Source to Sink: Heavy Metals in the Tinto-Odiel Mining Region

Project Highlights:

- Tracing acid mine drainage from source to sink in the Iberian Pyrite Belt, Spain.
- Assessing the resource potential of acid mine drainage from massive sulfide deposits.
- Investigating the final sink of acid mine drainage pollutants in the Huelva estuary and how stable they might be given future projected sea-level rise.

Overview:

The Iberian Pyrite Belt in Spain is one of the largest metallogenetic massive sulfide regions in the world, with original reserves estimated to have contained >1700 Mt of sulfide ores (Leistel et al., 1997). The local watershed is severely affected by acid mine drainage (AMD), whereby extreme Fe concentrations colour large sections of the Odiel and Tinto Rivers red.

AMD is rich in toxic heavy metals (e.g., Tl, Cu), and is a severe environmental problem (Canovas et al., 2022; Viers et al., 2023). Moreover, many elements of economic interest are released into the environment in AMD (e.g., rare earth elements, REE; Léon et al., 2023). Therefore, AMD is a potential secondary source of these elements. However, the sources, transport pathways, and sinks of metals derived from AMD remain poorly understood. The Tinto-Odiel region has been intensively mined for 4500 years, and it is the ideal environment to study AMD. This project will use REE patterns and the stable isotope fingerprints of Tl and Cu to trace these metals from Source to Sink in the Tinto-Odiel mining region. This will aid pollution tracking, future AMD resource estimation and also help assess whether sinks for pollutants will remain stable given future sea-level rise predictions.

Figure 1: Photographs from the Tinto-Odiel Mining Region. Left: Corta Atalaya open-pit mine, the largest open-pit mine in Europe. Right: Acid Mine Drainage colours the Tinto River dark red.

Key research questions:

This project aims to answer the following key research questions:

1) What are the sources of toxic heavy metals and REE in AMD?

2) What are the transport pathways of toxic heavy metals within the drainage basin?

3) What are the ultimate sinks for heavy metals and REE (e.g., in the Huelva estuary), and how stable are this sinks given future projected sea level rise?

Methodology:

Rare Earth Element patterns can be utilised as a distinctive source tracer in the AMD environment (Léon et al., 2023). For example, cerium (Ce) and europium (Eu) anomalies are inherited in rock leachates. Analysis of REE patterns will be carried out on samples collected from throughout the watershed, Huelva estuary, and Gulf of Cadiz. Preconcentration of high salinity samples will be carried out using a SeaFAST at UCL. REE concentration analyses will be carried out by quadrupole inductively coupled plasma mass spectrometry (ICP-MS)

Stable isotope ratios are another tool to identify sources and/or transport pathways. Different source rocks may have distinctive source isotope compositions, while biogeochemical processes occurring during transport can drive isotopic fractionation (e.g., Packman et al., 2023). This project will analyse the isotopic compositions of Cu and Tl by multiple collector ICP MS (MC-ICP-MS) in state-of-the-art metal-free clean laboratories at UCL and Imperial College London.

Possible timeline:

Year 1: Initial induction and training at UCL. Training in analytical methods and literature review. At this stage, the student will have the opportunity to contribute to project planning, with some flexibility on the final focus depending on interest. Second half of Y1: Sampling campaign with the University of Huelva team in Spain and method validation.

Year 2: Cu and Tl isotope analyses on diverse sample types from the Tinto and Odiel mining region, as defined during the project planning phase and collected during Y1 sampling campaign. Preparation of manuscripts for publication.

Year 3: REE element analysis on diverse sample types. Opportunity to attend an international conference to present project findings. Writing of manuscripts and PhD thesis.

Training and skills:

TARGET researchers will participate in a minimum of 40 days training over the 3.5 years of study composed of:

- an annual one-week workshop dedicated to their year group, and tailored to that cohort's needs in terms of skills development – *for the first three years of their study*;
- an annual all-TARGET workshop with cross-year interactions, advanced training and opportunities to specialise in particular areas – *all years of study*;
- a number of one-day workshops;
- additional online events and in-person workshops attached to relevant conferences.

In addition to the TARGET mandatory training the student will receive project-specific training in laboratory techniques. They will join a 60+ cohort of PhD students in a vibrant department and will be exposed to wide range of research topics in the field of Earth Sciences. They will have access to UCL's doctoral training, including academic writing, entrepreneurship, and presentation skills. They will also be trained to teach and will gain experience as a demonstrator in our department. The student will join the UCL Earth Resources Centre and be encouraged to attend and contribute to group meetings, seminars and-networking events.

Partners and collaboration:

Cu isotope analyses and REE concentration analyses will be carried out at UCL. Tl isotope analyses will be carried out at Imperial College London. As such, the student will be an active part of two world-leading isotope geochemistry groups (MAGIC, Imperial College London and LOGIC, UCL), with access to support from leading academics and a diverse group of PhD students and early career researchers.

Project support from the Environmental Mineralogy and Geochemistry Group at the University of Huelva, who have extensive expertise in Acid Mine Drainage, is also critical to the success of the project.

Requirements: Applicants should ideally have a MSci or MSc degree in Earth Science, Geology, Environmental Science, Chemistry, or related subject, with an interest in Geochemistry and Lab work.

Further reading:

Cánovas, C.R., Basallote, M.D., Macías, F., Olías, M., Pérez-López, R. and Nieto, J.M., 2022. Thallium in environmental compartments affected by acid mine drainage (AMD) from the Iberian Pyrite Belt (IPB): From rocks to the ocean. *Earth-Science Reviews*, p.104264.

Leistel, J.M., Marcoux, E., Thiéblemont, D., Quesada, C., Sánchez, A., Almodóvar, G.R., Pascual, E. and Saez, R.J.M.D., 1997. The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt Review and preface to the Thematic Issue: Review and preface to the Thematic Issue. *Mineralium deposita*, *33*, pp.2-30.

León, R., Macías, F., Cánovas, C.R., Millán-Becerro, R., Pérez-López, R., Ayora, C. and Nieto, J.M., 2023. Evidence of rare earth elements origin in acid mine drainage from the Iberian Pyrite Belt (SW Spain). *Ore Geology Reviews*, p.105336.

Packman, H., Little, S.H., Nieto, J.M., Basallote, M.D., Pérez-López, R., Coles, B., Kreissig, K., van de Flierdt, T. and Rehkämper, M., 2023. Tracing acid mine drainage and estuarine Zn attenuation using Cd and Zn isotopes. *Geochimica et Cosmochimica Acta*, *360*, pp.36-56.

Viers, J., Freydier, R., Grande, J.A., Zouiten, C., Marquet, A., Delpoux, S., Santisteban, M., Pokrovsky, O.S., Fortes, J.C., Davila, J.M. and Sarmiento, A., 2023. The use of copper isotopes for understanding metal transfer mechanisms within the continuum mine—river—dam (Huelva Region, Spain). *Environmental Science and Pollution Research*, *30*(18), pp.53275-53294.

Further details:

LOGIC group, University College London:

https://www.ucl.ac.uk/london-geochemistry-isotope-centre/london-geochemistry-isotope-centre

https://www.ucl.ac.uk/earth-sciences/people/academic/dr-susan-little

https://www.ucl.ac.uk/earth-sciences/people/academic/dr-katie-mcfall

MAGIC group, Imperial College London:

https://www.imperial.ac.uk/earth-science/research/research-groups/magic/

https://www.imperial.ac.uk/people/markrehk

Environmental Mineralogy and Geochemistry Group, University of Huelva:

http://www.uhu.es/rensma/en/introduction-mga/

UCL Earth Resources Centre:

https://www.ucl.ac.uk/earth-sciences/research/research-groups/earth-resources-centre