Geochemical Modeling of the Precipitation Process in SO_4-Mg/Na Microbialites

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INTRODUCTION

Longar is an endorheic mesosaline to hypersaline lake (> 10 $g{\cdot}L^{-1}$), with sulphate being the dominant anion over chloride (Cabestrero and Sanz-Montero, 2016). It is located in Lillo (La Mancha), a region with a continental semi-arid climate and is characterized by high evaporation (1300–1700 $mm{\cdot}yr^{-1}$) and low precipitation (300–500 $mm{\cdot}yr^{-1}$). The annual mean temperature is 14 ºC, and extreme values of -7 ºC and 40 ºC are registered in January and July, respectively (Sanz-Montero et al., 2015a). The most abundant mineral in the lake is lenticular gypsum and a suite of hydrated sulphates, such as hexahydrite, epsomite, pentahydrite, starkeyite, konyaite, bloedite, and thenardite. The major authigenic carbonates are calcite and aragonite, although dolomite, hydromagnesite, monohidrocalcite, magnesite and nesquehonite can also be found in smaller amounts (Cabestrero and Sanz-Montero, 2016).

After an extremely dry summer and autumn, in November 2016, the water lamina ponded in the lake was very thin and the concentration of the brine was the maximum recorded. The high salinity favored the subaqueous crystallization of a hard crust of evaporites on the bed. The up to 0.5 cm thick curst consisted of bloedite, epsomite, gypsum and mirabilite that occur within a microbial mat matrix as documented by Del Buey et al., this volume. There is increasing evidence that microbial mats proliferate in shallow lakes subjected to wet-dry cycles (Sanz-Montero et al., 2015b). It follows that the geochemistry of the environment, the idealized precipitation sequences and the mineral assemblages proposed by Eugster and Hardie (1978), are susceptible to change where microbes are present.

The purpose of this paper is the geochemical modeling of the mineral precipitation from the hyper-concentrated brine.

MATERIALS AND METHODS

Fieldwork was conducted in November 2016. Water samples taken were filtered (using 0.45 µm pure cellulose acetate (CA) membrane filters). The main cations and anions were analyzed by ion chromatography, using Dionex DX 500 ion and METROHM 940 Professional IC Vario chromatographs in the CAI for geological techniques in the Geological Sciences Faculty, Complutense University of Madrid. The carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ion concentration in the water was determined by titration. Hydrochemical parameters such as salinity (S), temperature (T), dissolved oxygen (DO), oxidation reduction potential (ORP), and pH values were measured in situ using a multiparameter meter.

Geochemical modeling was carried out using the PHREEQC program (Parkhurst and Appelo, 1999) in order to calculate ion activities and saturation indices of minerals commonly found evaporative environments and included in the Llnl database. In addition, a natural brine evolution during day and night was performed according the instructions provided in the software manual “Evaporation and Homogeneous Redox Reactions” of the PHREEQC program. The saturation indices (Table 1) for the day were calculated using the temperature registered in the field, but for the night, the temperature considered was the recorded in Tembleque weather station (AEMET), during the five previous days to the sampling. The program was constrained to reduce the temperature of the water mass of the brine considering night temperatures. Night temperatures in the area ranged between 1 and 7 ºC. Considering a 4 ºC average temperature and a temperature cushioning of 3 ºC, it means that temperature of the water during the night could decrease up to a minimum value of 7 ºC (equilibrium temperature).

RESULTS

As a result of the intense evaporation, the summer and autumn in 2016 year left a thinner water layer (< 10 cm). The water collected in Longar Lake watershed at 30 ºC was, with a salinity surpassing 400 $g{\cdot}L^{-1}$, the most concentrated in the last six years. Furthermore, pH values were the lowest ever measured, ranging from 7.1 to 7.3. In contrast, ionic composition did not show a significant variation compared to all other values found before (Mg^{2+}-SO_4^{2-}-Cl^- brine type). The absence of dissolved oxygen and ORP values ranging from -112.90 to -90.20 mV suggests reduction processes.

The simulation model of mineral precipitation during the day showed that only carbonates were supersaturated (Fig. 1). Dolomite and calcite had positive values of SI in the original brine solutions at noon temperatures (25-30 ºC). Glauberite, aragonite and gypsum were very close to the saturation with values of -0.01, -0.12 and -0.16 respectively (Table 1). All other phases were clearly undersaturated. Night model (decreasing temperature in steps of 1 ºC from 25 ºC) showed that glauberite oversaturated at temperatures lower than 25 ºC (Fig. 1). At temperatures lower than 13 ºC, mirabilite also oversaturated. Decreasing temperature, gypsum got even closer to saturation but was never

Mineral	Formula	SI Max
Mirabilite	$Na_2SO_4{\cdot}10H_2O$	**0.47**
Epsomite	$MgSO_4{\cdot}7H_2O$	-0.63
Bloedite	$Na_2Mg(SO_4)_2{\cdot}4H_2O$	-0.42
Gypsum	$CaSO_4{\cdot}2H_2O$	-0.06
Halite	NaCl	-0.19
Polyhalite	$K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$	**0.03**
Glauberite	$Na_2Ca(SO_4)_2$	**0.16**
Thenardite	Na_2SO_4	-0.01

Table 1. Modeled minerals with their formula and the maximum saturation indices (SI Max).

palabras clave: Lagunas, Costras salinas, Tapices bacterianos, Sulfatos.

key words: Shallow lake, Saline crusts, Microbial biofilms, Sulphates.

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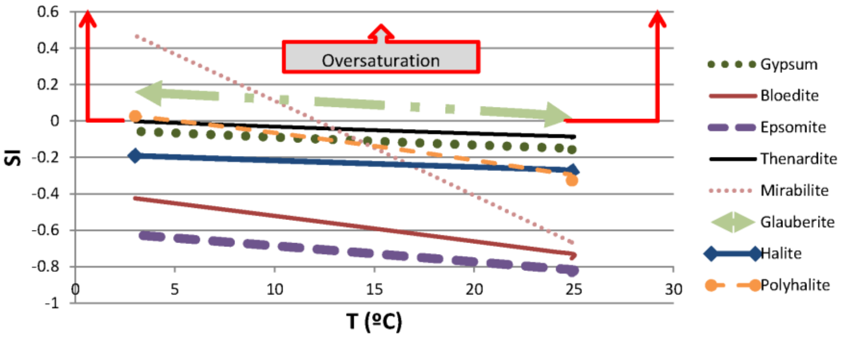

Fig 1. Saturation indices of the minerals while varying the temperature of the brine (Night and day). Only glauberite, mirabilite and Polyhalite are oversaturated.

oversaturated with a SI minimum value of -0.06. Dolomite stayed oversaturated, aragonite moved away from saturation point and calcite turned undersaturated at 10 ºC. Thenardite, halite and bloedite were very close to the saturation point at 3 ºC, with values of -0.01, -0.19, and -0.42, respectively. Polyhalite which was always undersaturated turned oversaturated under 5 ºC. All other sulphates were clearly still undersaturated.

DISCUSSION

Cabestrero and Sanz-Montero, 2016 presented a geochemical model of mineral precipitation considering lower values of salinity than those recorded in November 2016 in Longar. According to their results, except Gypsum, most sulphates and chlorides, cannot precipitate directly from the brine, because they are always undersaturated, even when most of the water is about to evaporate. Therefore, the authors attributed the increase of the saturation levels required for the precipitation of these sulphates to environmental changes induced by microorganisms. To explain the saline crusts that are grown intrasedimentary in microbial mats at very high concentrations as described by Del Buey et al. (this volume), a new geochemical model is required. The results of the geochemical model show that bloedite and epsomite are permanently subsaturated. The saturation indices calculated along with the close relationship between the minerals and the microbial mats suggest that microorganism's matrix play a role in the precipitation of the hydrated sulphates. In contrast, the presence of mirabilite, which has not been found before in a high concentration in Longar Lake, can be explained by inorganic precipitation. It would precipitate during the night when temperatures were clearly lower than the temperature of saturation, 12 ºC. Crust layering and the absence of organic matter in the crystals described by Del Buey et al., this volume is coherent with this type of precipitation. Glauberite was also oversaturated, although was not detected by XRD. Thus, it may require specific conditions of nucleation that will be assessed in a near future. Polyhalite was oversaturated below 5 ºC, but this temperature was not presumably reached for enough hours during the night, or re-dissolved during the day. Thenardite was very close to the saturation at 3 ºC, but the brine may not have reached these temperatures, as 3 ºC is below the equilibrium temperature calculated (7 ºC). Gypsum was also undersaturated, although its presence in the crusts is lower than in the paragenesis commonly found in the lake. The ability of gypsum to nucleate in the organic matrix explains its precipitation (Cabestrero and Sanz-Montero, 2016). Halite was also undersaturated.

This paper provides a geochemical model dealing with unusual hyper-concentrated brines (over 400 g·L-1) and gives evidence on the role of microorganisms in the precipitation of subsaturated sulphates. Thus, interactions between microorganisms and sulphates at extreme hypersaline conditions are of more importance than previously supposed.

CONCLUSIONS

The increase of salinity that occurs when the brine is extremely concentrated cannot explain the presence of most of the minerals found in Longar Lake, except for mirabilite. The precipitation of mirabilite can take place physicochemically at the concentration of the brine and temperature recorded during the night. Though waters are supersaturated in carbonates and subsaturated in sulphates and chlorides, the precipitation of most of the minerals is only related with physicochemical conditions promoted by microbial activities. Organic matter can absorb or expel ions promoting hydrochemical changes.

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