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Biomineralization in relation with endoevaporitic microbial communities. Miocene lake deposits of the Madrid Basin, Central Spain.

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1 Introduction

This work deals with the role played by endoevaporitic microorganisms in the formation of minerals such as dolomite and celestite associated with gypsum, which is an emerging, frontier-subject in view of recent findings of sulphate deposits in Mars.

The research is centred on Miocene gypsum deposits cropping out in the easternmost part of the Madrid Basin. The deposits accumulated in a saline lake during the lower Miocene and are characterized by a quite spectacular, distinctive “Christmas’s tree” morphology, which is indicative of an atypical growth style of gypsum. In detail, Christmas-tree gypsum consists of twinned macrocrystals formed by mm- to cm-sized subcrystals that grew epitaxially according to a regular pattern (Rodríguez-Aranda et al., 1995). The boundaries of these subcrystals appear unevenly outlined by fossil organic matter, micro-dissolutional surfaces, and different minerals (dolomite, celestite...) that have been interpreted as products of microbial endoevaporitic communities that throve in the gypsum (Rodríguez-Aranda et al., 2004). The term endoevaporitic communities was coined by Rothschild et al. (1994) referring to microbes living embedded within a few-mm of the surface gypsum crust. This adaptation represents the conquer of an ecological niche that allow microorganism to live in an otherwise hostile environment.

Endoevaporitic communities have been described, generally from a microbiological point of view, in different modern saline environment. Such is the case of the Death Valley studied by Douglas and Yang (2002) who also suggested that endoevaporitic microbial communities are tied to evaporite mineralogy affecting its composition.

In this work we place emphasis on describing the minerals formed by mediation of the microbial communities that inhabited the gypsum crystals, especially dolomite and celestite. Besides, the influence of these microorganisms in the boring (endolithic action) and further replacement of gypsum by dolomite have been subject of study by Sanz Montero et al., 2004; and Sanz Montero et al. (in prep.)

2 Dolomite biomineralization

Dolomite outlining gypsum subcrystals has been interpreted as a primary mineral phase and formed through microbial mediated processes (Sanz Montero et al., 2003). A number of sedimentological, geochemical, mineralogical and textural features support this interpretation.

Sedimentological features and facies association:

Gypsum layers are composed of growth aligned selenite crystals displaying a habit characterised by the twin re-entrant angle systematically opening downward. These precipitated in periods of brine concentration in the saline lake. In concurrence with brine freshening, gypsum growth was regularly interrupted what allowed the outlines of the subcrystals to be colonized by microbial mats. In the dry season gypsum precipitation proceeded sealing the mats in relation with which took place the dolomite precipitation. The seasonal character of the dilution events, probably correlative with the input of meteoric water to the lake, is suggested by the uniformity in the spaced of the vertically stacked subcrystals of gypsum.

Dolomite not only occurs between gypsum subcrystals but also forms distinctive cm-thick beds exhibiting typical morphologies of stromatolites such as pustular, domal and reticulate. These stromatolites represent mineralised microbial mats that throve during major dilution stages of the lake. Sedimentary interruptions are further reflected by early replacements of gypsum and dolomite by anhydrite.

Geochemical and mineralogical evidences.

Different petrographic examinations, especially under fluorescence microscopy, have revealed the presence of organic matter intimately associated with dolomite. Organic matter occur as massive forms or microfibrils interpreted in general, as remains of extrapolymeric substances produced by microorganisms. Occasionally, these occur together with clusters of coccoidal cells partially mineralised in dolomite that corroborates this interpretation. The contribution of organic matter from bacterial and eukaryotic sources in Tertiary hypersaline lakes have been elsewhere reported by Wang et al. (1998)

Isotopic analysis of the dolomite samples yielded $\delta^{13}C_{PDB}$ values ranging from -7.35 to -4.65‰; this is, significantly enriched in ^{12}C which can be related with organic matter contribution. Moreover, values of $\delta^{18}O_{PDB}$ range from –7.79 to –2.65‰ suggesting a probable metabolic origin for the oxygen present in the mineral structure.

Mineralogical analysis by X-ray diffraction show that the carbonate is pure dolomite, nearly stoichiometric and generally slightly Ca-rich. The degree of ordering ranges from 0.3 to 0.6.

Systematic microanalytical determinations carried out with electronic microprobe and EDS techniques indicate a total lack of Sr in the dolomite crystals. In addition, the carbonate mineral that pervasively forms facies association with the gypsum is dolomite. Both evidences also support a primary origin for dolomite. When other carbonate precursor is absent, microbial activity provides appropriate conditions for overcoming kinetic factors that inhibit the formation of dolomite in earth-surface environments (Vasconcelos and McKenzie, 1997).

Crystal textures:

The detailed petrography of the dolomite has been carried out by using SEM imagery. Most of dolomite crystals are between 5 and 25 μm in size. These crystals are spheroidal in shape or exhibit wheat grain morphologies. Whatever the case, the crystals pervasively show spheroidal inner holes. Some crystals appear isolated but typically they form distinctive “8”-shaped couples, tetrads, or clusters. In the case of tetrads, and sometimes also in couples, the inner wall separating crystals is quite thin and discontinuous. In other situations a single dolomite envelope surrounds the group. Layers of thin platelets arranged tangentially around the core compose individual spheroidal crystals that towards the edges develop rhombohedral terminations. The wheat grain morphologies are also formed by stacked platelets of dolomite that exhibit helicoidal dislocation lines.

Formation of dolomite with microbial participation

Evidences provided above support that dolomite crystals associated with gypsum precipitated with microbial involvement. Likewise, crystalline textures indicate that spheroidal crystals represent mineralised coccoidal cyanobacteria. The formation of dolomite in relation with cyanobacteria activity is a striking phenomenon scarcely documented, with the exception of descriptions of microbialites in Rao et al. (2003). In the case study the biomineralization of cyanobacterias in dolomite took place not only in typical surficial microbial mats developed on the lake bottom but also in endoevaporitic microbial communities while enclosed in gypsum. In spite of these conditions, mineralization was prompted when microbes were still in a turgent stage, as suggested by the good morphological preservation of the cells. The mineralization proceeded on the cell wall before bacteriolysis. Specific microenvironment created around microbial cells may have favoured the precipitation of dolomite. These conditions include: cell walls enriched in Ca^{2+} and Mg^{2+}, CO_2supplied by respiratory processes (Ehrlich, 1999), suitable pH, and, possibly a proper substrate, since some groups of cyanobacteria are provided with a paracrystalline proteinaceous layer which forms the outermost surface of the cells that subsequently can act as nucleation site for minerals (Schultze-Lam and Beveridge, 1994).

3 Celestite occurrences

Celestite minerals are ubiquitous in gypsum crystals. They occur intimately associated with dolomite and/or embedded in organic matter. Celestite crystal exhibit prismatic habits, less than 20 μm in length. Its morphology ranges from euhedral to subeuhedral depending on its relation with dolomite crystals, this revealing a coeval precipitation.

Formation of celestite

Traditionally, celestite has been thought to be purely an evaporitic mineral. However, recent findings tie celestite with microbial microenvironments. So, experiments carried out by Schultze-Lam and Beveridge (1994) led to the epicellular precipitation of celestite on unicellular cyanobacteria. In the same way, Douglas (2002) found that celestite formed in the exopolymers surrounding purple sulphur bacteria in microbial mats from a Bahamian hypersaline pond. Additionally, Taberner et al. (2002) interpreted celestite as a by-product of sulphate reducer bacteria.

In the case study, textural and mineralogical relations allow us consider the two latter mechanisms as plausible for the precipitation of celestite, since this mineral also appears associated with iron sulphide. Moreover, Christmas tree gypsums are characterised by significant proportions of Sr (with average values higher than 1000 ppm) which may have been released by dissolution or sulphate-reduction mechanisms, and later incorporated in celestite structure.

By contrast, there are no signs of strontianite (CaSr $(CO_3)2$), the mineral that accompany celestite in the epicellular model of formation proposed by Schultze-Lam and

Beveridge (1994).

4 Conclusions

This paper provides evidences confirming that the imprints due to microbial endoevaporitic communities can be preserved in the geological record of saline settings. The signatures are diverse (isotopic values, gypsum microdissolution, etc.,) but those concerning biomineralization processes prevail. Specifically, textures recognised in dolomite crystals support that coccoid cyanobacteria mediated the epicellular precipitation of dolomite. Celestite appears pervasively associated to dolomite. Like in Miocene samples, in some modern environments celestite occurs embedded in organic matter, concretely in exopolymers surrounding purple sulphur bacteria (Douglas, 2002), which imply some microbial involvement in celestite formation. The ubiquitous presence of iron sulphides in gypsum facies indicates that sulphate reducer bacteria also played a role in the processes of mineral formation.

These results suggest that typical layering found in modern microbial mats might be indicated in ancient saline deposits by specific biomineral distribution.

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