

Characterisation of the bio-mineralogical and isotope geochemical signatures of past life in a Mars analogue environment of Rio Tinto, SW of Spain.

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Abstract

Iron-rich sulfate minerals are present on Mars hence sulfur, oxygen and iron isotopes could be a key tool for the detection of any past or present life. Experiments with flow through reactors and enrichment cultures have been conducted to investigate the link between the activity of microbial communities and sulfur, oxygen and iron isotope fractionation in Martian like minerals. Sediments from a modern hyper-acidic, Fe-rich subareal environment at Rio Tinto, SW Spain were used in the experiments. 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]. Initial data from the flow through reactor experiments indicate an extreme sulfur isotope fractionation in the Moguer estuarine part, extending beyond the maximum of 47‰ predicted by the standard Rees model [2]. These data suggest that, at least, sulfur isotopes have a potential to be sensitive indicators of biotic activity in Martian environments that contain sulfate minerals.

1. Introduction

The development of geochemical proxies for possible early life on Mars is important in preparation for future space missions, especially those that will return samples to Earth. We are developing an approach to evaluate the presence of a biosphere on Mars through an integrated mineralogical, chemical and stable isotope study with Rio Tinto material as a terrestrial analogue of Mars. The extreme geochemical characteristics of Rio Tinto water and sediment 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]. These conditions result in the precipitation of ferric-bearing and sulfate-bearing minerals, including jarosite (KFe³⁺₃(SO₄)₂(OH)₆), goethite (Fe³⁺O(OH)) and hematite (Fe₂O₃), minerals that have been reported widely in Hesperian Martian deposits [5]. This multi-discipline study (microbiology, mineralogy, S-Fe-O isotopes and trace-element) will characterize the biogeochemical and bio-mineralogical response to the presence of life.

2. Flow-through reactors.

Flow-through reactor experiments were performed using sediments from Río Tinto. The sediments were collected from localities where the potential for sulfate-reducing activity was previously identified. Sediments were taken 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 following 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. 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 $^{34/32}S$ and $^{18/16}O$ isotope fractionation.

3. Batch cultures.

Enrichment culture experiments were performed with Rio Tinto sediments for sulfate and iron reducer microorganism. Sediments were again taken both from Marismilla, close to the source of the river, and from Moguer, in the estuarine part, The sulfate reducer enrichment culture experiments were performed at 30°C, pH 7 with lactate and acetate as electron donors. The next experiments in this project will be enrichment cultures for sulfate reducers at pH 4 and iron reducer cultures at pH 2.5 with glycerol as electron donor.

4. Results

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). We detect moderate sulfate reduction rates between 5 and 90 nM cm⁻³ h⁻¹ in Rio Tinto Sediments. Although the input pH does not seem to have a major influence in the reactors behavior, active buffering has been observed inside the reactors producing close to neutral pH with sulfate-reducing activity. The pH remains around 5 when the sulfate reducing activity has been inhibited.

The data from the batch cultures are still in process.

5. Conclusions

After the incubation of sediments from the source and estuarine areas of Rio Tinto using flow-through reactors, they were observed 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, these data could be explained by several cycles of reduction and re-oxidation of sulfate inside the reactors.

These data suggest that, at least, sulfur isotopes have the potential to be sensitive indicators for biotic activity in Martian environments that contain sulfate minerals.

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5. References

[1] Stam, M.C., et al., Sulfate reducing activity and sulfur isotope fractionation by natural microbial communities in sediments of a hypersaline soda lake (Mono Lake, California). Chemical Geology, 2010. **278**(1-2): p. 23-30.

[2] Rees, C.E., A steady-state model for sulphur isotope fractionation in bacterial reduction processes. Geochimica et Cosmochimica Acta, 1973. **37**(5): p. 1141-1162.

[3] Habicht, K.S. and D.E. Canfield, Isotope fractionation by sulfate-reducing natural populations and the isotopic composition of sulfide in marine sediments. Geology, 2001. **29**(6): p. 555-558.

[4] Amils, R., et al., Extreme environments as Mars terrestrial analogs: The Rio Tinto case. Planetary and Space Science, 2007. **55**: p. 370-381.

[5] Fernández-Remolar, D., et al., The Río Tinto Basin, Spain: Mineralogy, sedimentary geobiology, and implications for interpretation of outcrops rocks at Meridiani Planum, Mars. Earth and Planetary Science Letters, 2005. **240**: p. 149-167.

[6] Canfield, D.E., Isotope fractionation by natural populations of sulfate-reducing bacteria. Geochimica et Cosmochimica Acta, 2001. **65**(7): p. 1117–1124.

[7] Brunner, B. and S.M. Bernasconi, A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. Geochimica et Cosmochimica Acta, 2005. **69**(20): p. 4759-4771.