preferentially associated to this mineral.

Small (< 700 μ m), interstitially-grown, gypsum crystals, are widely distributed throughout the crust. They occur as isolated lenticular-shaped crystals (fig 2B).

palabras clave: Microbialitas, Costras salinas, Sufatos hidratados	**key words:** Microbialites, Saline crusts, Hydrated sulfates.

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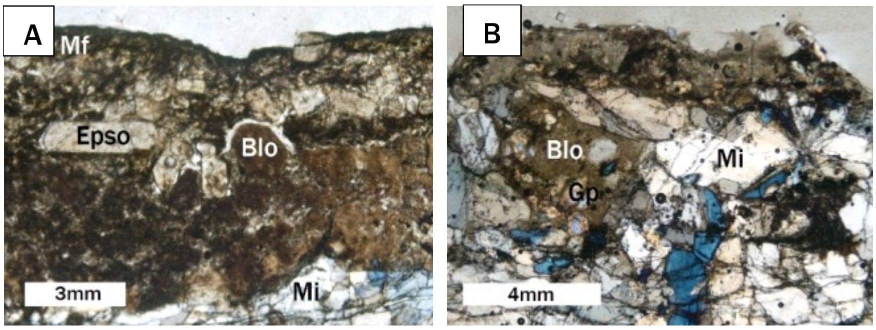

Fig 2. *(A) General laminated structure of a saline crust. Alotriomorphous bloedite (Blo), subidiomorphous epsomite (Epso) and idiomorphous gypsum (Gp) embedding by microbial filaments (Mf). (B) Subidiomorphous (fibrous radiated aggregates) and alotriomorphous mirabilite (Mi) at the base of the saline crust. Bloedite, Epsomite and Gypsum grown in close relation with organic matter.*

Sample	***Bloedite $Na_2Mg(SO_4)_2 \cdot 4H_2O$***	***Epsomite $MgSO_4 \cdot 7H_2O$***	***Gypsum $CaSO_4 \cdot 2H_2O$***	***Mirabilite $Na_2SO_4 \cdot 10H_2O$***
LG -7	*28%*	*14%*	*13%*	*45%*
LG-11	*39%*	*25%*	*7%*	*29%*
LG-12	*54%*	*11%*	*10%*	*26%*

mineralogical analyses undertaken in the three saline

DISCUSSION AND CONCLUSIONS

We provide new insight into the formation of hydrated sulfates from hyper-concentrated brines.

The formation of biolaminated crystalline crusts on the bed of this lake has not occurred previously because the extreme conditions required for their formation were not recorded before. The hyper-concentrated brine was enriched in magnesium sulphates and sodium sulphates, consistent with the mineralogy of the crust, composed by hydrated sulphates. However, Cabestrero et al. (2017, this volume) calculated that the saturation indices of epsomite and bloedite in the brine are negative and decrease significantly with temperature. These calculations are consistent with our observation concerning to the nucleation and growth of the mineral phases, restricted to the microbial matrices. Thus, we suggest that the precipitation of bloedite, epsomite and gypsum results from a complex interplay between the organic matrices and physico-chemical conditions. The intrasedimentary growth of gypsum in the microbial mat has been previously reported in El Longar and other environments (Cabestrero et al. 2013, among others). By contrast and despite some authors had described the incorporation of organic matter in epsomite (De la peña et al. 1982), the bioformation of bloedite and epsomite has not been previously documented in this type of crusts (Last, 1994; Mees et al. 2011).

Although bioinduced mineralization of Mirabilite was suggested by Dongyan et al. (1998), nor our textural observations nor the geochemical modeling of mirabilite precipitation support unequivocally this type of origin in El Longar crust.

Our results offer strong evidence for the bioinduced formation of hydrated sulphates mainly bloedite, epsomite and gypsum in biolaminated crusts (microbialites).

A solid understanding of these geobiological processes in hypersaline lakes might be useful to unravel the origin of hydrated sulfates of Europa and Ganymede (Zolotov, 2016).

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