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

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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. Sulphur isotopes are likely to be a key tool for this purpose since abundant sulphate minerals on the surface of Mars [1], such as jarosite ($KFe^{3+}{}_3(SO_4)_2(OH)_6$), may record the activity of sulphur metabolizing microorganisms. Little is currently known about the sulphur isotope effects associated with sulphate 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 [6], but they can not been explained by previous work in pure bacterial cultures, and in natural populations from highly active microbial mats, where maximum depletions in ^{34}S of 46 ‰ had been observed, supporting the Rees model in microbial sulphur fractionation activity.

Here we investigate the relationship between sulphate reducing activity and sulphur isotope fractionation in a modern hyper-acidic environment at Rio Tinto, SW Spain [2,3,4]. 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 sulphur compounds by chemolithotrophic microorganisms. 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.

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

Flow-through reactor experiments were performed using sediment samples from Río Tinto, from localities where the potential for sulphate-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^{o}C, using an artificial input solution with sulphate in excess using techniques developed by Stam et al. [5]. Two sets of 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. Initial data indicate moderate sulphate 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, at both pH 7 and pH 3. Although the input pH seems not to have a major influence in reactor behaviour, active buffering has been observed inside the reactors producing close to neutral pH with sulphate-reducing activity. The pH is maintained around 5 when we inhibited the sulphate reducing activity.

Extreme sulphur isotope fractionation has been observed in the Moguer estuarine, where has been recorded an inverse correlation between sulphate reducing rates and isotope fractionation, which extends beyond the maximum value of 46‰ predicted by the Rees model [7].

We expect our results to further help in the targeting of sampling sites in the search for traces of life on Mars.

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