Marine Micronutrient Cycling between Sediments and Seawater: What controls the concentration and isotopic composition of micronutrient trace metals in the global oceans?

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In this project you will use new and exciting experimental and analytical approaches to investigate how marine sediments help control the concentration and isotopic composition of micronutrient trace metals in seawater. This is important because trace metals are required by photosynthetic algae, and their abundance in seawater is intimately linked to the drawdown of atmospheric CO2 and the regulation of global climate.

Introduction

Micronutrient trace metals 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 the overlying water column and from sediment pore-waters and lock up 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. Moreover iron and manganese minerals can undergo partial dissolution as sediments become sub-oxic, which may also lead to a release of their metal load. In particular new research from our group shows that as the manganese oxide birnessite ages and transforms it can release up to half of its nickel content (Atkins et al., 2016). Nickel is an important micronutrient in seawater because it is required for photosynthesis and thus nickel concentrations and isotopic compositions in sediments and seawater might both influence and reflect modern and ancient primary productivity.

While it is clear for nickel that the aging and transformation of birnessite might have a drastic impact on nickel cycling, a number of important questions are still unclear:

Is nickel released from other sediment minerals as they age and transform?

Is nickel released from marine sediment minerals as they partially dissolve?

Are other micronutrient trace metals like cobalt, copper and zinc released from marine sediment minerals as they age and transform, and undergo partial dissolution?

How does the presence of sedimentary organic matter affect the uptake and release of micronutrient trace metals?

Does the uptake and release process impart an isotopic signal to micronutrient trace metals that we can use to track the global cycling of these important elements in the oceans?

In this project you will investigate the behaviour of nickel and other micronutrient trace metals 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 in the Isotope Geochemistry and Cosmochemistry Group at ETH Zurich.

Objectives

In this project you will:

1. Prepare iron and manganese (hydr)oxide minerals in the laboratory and dope these with nickel and other metals to produce synthetic samples that are analogous to iron and manganese (hydr)oxides found in marine sediments.

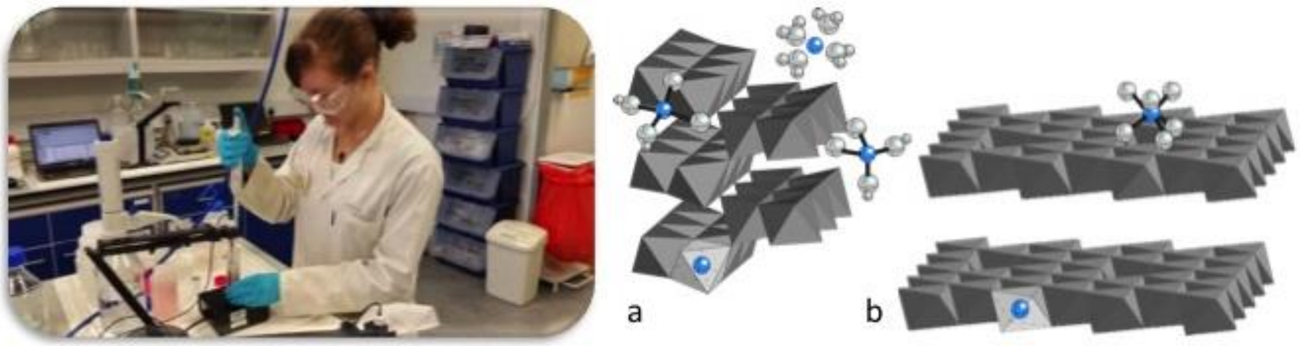
2. Age, transform and partially reductively dissolve these metal-mineral samples in laboratory experiments designed to simulate the diagenesis of marine sediments. During diagenesis you will take samples of the experimental solution and the metal-mineral solids to form a time series.

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

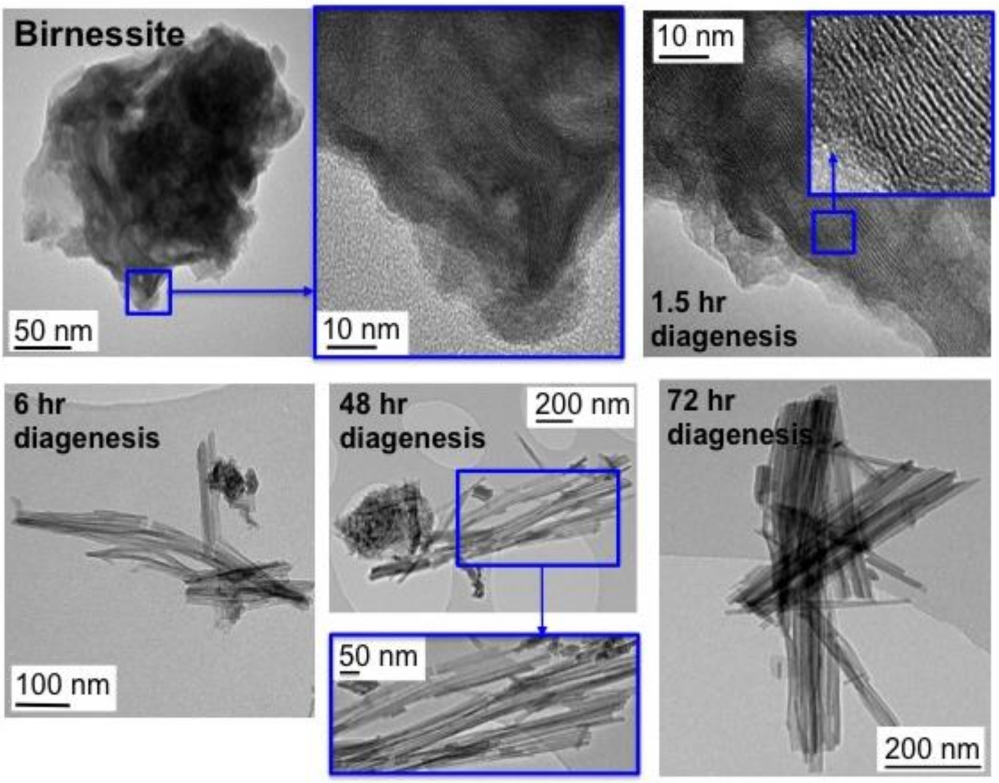
4. Analyse the solid time series samples in detail using new nanoscale spectroscopy and microscopy probes at Diamond Light Source, to determine how and why the metals are released or retained in the remaining mineral products, and how sedimentary organic matter effects the release or retention process.

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 (hydr)oxide mineral doped with cobalt, another important micronutrient trace metal. On the right you can see the structures of two of the most important iron and manganese (hydr)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 up to half the nickel in the birnessite is lost to solution (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 Dr Susan Little at University College London and Prof Derek Vance at ETH Zürich, who are experts in the oceanic cycling of micronutrient trace metals and the analysis of metal stable isotope compositions in experimental and real-world samples.

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 Barcelona in 2019 and Hawaii in 2020.

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. The applicant should have a good command of both written and spoken English.

Background Reading (copies available on request)

On the biogeochemical cycling of micronutrient trace metals in the oceans:

- Anbar A.D. and Knoll A.H. (2002) Proterozoic ocean chemistry and evolution: A bioinorganic bridge? *Science* 297, 1137-1142.
- Bruland K.W., Lohan M.C. and Middag R.H. (2014) Controls of trace metals in seawater. In: Mottl M.J., Elderfield H. (Eds) *Treatise on Geochemistry*, 2nd edn, vol 8, pp 19–51.
- Morel F.M.M., Milligan A.J. and Saito M.A. (2014) Marine bioinorganic chemistry: The role of trace metals in the oceanic cycles of the major nutrients. In: Mottl M.J., Elderfield H. (Eds) *Treatise on Geochemistry*, 2nd edn, vol 8, pp 123–149.
- Morel F.M.M. and Price N.M. (2003) The biogeochemical cycles of trace metals in the oceans. *Science* 300, 944-947.

- **Vance D.**, Archer C. **Little S.H.**, Köbberich M. and de Souza G.F. (2017) The oceanic cycles of the transition metals and their isotopes. *Acta. Geochim*. 36, 359-362.

On the biogeochemical cycling of nickel in the oceans, including the aging and transformation of birnessite in marine sediments and release of nickel:

- 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. *Geochim. Cosmochim. Acta* 189, 158-183.
- Atkins A.L., Shaw S., **Peacock C.L.** (2014) Nucleation and growth of todorokite from birnessite: Implications for trace-metal cycling in marine sediments. *Geochim. Cosmochim. Acta.* 144, 109-125.
- Ciscato E.R., Bontognali T.R.R. and **Vance D.** (2018) Nickel and its isotopes in organic-rich sediments: Implications for oceanic budgets and a potential record of ancient seawater. *Earth. Planet. Sci. Lett.* 494, 239-250.