High enrichment of molybdenum in hypersaline microbial mats of Guerrero Negro, Baja California Sur, Mexico

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ABSTRACT

Analysis of modern microbial mats from the Guerrero Negro (Mexico) hypersaline region showed substantial Mo enrichment factors ($EF_{Mo} = (Mo/Al)_{sample}/(Mo/Al)_{background}$) ranging from 63 to 558, with an average molar ratio value of 297 ± 135. These enrichments are caused by authigenic biogeochemical processes, which are independent of the local abundance of Mo. Our calculations indicate that approximately a half of the Mo enrichment in the microbial mats may be explained by geochemical processes (e.g., coprecipitation with authigenic sulfides such as pyrite), while the remaining half are included in our operationally defined residual fraction. Generally, it is accepted that the elevated concentrations of Mo found in ancient anoxic sediments are a consequence of high biological production. Our calculations of EF_{Mo} based on concentrations of Mo and Al taken from the literature for different ancient environments (74 to 155 Ma) suggest that some of these elevated enrichments (EF_{Mo} of up to 1261) could have been the result of benthic microbial mats colonizing such environments. Considering that modern microbial mats may be used as proxies to those which have existed on Earth 3.5 billion years ago, the results obtained in this work suggest that these consortia of microorganisms may have represented an important sink for Mo during periods in Earth's history when microbial mats were more abundant. This characteristic leads us to propose high EF_{Mo} values, slight Fe impoverishments, low reactive Fe availability, and intermediate Degree of Pyritization (12 to 50%) as a new geochemical tool to indicate conditions associated with the presence of microbial mats in ancient hypersaline environments.

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1. Introduction

Studies of microbial communities thriving in extreme environments are important because they give insights into the early life imprints from the Earth's geologic past (Fenchel et al., 1998). Some of these microorganisms group themselves to form what are known as microbial mats, defined as accumulations of microorganisms that reach macroscopic dimensions (Des Marais, 1995). These mats are made up of heterotrophic and autotrophic organisms, which are organized into independent, vertical laminated layers (Pinckney and Paer, 1997. Modern microbial mats are considered to be analogs to those which existed on Earth approximately 3.5 billion years ago (Walter, 1976; Walsh and Lowe, 1985; Walsh, 1992) and are ideal for the study of microbial interactions (Van Gemerden, 1993), elemental cycles (Visscher and Van Gemerden, 1993; Paerl et al., 2001), and interactions between microorganisms and minerals (Visscher et al., 1998; Reid et al., 2000; Krumbein et al., 2003; Dupraz et al., 2004). Currently, the distribution of microbial

mats is not limited to extreme environments; however, the best coherent laminated ecosystems are formed under extreme conditions of temperature, salinity, and light intensity. For these reasons they can be found on the surface of sediments of fresh water springs, streams and thermal springs (Bauld, 1981; Jørgensen and Nelson, 1988) and, especially, in hypersaline environments (Van Gemerden et al., 1989). One of the most important examples of microbial mats thriving in hypersaline environments is found in the various evaporation ponds of the saltern of Guerrero Negro (GN). This hypersaline region, located in Baja California Sur, Mexico, presents adequate conditions for their formation and development (Canfield and Des Marais, 1993; Huerta-Diaz et al., 2011).

From a biogeochemical point of view, the microbial mats, such as those present in the evaporation ponds of GN, are characterized by the co-occurrence of the processes of dissimilatory sulfate reduction and photosynthesis, two reactions that are mutually exclusive from the thermodynamic point of view. The high rates of oxygenic photosynthesis (up to 1000 μM min^{-1}) and sulfate reduction (up to 34 μM min^{-1}) close to the mat–water interface (Canfield and Des Marais, 1993) create microgradients of dissolved oxygen, H$_2$S, dissolved inorganic carbon (DIC), and pH within the mat (Jørgensen and Des Marais, 1986b). The high rates of sulfate reduction are conducive to the production of

substantial amounts of H_2S, with concentrations that reach as much as 250 μM (Jørgensen and Des Marais, 1986a) at a pH of 7.4 (Des Marais, 1995). High concentrations of H_2S may imply the formation of large amounts of authigenic Fe sulfide minerals such as pyrite (and associated trace metals), amorphous FeS, mackinawite, etc. These high rates of sulfate reduction, however, do not reflect the quantity of authigenic pyrite which forms in the microbial mats of GN. Previous studies have reported low concentrations (0.21 to 11 μmol g^{-1}) of pyrite in the mats (Yévenes-Burgos, 2004; Huerta-Diaz et al., 2011) in relation to concentrations reported for anoxic (e.g., Black Sea: 0.15 to 197.5 μmol g^{-1}; Wijsman et al., 2001) and anoxic hypersaline (e.g., Orca Basin: 2 to 134 μmol g^{-1}, Hurtgen et al., 1999; Bannock and Tyro Basins: 28 to 178 and 79 to 149 μmol g^{-1}, respectively, Henneke et al., 1997) sediments. Furthermore, evidence that Fe limitation prevents pyrite formation in mats and underlying anoxic–sulfidic sediments from the saltern of GN was reported by Huerta-Diaz et al. (2011). These authors found very low concentrations of reactive Fe (10–33 μmol g^{-1}) relative to other sedimentary environments, a slight impoverishment of total Fe, intermediate degrees of pyritization (12–50%), and high (up to 100%) degrees of sulfidization (the percentage of reactive Fe bound to sulfides).

Previous studies of the influence of geochemical processes on the formation of authigenic pyrite and associated metals in reducing sedimentary environments have demonstrated that the degree of trace metal pyritization (DTMP) generally increases as the degree of pyritization (DOP) increases (Huerta-Diaz and Morse, 1992). For the particular case of Mo, an element sensitive to environmental changes (Morford and Emerson, 1999; Boothman and Coiro, 2009) and high affinity for pyrite under reducing conditions, it has been shown to be almost completely associated to this mineral, even at low DOP values in both, anoxic–sulfidic and anoxic–non-sulfidic sedimentary environments (Huerta-Diaz and Morse, 1992). In contrast, other metals such as Mn and Zn present moderate (Mn-DTMP: ~35%) to low (Zn-DTMP: <20%) association to pyrite (Huerta-Diaz and Morse, 1992). Additionally, Huerta-Diaz et al. (2011) found that in the microbial mats of GN the metals Cd, Pb, and Co were enriched 35 ± 10, 2.8 ± 1.6, and 2.2 ± 0.4 times the average values of the Earth's crust, respectively.

This work presents for the first time, vertical distributions of total concentrations of Mo and its speciation in two operationally defined fractions (HCl and HNO_3) in a microbial mat collected from the GN hypersaline region, an ecosystem where the formation of pyrite is limited by the availability of reactive Fe (Huerta-Diaz et al., 2011). Additionally, the elements Fe, Mn and Zn were also measured in the same geochemical fractions. The objectives of this study were to evaluate the geochemical distribution of Mo in a microbial mat from a hypersaline environment, and to use its anomalous concentrations as a potential biomarker of the past presence of this kind of consortium of organisms in the geologic past. Our results show that there is a substantial enrichment of Mo in the mats of GN, which is considerably higher than those reported for anoxic marine sediments. Our findings suggest that benthic microbial ecosystems from ancient hypersaline environments, which were more important in the geologic past, may have been important sinks for Mo. Finally, we propose that high enrichment values of Mo (>297), combined with slight impoverishment of Fe and intermediate degrees of pyritization (12–50%), can be used as geochemical indicators of reducing conditions associated with the presence of microbial mats in ancient hypersaline environments.

1.1. Study area

The GN salt evaporation zone (or saltern) is located on the west coast of the Baja California peninsula, in Mexico (Fig. 1), approximately 600 km from the Mexico-United States border. This area, part of the Vizcaino Biosphere Reserve and considered as one of the few protected hypersaline ecosystem regions in Mexico (López-Cortés, 1998), is concessioned to the Exportadora de Sal (ESSA) company. ESSA extracts

salt from ocean water via a series of evaporation and crystallization ponds (Fig. 1). The evaporation ponds have a water depth of approximately 1–1.5 m and are separated by dykes. Water from the Ojo de Liebre Lagoon (OLL), with a salinity of 47 psu, is pumped directly into pond 1 (Pumping station 3-A; Fig. 1) and from there the water is transferred to the rest of the ponds. In this way, the salinity increases with the number of the evaporation pond, with the last ponds (12 and 13) presenting salinities that may reach (and often exceed) 220 psu. The salinity within the individual ponds, however, is relatively constant. It is on the bottom of some of these ponds where conditions are suitable for the formation of microbial mats, particularly in pond 5 (Fig. 1), which presents a salinity of approximately 105 psu. The mats in this pond exist year round, with a formation/growing period of about 3 months (López-Cortés, 1998). The evaporation ponds are isolated from the town of GN (approximately 28 km from the town), a fact that severely limits the impact of anthropogenic trace metal contributions to the study area (Fig. 1).

2. Materials and methods

All the materials used in the collection and processing of samples were washed with phosphate-free soap, rinsed three times with distilled water, left for five days in a 5% HCl solution, and then rinsed another three times in deionized water (>18.2 MΩ cm^{-1}). Materials were dried at ambient temperature inside a laminar flow hood. All the reagents used in this work were reagent grade or better. Procedural blanks were routinely analyzed and included in each batch of samples, and all were found to be below their corresponding detection limit.

2.1. Sample collection

Microbial mat samples from pond 5 (labeled as 5 in Fig. 1) were collected in September of 2002 by a diver using a 7.5 cm interior diameter and 10 cm long acrylic tube. The microbial mat, with a thickness of 40 mm, was extracted from the tube using a hydraulic piston and then sectioned in the field every two mm with a nylon string, taking advantage of the mucilaginous structure of the mat. The 20 samples that were obtained from the mat core were stored in 50-ml plastic centrifuge tubes and kept in an ice chest at approximately 4 °C for less than two hours. They were then transferred to a freezer and kept at −20 °C until the time of analysis in the laboratory. Trace metal distributions previously reported in the literature (Co, Cu, Pb, Zn, Ni Cd, Fe, and Mn) have indicated minimum horizontal (data from six mat cores from GN; Yévenes-Burgos, 2004) and vertical (data from two mat cores collected from different evaporation ponds; Huerta-Diaz et al., 2012) variability. These results suggest that sample collection is not strongly dependent on number and distribution of mat samples. Results in this work, however, should be taken with precaution until a more detailed study is carried out to corroborate that our Mo results are consistent with the spatial distribution results obtained for other metals. An ongoing research is in the process to address this question. Additionally, nine superficial sediment samples were analyzed from the Ojo de Liebre Lagoon (Fig. 1), which were collected during a previous field trip in March 2000. Their description and collection procedures are described in Macías-Zamora et al. (2008). Finally, in March 2009, additional microbial mat samples from pond 5 were collected for the analysis of dissolved oxygen microprofiles. Herein, all metals associated to the sediments of OLL and the microbial mats will be referred to as trace metals (Me), regardless of their concentration level.

2.2. Extraction of total Fe, Mn, Zn, Mo, and Al

Total extractions of Fe, Mn, Zn, Mo, and Al (the latter used as a normalizing element) in the microbial mats of pond 5 and the sediments of OLL were carried out following the method of Carignan and Tessier (1988). For this method, approximately 0.5 g (dry weight of