The Bottom-Up Ocean: Do marine sediments control ocean chemistry?

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In this project you will use new and exciting experimental and analytical approaches to investigate how minerals in marine sediments help control the concentration and isotopic composition of rare earth elements (REE) in sediment porewaters and seawater. This is important because REE concentrations and isotopes in the marine environment are used as powerful tracers of biogeochemical processes that can shed light on the Earth system, including the global carbon cycle and climate change. A better understanding of the controls on REE concentrations and isotopes will therefore improve our interpretation of REE signals and how we understand and sustainably coexist with our planet.

Introduction

The rare earth elements (REE) are delivered to the oceans via a range of sources, including rivers, and end up being deposited into a number of sinks, including marine sediments. For many metals, marine sediments provide the most important sink, and sediment minerals provide the most important sedimentary hosts. In particular, iron and manganese oxides are able to scavenge metals from porewaters and the overlying water column and lock up these metals over long timescales. As the sediments are buried and subducted, these metals eventually resurface on the continents and are once again weathered and transported back to the oceans by rivers. Over shorter timescales, iron and manganese oxides can age and transform, and new research shows that during transformation these minerals can release some of their metal inventory. In particular, research from our group shows that as the manganese oxide birnessite ages and transforms it can release some of its metal content into porewaters, which potentially provides an important benthic flux of metals into seawater (Atkins et al., 2016).

While it is clear for some metals that the aging and transformation of birnessite might have a drastic impact on metal concentrations and isotopic compositions in porewaters and seawater, whether and to what extent mineralogical processes control the cycling and reactivity of REE is still unclear and a number of key questions remain unanswered:

Are REE released from sediment minerals as they age and transform?

Are REE released from sediment minerals as they partially dissolve?

How does the uptake and release of REE from sediment minerals effect REE concentrations and isotopic compositions in porewaters and seawater?

Does the presence of sedimentary organic matter affect the behaviour of REE?

In this project you will investigate the behaviour of REE during the aging, transformation and partial reductive dissolution of iron and manganese oxides, using a combined experimental and analytical approach, with the opportunity to use state-of-the-art nanoscale probes at Diamond Light Source synchrotron and stable isotope facilities at the Keck Collaboratory for Plasma Spectrometry at Oregon State University.

Objectives

In this project you will:

1. Prepare iron and manganese oxide minerals in the laboratory and dope these with REE to produce synthetic samples that are analogous to iron and manganese oxides found in marine sediments.

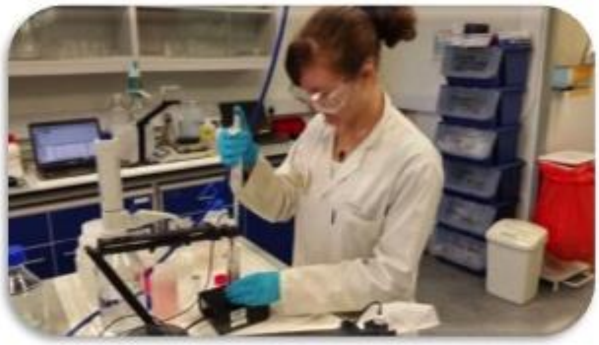
2. Age, transform and partially reductively dissolve these metal-mineral samples in laboratory experiments designed to simulate the diagenesis of marine sediments. During diagenesis you will take samples of the experimental solution and the metal-mineral solids to form a time series.

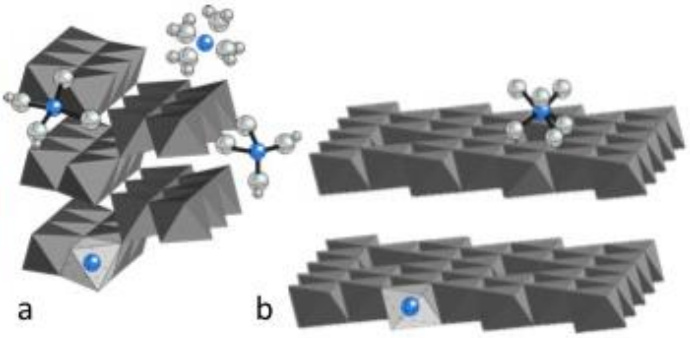
3. Analyse the solution and solid time series samples with a suite of state-of-the-art geochemical techniques, including X-ray diffraction, electron microscopy and mass spectrometry, to determine the amount of metals that are released into solution vs the amount that are retained in the remaining mineral products.

4. Analyse the solid time series samples in detail using nanoscale spectroscopy and microscopy probes at Diamond Light Source, to determine how and why the metals are released or retained in the remaining mineral products, and how sedimentary organic matter effects the release or retention process.

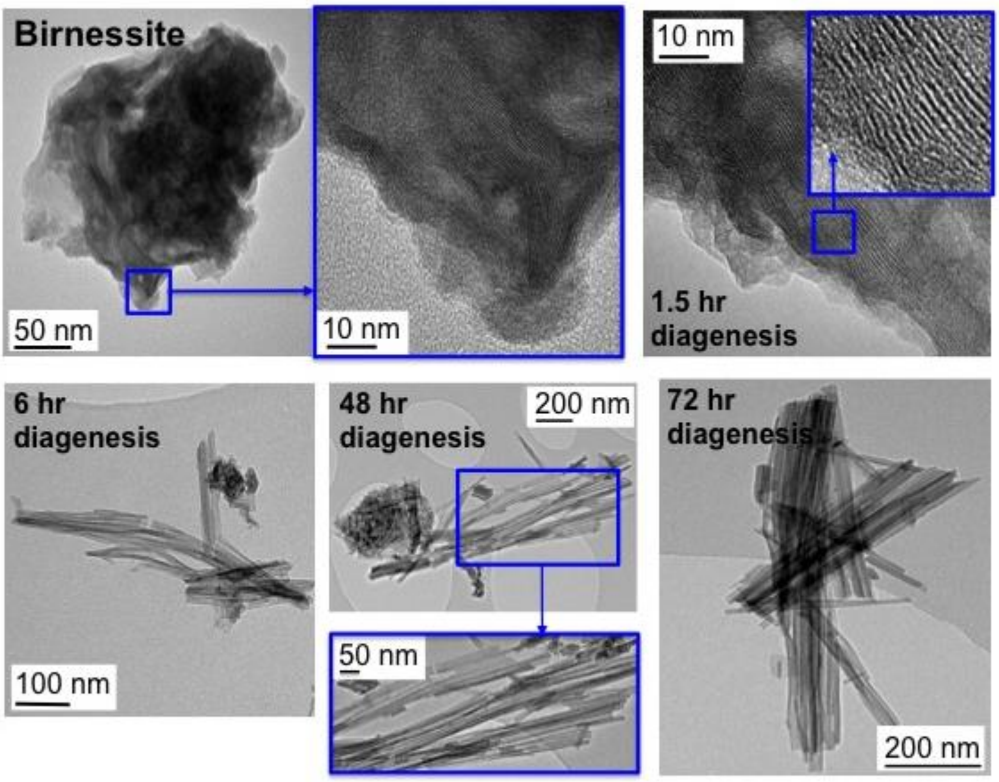
5. Analyse the solution and solid time series samples using state-of-the-art multi collector mass spectrometry to determine the isotopic composition of the metals in both the solution and solid phases.

6. Investigate metal concentrations and isotopic compositions in a suite of natural iron- and manganese-rich sediments deposited in a range of diagenetic regimes, to relate the experimental results to real-world environments.





PhD student in the Cohen Geochemistry Labs preparing an iron oxide mineral doped with nickel, another important tracer of biogeochemical processes. On the right you can see the structures of two of the most important iron and manganese oxides in marine sediments – ferrihydrite (a) and birnessite (b).



Electron microscopy images of birnessite aging and transforming – after 1.5 hours of experimental diagenesis you can see the layers of the birnessite mineral becoming rumpled, before the growth of long needle-like fibers. During the aging and transformation process nickel in the birnessite is lost to solution, and in sediments this process may provide an important benthic flux of nickel into seawater (see Atkins et al., 2016).

Training

You will work under the supervision of Prof Caroline Peacock within the Cohen Geochemistry Group at Leeds, and, depending on your interests, you will have the opportunity to work with Prof Brian Haley at Oregon State University, who is expert in the oceanic cycling of REE and the analysis of REE stable isotope compositions.

You will receive specialist scientific training in state-of-the-art biogeochemical, mineralogical, experimental and analytical techniques and computational geochemical modelling. Specifically you will have the opportunity to analyse your samples using world-leading synchrotron spectroscopy and microscopy techniques at the Diamond Light Source.

In addition you will be trained in a wide variety of key transferable skills within the *PANORAMA* NERC DTP, from computer programming and modeling, to media skills and public outreach. You will also be encouraged and supported to present your research at national and international scientific conferences, for example at Goldschmidt, the premier geochemistry conference held in Hawaii in 2022.

Diamond Light Source synchrotron in Oxfordshire UK, with two of the beamline scientists helping to set up nanoscale analyses of our solid time series samples (all images from diamond.co.uk).

Eligibility

You must satisfy the requirements to register as a doctoral student at the University of Leeds, which involves holding an appropriate Honours, Diploma or Masters Degree and having passed the appropriate English language tests. Applications are invited from graduates who have, or expect to gain, a good degree in chemistry, environmental science, geology, materials science, or another relevant science discipline. Relevant Masters level qualifications are welcomed. You should have a good command of both written and spoken English.

Background Reading (copies available on request)

On the biogeochemical cycling of metals and REE in the oceans:

- **Homoky W.B.**, Weber T., Berelson W.M., Conway T.M., Henderson G.M., van Hulten M., Jeandel C., Severmann S. and Tagliabue A. (2016) Quantifying trace element and isotope fluxes at the ocean-sediment boundary: A review. *Philosophical Transactions of the Royal Society A* 374, 20160246. https://doi.org/10.1098/rsta.2016.0246

- Abott A.N., **Haley B.A.**, McManus J. and Reimers C.E. (2015) The sedimentary flux of dissolved rare earth elements to the ocean. *Geochimica et Cosmochimica Acta* 154, 186-200. https://doi.org/10.1016/j.gca.2015.01.010

- **Haley B.A.**, Du J., Abbott A.N. and McManus J. (2017) The impact of benthic processes on rare earth element and neodymium isotope distributions in the oceans. *Frontiers in Marine Science* https://doi.org/10.3389/fmars.2017.00426

- Abbott A.N., Löhr S. and Trethewy M. (2019) Are clay minerals the primary control on the oceanic rare earth element budget? *Frontiers in Marine Science* https://doi.org/10.3389/fmars.2019.00504

On the aging and transformation of birnessite and release or retention of metals:

- Atkins A.L., Shaw S., **Peacock C.L.** (2014) Nucleation and growth of todorokite from birnessite: Implications for trace-metal cycling in marine sediments. *Geochimica et Cosmochimica Acta* 144, 109-125. http://dx.doi.org/10.1016/j.gca.2014.08.014

- Atkins A.L., Shaw S., **Peacock C.L.** (2016) Release of Ni from birnessite during transformation of birnessite to todorokite: Implications for Ni cycling in marine sediments. *Geochimica et Cosmochimica Acta* 189, 158-183. http://dx.doi.org/10.1016/j.gca.2016.06.007

- Wu Z., **Peacock C.L.**, Lanson B., Yin H., Zheng L., Chen Z., Tan W., Qiu G., Liu F. and Feng X. (2019) Transformation of Co-containing birnessite to todorokite: Effect of Co on the transformation and implications for Co mobility. *Geochimica et Cosmochimica Acta* 246, 21-40. https://doi.org/10.1016/j.gca.2018.11.001