# Carbonates and Sulfates in Hot Spring Microbialites (Baños de Mula, Betic Range)

/ Mª ÁNGELES GARCÍA-DEL-CURA (*1, 2), Mª ESTHER SANZ-MONTERO (3), DAVID BENAVENTE (2,4), SALVADOR ORDÓÑEZ (2,4)

(1) IGEO, CSIC-UCM. Facultad de Geología. c/ José Antonio Novais, 12, 28040 Madrid (España)
(2) Laboratorio de Petrología Aplicada, Unidad Asociada UA-CSIC. San Vicente del Raspeig, 03690 Alicante (España)
(3) Departamento de Petrología y Geoquímica. UCM, c/ José Antonio Novais, 12, 28040 Madrid (España)
(4) Departamento de Ciencias de la Tierra y del Medio Ambiente. Universidad de Alicante, San Vicente del Raspeig, 03690

## INTRODUCTION

In this paper the association of various minerals, mainly carbonates, to microbial mats that cover the surfaces of a hot spring is documented. In addition, the influence of microorganisms in the formation of the travertine is discussed.

The hot spring is located in Baños de Mula (Murcia province), in the Eastern Betic Range, in a Neogene- Quaternary post-tectonic basin, the Mula-Archena basin, considered a sub-basin of the Fortuna basin (Meijninger, 2007). In this area there are ancient travertine deposits (Upper Pleistocene - Holocene?); mantle travertine deposits (García del Cura et al. 2014) and ridge travertines.

These deposits are related to the so-called "Limit fault or Mula-Archena fault" which it is still active. This paper is focused on actual deposits that are the latest petrogenetic manifestation of such fault because the hot water can be considered the last event of tectonic origin in the area at the moment.

Some of the studied deposits could be defined as travertine (thermogene travertine) and others as stromatolites and tufas of bryophytes (microbialites). Recent minerals are formed in an active hot spring. Today the water of this hot spring is used for the operation of a spa (El Pozo Spa). The location of upwelling of hot water was shifted as a result of tectonic activity, and more specifically with an earthquake which occurred in the 18th century.

Travertines typically consist of crystalline and fibroradiate layers (García-del-Cura et al., 2012), whereas stromatolites are dominantly formed by bacterial shrubs and clotted micrite. Depending on the chemical and physical characteristics of the thermal waters, irregular masses of filamentous bacteria may colonize locally travertine surface and create shrubs structures (Capezzuoli et al 2014) in banded travertine facies (García-del-Cura et al., 2012).

We agree with the definition of stromatolite as laminate category of microbialites after Awramik & Margulis (1974) (cit in Riding 1999), modified by Reading 1991, as stromatolite is a laminated benthic microbial deposit, benthic including the sediment – water surface and some sub-surface layers.

Several types of microbial-mediated mineralization can be distinguished in sedimentary environments, including biologically-induced and biologically influenced mineralization. Biologically-induced mineralization results from the interaction between biological activity and the environment. Biologically-influenced mineralization is defined as passive mineralization of organic matter (biogenic or abiogenic in origin), whose properties influence crystal morphology and composition (Dupraz et al. 2009). The delicate balance of a combination of microbial and physicochemical processes, which is different in different environments, is ultimately responsible for the formation of the microbialite (Dupraz et al. op cit.).

The studied spring deposits in this paper will help determine the degree of microbial contribution to the mineralization of calcium carbonate and Sr and Ba sulfates at temperature of about 40 º C.

## METHODS

The mineralogy was studied by X-ray diffraction (XRD), optical microscopy and SEM with EDS. Sample surfaces were observed with FESEM (SUPRA40VP) and VPSEM (Hitachi S3000N), in back scattered electron mode and low pressure, with a Bruker XFlash 3001 EDS to examine the composition. Thin sections of samples embedded in resin were observed with an Axioscop Zeiss TLM and Hitachi S3000N VPSEM.

Spring water was sampled in different seasons. Anions and major cations of water were determined by ion chromatography and trace composition was performed by ICP-MS. The saturation index of different minerals (SI) was calculated using the PHREEQC program.

## MATERIALS

Current hot spring emerges in a small outdoor fountain and has three types of deposits: A) Multilayer laminated crusts make contact with water flowing at a temperature of 39-40 ° C with well-developed multispecie microbial mats could be defined as travertine. B) Spongy bryophyte tufa and stromatolites in the splash zone next to the deposit previously described and in gradual transition with it. C) Laminated crusts with mamelonar surface are located on far wall points with poorly developed biofilms.

### Mineralogy and Hydrochemistry

LMC calcite, gypsum, quartz, illite and dolomite have been characterized by XRD. Celestite-barite, Mg minerals and feldspars, micas and clay minerals (caolinite) have been identified by SEM and EDS.

The composition of spring waters (autumn) show this saturation index (SI), calculated using the PHREEQC program. Water is oversaturated with respect to calcite (0.61), aragonite (0.47), ordered dolomite (1.26), disordered dolomite (0.77), barite (0.26) and undersaturated in gypsum (-0.46), magnesite (-0.92) celestite (-0.37) and hydromagnesite (-10.54). Summer and winter waters

| palabras clave: Travertino, Carbonato continental. | key words: Travertine, Terrestrial carbonate. |
|---|---|


* corresponding author: agcura@geo.ucm.es

present minor variations.

***Petrographic data***

Multilayer laminated crusts are the most complex deposits, these are associated with biofilms and EPS of living cyanobacteria (carbonates, aggregates from 10 to 40 µm in diameter, (Fig. 1B), bacteria (barite-celestite spherical particles of ≈2 µm in diameter, Fig. 2) and diatoms are observables. The holes corresponding to the stalks of diatoms in the calcite crystals (arrows in Fig. 2A) are frequently observed. Calcite and dolomite are associated with EPS of living cyanobacteria (Fig. 1B), in travertine and stromatolite surfaces.

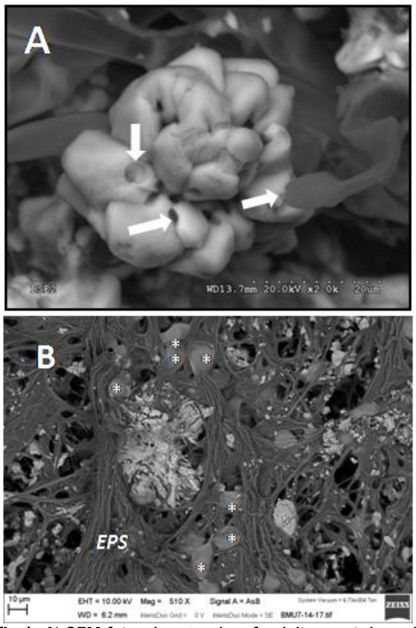


**fig 1.** *A) SEM fotomicrography of calcite crystals and stalks of diatoms. B) SEM fotomicrography of carbonates associated to living cyanobacteria (*) and their EPS.*

***DISCUSSION***

The presence of the allochthonous carbonates trapped in the biofilms makes it difficult to the XRD characterization carbonates generated in the microbial mats. The size and morphology of the celestite-barite are related to bacteria (Fig. 2).

At some points away from the flow of the water, evaporation also could intervene in the genesis of gypsum, which it is markedly more abundant in zones undergoing episodes of dryness.

Similar paragenesis (gypsum-calcite-dolomite-barite) has been documented in other recent spring biofilm, (Almería, Spain) by García-del-Cura et al., 2014 and in the geological record in the Miocene lacustrine sequences in Madrid and Duero Basins (Sanz-Montero et al. 2009).

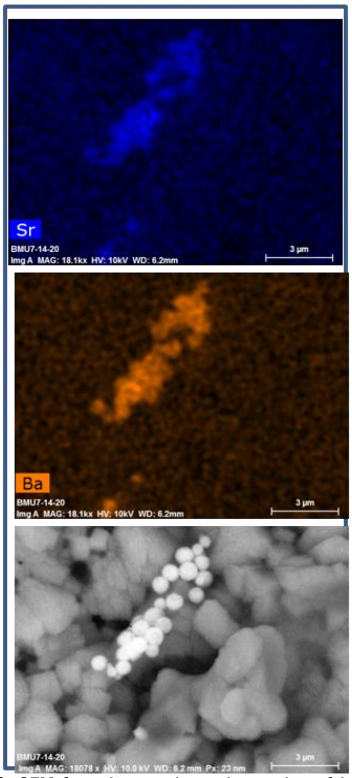


**fig 2.** *SEM fotomicrography and mapping of barite and celestite on recent travetine surface.*

***CONCLUSIONS***

Travertines are currently formed in a hot springs of Baños de Mula (Betic Range) and they gradually convert to Bryophytes tufas with stromatolites (microbialites).

We consider stromatolites to be carbonate deposits induced by biological activity, whereas some travertine layers are biological influenced deposits. In some laminated studied deposits (travertines), there are crystalline layers alternating with layers of biogenic texture.

Complex biofilms are formed on the surface of these travertines and microbialites. The precipitation of calcite, dolomite and barite-celestite take place on the EPS of biofilms, and sometimes are attached to the microbial cells. Their genesis may be related to the physiological activity of the different components of biofilm or microbial mat community; cyanobacteria and bacteria mainly through changes in water composition.

Minerals trapped in these biofilms may be derived from mineral matter in suspension in the wind.

**ACKNOWLEDGEMENTS:**

This study was financed by the Spanish Ministry of Economy and Competitivity (Projects CGL2011-25162 and CGL2011-26781).

**REFERENCES**

*Capezzuoli, E., Gandin, A., Pedley, M. (2014): Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art. Sedimentology, **61**, 1-21, doi: 10.1111/sed.12075.*

*Dupraz, C.; Reid, P., Braissant, O., Decho, A.W., Norman, R.S., Visscher, P. (2009): Processes of carbonate precipitation in modern microbial mats. Earth Sci. Rew., **96**, 141-162. doi:10.1016/j.earscirev.2008.10.005*

*Garcia-del-Cura, M.A., Benavente, D., Martinez-Martinez, J., Cueto, N. (2012): Sedimentary structures and physical properties in travertine and carbonate tufa building stone. Const. Build. Mat., **28**, 456-467. doi:10.1016/j.conbuildmat.2011.08.042*

*–, M.A., Sanz-Montero, M.E., De-los-Rios, M.A., Ascaso, C. (2014): Microbial dolomite in fresh water carbonate deposits. Sedimentology, **61**, 41-55. doi: 10.1111/sed.12047*

*-, M.A., Benavente, D., Martínez-Martínez, J.; Ordóñez, S. (2014): Los travertinos de Baños de Mula. Una roca de interés sedimentológico y arqueológico. Geogaceta, **56**, 75-78*

*Meijninger, B.M.L. (2007): "Late-orogenic extension and strike-slip deformation in the Neogene of southeastern Spain". Geologica Ultraiectina. Mededelingen van de Faculteit Geowetenschappen. Universiteit Utrecht {Communications of the Faculty of Geosciences, Utrecht University}, **269**, 176 pp*

*Riding . R. (1991): Classification of microbial carbonates. In Riding. R. (ed.): Calcareous algae and stromatolites, 21-51. Springer-Verlag, Berlin.*

*- (1999): The term stromatolite: towards an essential definition. Lethaia, **32**, 321-330.*

*Sanz-Montero, M.E., Rodríguez Aranda, J.P., García-del-Cura, M.A. (2009): Bioinduced precipitation of barite and celestite in dolomite microbialites. Examples from Miocene lacustrine sequences in the Madrid and Duero Basins, Spain. Sediment. Geol., **222**, 138 – 148. doi:10.1016/j.sedgeo.2009.05.009*