

Out of this world! Sulfur cycling in Rio Tinto, Andalucia, Spain: an Earth analogue for extraterrestrial environments

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University of Stirling, Biological and Environmental Sciences
In partnership with **University of Glasgow, Scottish Universities Environmental Research Centre**
Universidad de Huelva, Departamento Geología

Supervisory Team

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Key Words

1. Isotope biogeochemistry; sulphate minerals; acid mine drainage

Overview

The Rio Tinto is an Acid Mine Drainage (AMD) system in southwestern Spain. Its characteristic red colour (Figure 1) is derived from iron dissolved in its acidic waters. The area has been mined for metals since the Bronze Age. However, there is evidence that the river waters have been naturally acidic for at least two million years. Hence, Rio Tinto offers the unique opportunity to compare the influence of modern mining and toxic heavy metal pollution on the biogeochemical sulphur cycle and, in turn, the influence of microorganisms in sequestering toxic heavy metals in the form of sulphate and iron oxide minerals. Additional interest comes from the field of astrobiology: Rio Tinto's extreme acidic environment serves as an analogue for potentially habitable environments on Mars and Jupiter's icy moon Europa.

In order to understand microbial sulphur cycling at Rio Tinto, we will investigate S and O isotopes in sulphates from modern and ancient sediments, as well as S, H, O and C isotopes on water samples. This project will also lay the foundations for a follow-on project in which we would like to add Fe and Mg

isotope analyses to understand more about the formation pathway of sulphate minerals.



Figure 1. The Rio Tinto's red colour stems from iron dissolved in its acidic waters.

Oxidation, thought to be biologically mediated, of pyritic ore bodies by groundwaters in the source area of the Rio Tinto generates headwaters enriched in sulfuric acid and ferric iron. Seasonal evaporation of river water drives precipitation of hydronium jarosite and schwertmannite, while (Mg,Al,Fe³⁺)-copiapite, coquimbite, gypsum, and other sulfate minerals precipitate nearby as efflorescences where locally variable source waters are brought to the surface by capillary action. During the wet season, hydrolysis of sulfate salts results in the precipitation of nanophase

goethite. Holocene and Plio-Pleistocene terraces show increasing goethite crystallinity and then replacement of goethite with hematite through time. Early and later diagenesis are recorded in terrace deposits formed about one thousand and two million years ago, respectively. These sedimentary deposits formed under physical and chemical conditions comparable to those of modern Rio Tinto sediments. As part of the research and training proposed here, samples shall be collected during two field trips from modern deposits and million year old deposits.

Methodology

The student will be based in the Biological and Environmental Sciences division at the University of Stirling. We will collect both modern and ancient sulphate minerals and modern water samples during two field trips to the Rio Tinto – one during the dry season, another one during the wet season. The rock and water samples will be microscopically and geochemically characterised in Stirling. S and O isotopes on sulphates, as well as S, H, O and C isotopes on water samples, will be analysed at the Scottish Universities Environmental Research Centre (SUERC) in East Kilbride. Stirling and East Kilbride are within easy commuting distance of each other, and short-term accommodation is available at SUERC.

Timeline

Year 1: Literature review, Rio Tinto field trip 1, geochemical sample characterisation.

Year 2: Isotopic analysis of samples from field trip 1, paper 1, Rio Tinto field trip 2, geochemical sample characterisation.

Year 3: Isotopic analysis of samples from field trip 2, international geochemistry conference (Goldschmidt), paper 2.

Year 4: Thesis, further papers.

Training & Skills

Some of the [Natural Environment Research Council's most wanted skills](#) will be developed through this project, in particular multi-disciplinarity and fieldwork. Specific skills include: Development of and planning for detailed sampling programmes in Spain; Sample collection and storage protocols (both abiological and microbial); Scanning electron microscopy and Energy-dispersive X-ray spectroscopy; X-ray diffraction; X-

ray fluorescence spectroscopy; Mössbauer spectroscopy; Principles and practice of stable isotope geochemistry, including sample precipitation protocols; use of vacuum extraction systems; dual inlet and continuous flow mass spectrometry; *in situ* laser extraction; Training and experience in national and international conference presentations; Preparation and submission of papers to international, peer-reviewed journals.

References & Further Reading

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