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Exceptional preservation of Mn-oxidizing microbes in cave stromatolites (El Soplao, Spain)

Rafael P. Lozano [a,*], Carlos Rossi [b]

[a] Museo Geominero, Instituto Geológico y Minero de España, Ríos Rosas 23, Madrid 28003, Spain
[b] Departamento de Petrología y Geoquímica, Facultad de Ciencias Geológicas, Universidad Complutense, Madrid 28040, Spain

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ABSTRACT

Many ferromanganese stromatolites of El Soplao Cave (N Spain) are characterized for the exceptional preservation and high diversity of microbial fossils, probably representing the best example of microbial preservation described in ferromanganese deposits so far.

The El Soplao stromatolites are mainly formed by polymetallic Mn-rich oxides with subordinate and variable amounts of detrital material, and consist of both dendritic and laminar microfacies. In both microfacies, microbial forms are abundant in the relatively pure Mn-oxide rich material, whereas they are scarce in areas with significant detrital material. Microbial forms are observed either in cross section, completely embedded in the Mn-oxide-rich matrix, or in three dimensions lining the walls of pores. Based on their morphology, we have separated the most abundant microbial forms into six main morphotypes and six additional submorphotypes, most of which can be assigned to bacteria. Most morphotypes consist of coccoid, coccobacilus, or filamentous forms. Therefore they are not diagnostic of any particular bacterial group. However, the ovoid cells of morphotype B show cylindrical polar protuberances typical of prosthecate alpha-*Proteobacteria*. On the basis of characteristic morphological features, three submorphotypes of morphotype B can be assigned to three alpha-*Proteobacteria* genera: *Hyphomicrobium*, *Pedomicrobium*, and *Caulobacter*. This ascription is supported by the well known Mn-oxidizing behavior of both *Pedomicrobium* and *Caulobacter*, and by the common presence of *Hyphomicrobium* in ferromanganese deposits elsewhere.

The excellent microbial preservation is partly related to the origin of the ferromanganese oxides, i.e. extracellular precipitation induced by microbial metabolism. Other factors contributing to the good microbial preservation are the relatively low degree of diagenetic alteration, and the relatively high accretion rates of stromatolites compared to other ferromanganese deposits. The generally low degree of diagenesis is likely because the stromatolites have remained relatively stable and at a rather low temperature since they were formed at least 1 Ma ago. Still, some stromatolites have suffered diagenetic alteration (partial dissolution and replacement by calcium carbonates and Fe-rich oxides), obscuring or even obliterating their bioforms. The El Soplao case represents an example of how easily biogenic Mn oxides can be altered, and their bioforms blurred, in a relatively short geological time span in spite of being in a relatively stable, alkaline, and low-temperature setting. A geological implication is that the absence of bioforms in other ferromanganese deposits, including rock varnish and Precambrian iron formations, does not disprove their possible biogenic origin, since the high chemical reactivity of biogenic manganese oxides makes them highly vulnerable to diagenesis.

1. Introduction

Deposits rich in manganese and iron oxides form in a variety of earth surface and shallow subsurface environments, including rock outcrops (i.e. rock varnish: Liu and Broecker, 2000; Dorn, 2007), sea-floor nodules (Ehrlich, 2000), hot springs (Chafetz et al., 1998), lakes (Asikainen and Werle, 2007), and caves (Spilde et al., 2005). In surface waters, the oxidation of dissolved Mn^{2+} and Fe^{2+} to form insoluble oxides can be achieved inorganically, for example by increasing the oxygen content (i.e. the oxidizing potential) and/or pH (Stumm and Morgan, 1981). However, it is believed that most earth-surface ferromanganese deposits are induced by microbes, especially bacteria, which catalyze the oxidation of aqueous Mn^{2+} leading to the precipitation of extracellular Mn oxides (Nealson, 2006). Furthermore, some ferromanganese deposits have been recognized as stromatolites, i.e. as the result of the trapping and binding of sediment on microbial biofilms, as well as of metabolically-induced mineral precipitation. While recent examples of ferromanganese stromatolites are relatively rare (e.g. Sommers et al., 2002; Rossi et al., 2010), there

* Corresponding author. Tel.: +34 913495938; fax: +34 913495830.
E-mail addresses: r.lozano@igme.es (R.P. Lozano), crossi@geo.ucm.es (C. Rossi).

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are many known examples in the marine fossil record, especially in the Proterozoic (e.g. Planavsky et al., 2009).

Despite their alleged microbial origin, most sedimentary ferromanganese oxides (including stromatolites) hardly preserve fossil microbes, at least at the scale of observation of standard scanning electron microscopes (SEM) (e.g. Spilde et al., 2005). Besides, the simple presence of microbioforms in ferromanganese deposits does not prove a biogenic origin: the microbes could be accidental or have developed after the initial oxide precipitation. The paucity of microbial forms in ferromanganese oxides has led to some controversy regarding their origin (biogenic vs. inorganic), especially in rock varnish (Kuhlman et al., 2006). In some cases, the biogenic origin of modern Mn-rich crusts has been proved using molecular techniques (Northup et al., 2003; Northup et al., 2010). In other cases, the preservation of typical stromatolitic textures, such as laminated microdomes–botryoids, has been used in support of the biogenicity of Mn-oxide rich crusts. However, this criterion should be taken with caution, since similar textures can be produced by inorganic precipitation.

Recently, we have described the occurrence of ferromanganese stromatolites that preserve an exceptional abundance of fossil microbes (Rossi et al., 2010). The stromatolites formed in a cave (El Soplao) and present macroscopic features very similar to those observed in typical $CaCO_3$ stromatolites. The abundance of fossil microbial forms in freshly broken surfaces of unaltered Mn-oxide-rich material is extreme, and the excellent microbial preservation allows the SEM observation of external and internal morphological details of microbial cells. Besides, most of the microbes are completely embedded in the Mn-oxide-rich matrix and are commonly aligned parallel to the lamination of microdomes, indicating that the microbes were instrumental in the stromatolitic growth (Rossi et al., 2010).

A closer and more systematic examination of stromatolite samples from El Soplao cave has revealed that the diversity of microbial forms is greater than what we initially envisaged. To our knowledge, the El Soplao case represents the best example of microbial preservation in ferromanganese deposits described so far. In this paper we describe in detail the most abundant microbial forms fossilized in the El Soplao stromatolites, and we assign tentatively some of the morphotypes to specific microbial groups based on key diagnostic characteristics. Also, we discuss the causes of the excellent microbial preservation in the El Soplao stromatolites. Since some of the stromatolite samples show signs of diagenetic alteration, we also evaluate the impact of diagenesis on the preservation of bioforms in El Soplao. This exercise can help to elucidate why microbial fossils are so rare in other ferromanganese deposits such as rock varnish or ancient iron formations.

2. Methods

This study is based on the analysis of nine stromatolite samples from El Soplao cave. Using a diamond saw, those samples were cut into slabs oriented perpendicular to the growth banding. Based on textural differences, one or more growth bands were subsampled to be examined using a JEOL 6400 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometer. Some of the images, especially those at high magnification, were collected in a JEOL JSM-6335F field-emission SEM. Prior to SEM

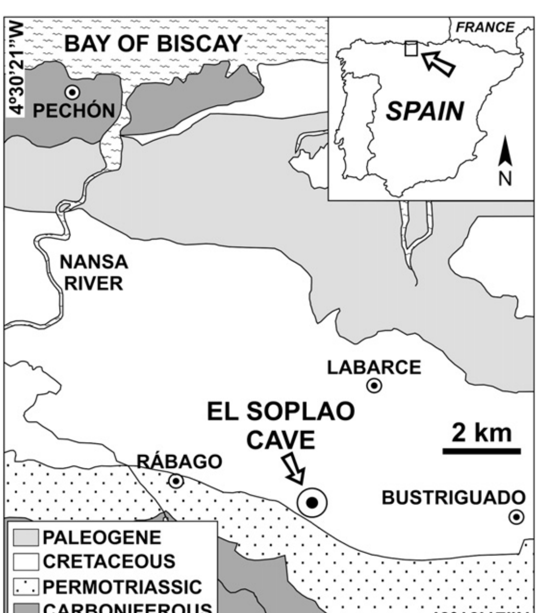

Fig. 1. Geological sketch map of northwestern Cantabria, showing the location of El Soplao cave.

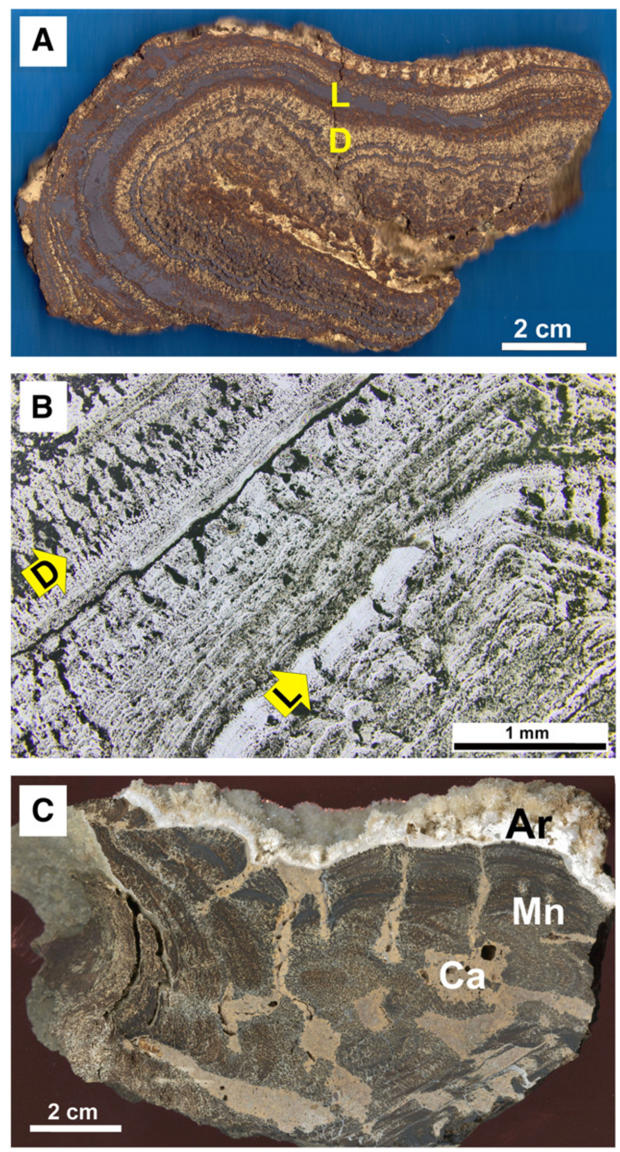

Fig. 2. Stromatolite slab (A) and reflected-light image of a polished thin section (B), both showing the alternation of laminar (L) and dendritic (D) layers. C: Cross section of an altered dendritic stromatolite, showing extensive replacement by inclusion-rich calcite ("Ca", orange colored), remnants of the original dendritic Mn-rich oxides ("Mn"), and a crust of fibrous aragonite ("Ar") that precipitated on the exposed surface of the stromatolite.