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Microbial sulfur isotope fractionation in a Mars analogue environment at Rio Tinto, SW Spain

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Abstract

Abundant sulfate minerals are present on Mars hence sulfur isotopes are likely to be a key tool for the detection of any past or present life. To investigate the link between the activity of sulfate reducing microorganisms and sulfur isotope fractionation, we incubated sediments from a modern hyper-acidic, Fe-rich subareal environment at Rio Tinto, SW Spain. This site has been frequently used as a geochemical analogue of Mars. Sediments were sampled from the upper part of Rio Tinto (Marismilla) and the estuary (Moguer). Laboratory incubations were carried out at 30°C, using an artificial input solution with sulfate in excess [1]. Electron donors were provided by the natural substrate. Initial data indicate moderate biological sulfate reduction rates of between 5 and 90 $nmol \cdot cm^{-3} \cdot h^{-1}$ both in Marismilla and in Moguer, independent of the pH of the input solution. Sulfur isotope fractionation was extreme in the Moguer estuary, extending beyond the maximum of 47‰ predicted by the standard Rees model [2]. These data indicate that sulfur isotopes have a potential to be sensitive indicators of biotic activity in Martian environments containing sulfate minerals.

1. Introduction

The development of geochemical proxies to detect evidence of possible early life on Mars is important in preparation for future space missions, especially those that will return samples to Earth. Sulfur isotopes are likely to be a key tool for this purpose since abundant sulfate minerals on the surface of Mars [3], such as jarosite ($KFe^{3+}_3(SO_4)_2(OH)_6$), may record the activity of sulfur metabolizing microorganisms. Little is currently known about the sulfur isotope effects associated with sulfate reduction in hyper-acidic environments where jarosite and associated minerals are likely to have precipitated.

In the geological record ^{34}S depletions of >45 ‰ and up to 70‰ are typically found [3], but they can not been explained by previous work using pure bacterial cultures, and in natural populations from highly active microbial mats, where maximum depletions in ^{34}S of 46 ‰ have been observed. These latter data support the microbial sulfur fractionation activity model of Rees [2].

Here we investigate the relationship between sulfate reducing activity and sulfur isotope fractionation in a modern hyper-acidic environment at Rio Tinto, SW Spain. The geochemical characteristics of Rio Tinto are the consequence of modern weathering of pyrite-rich ores in the Iberian Pyritic Belt, and the metabolism of iron and sulfur compounds by chemolithotrophic microorganisms [4]. This results in a high concentration of ferric iron that is soluble under the acidic conditions generated by the biological activity. These conditions cause the precipitation of ferric-bearing minerals, including amorphous phases and hydronium jarosite [5].

Despite the fact that Rio Tinto, the microbial iron cycle is dominant, and high concentrations of ferric iron can inhibit microbial sulfate reduction, sulfate reducing bacteria have recently been isolated from Rio Tinto sediments suggesting their survival in local microniches.

2. Flow-through reactors.

Flow-through reactor experiments were performed using sediment samples from Río Tinto, from localities where the potential for sulfate-reducing activity was previously identified. Sediments were taken both from Marismilla, close to the source of the river, where acidic water from the river is mixed with waste waters from the village of Nerva, and from Moguer, in the estuarine part, where tidal effects create a dynamic environment, with mixing between hyperacidic and marine conditions.

Sediments were incubated in the laboratory at 30°C, using an artificial input solution with sulfate in excess using techniques developed by Stam et al. [1]. Experiments were performed at pH 7 and pH 3 with electron donors provided by the natural substrate. Duplicate reactors were incubated for a total of 10 weeks.

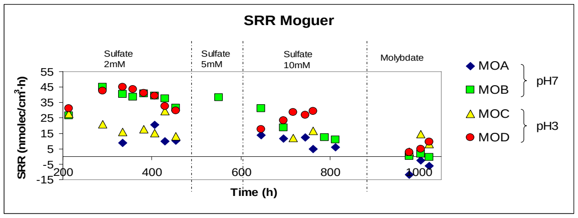

Figure 1: Sulfate reducing rates (SRR) in Moguer sediments. The reactors were incubated with an artificial input solution with a sulfate concentration of 2 mM, 5 mM and 10 mM. At the end of the experiment, with a mixed sulfate (10 mM) molybdate (10 mM) solution was added in order to inhibit the sulfate reducing prokaryote metabolism. Two duplicate reactors (MOA and MAB) were incubated with an input solution of pH 7 and another two (MOC and MOD) at pH 3.

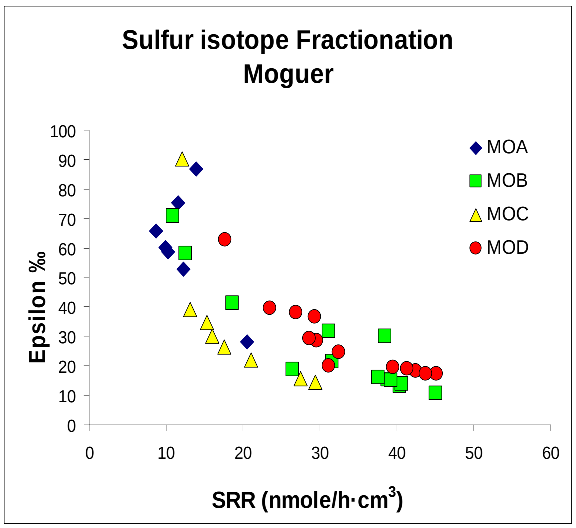

Figure 2: Relation between sulfate reducing rates (SRR) and sulfur isotope fractionation (Epsilon), observed in Moguer estuarine site. Two replicate reactors were incubated with an artificial inflow solution at pH 7 (MOA and MOB) and two duplicate reactors were incubated at pH 3 (MOC and MOD)

Initial data indicate moderate sulfate reduction rates of between 5 and 90 nM cm^{-3} h^{-1} in the Marismilla and between 5 and 45 nM cm^{-3} h^{-1} in Moguer (Figure 1), at both pH 7 and pH 3. Although the input pH seems not to have a major influence in reactor behavior, active buffering has been observed inside the reactors producing close to neutral pH with sulfate-reducing activity (Figure 2). The pH is maintained around 5 when we inhibited the sulfate reducing activity. At the end of the experiment, a molybdate solution was added, in order to inhibit the sulfate reducing prokaryote metabolism and contrast if there were some possible abiotic effect in the sulfate reducing rates or in the ^{34}S isotope fractionation.

Extreme sulfur isotope fractionation (ε [1, 6]) has been observed in the samples from the Moguer estuarie with an inverse correlation between sulfate reducing rates and isotope fractionation, which extends beyond the maximum value of 46 ‰ predicted by the Rees model[2] (Figure 2).

3. Conclusions

After the incubation of sediments from the specific areas of Rio Tinto, using flow-through reactors, it was established that:

-Bacterial sulfate reduction occurs in Rio Tinto sediments with an excess of sulfate and the absence of ferric ion.

-Similar sulfate reduction rates and isotope fractionation occur with inflow solutions of pH 7 and pH 3. Moreover, it was observed that the pH was buffered close to neutral values in the reactors.

-Extreme isotope fractionation (> 70‰) occurs in Moguer estuarine sediments, which could support the Brunner and Bernasconi model for sulfate reducer bacteria metabolism [7]. Alternatively the data could be explained by several cycles of reduction and re-oxidation of sulfate inside the reactors.

These data indicate that sulfur isotopes have the potential to be sensitive indicators of biotic activity using sulfate minerals in a Martian environment.

4. Acknowledgements

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5. References

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