Ironing out the carbon cycle: Carbon burial associated with iron oxides in Arctic shelf sediments

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Background:

Over the last decades, a huge body of scientific research has proven that increased CO_2 in the atmosphere since the industrial revolution is one of the main drivers of accelerated global climate change. As marine geoscientists, we are interested in the capability of the world's oceans to sequester atmospheric CO_2 into photosynthetic algal biomass, and to ultimately lock it away in seafloor sediments when this biomass dies and sinks to the ocean depths. This sequestration of CO_2 though organic matter burial **has regulated global climate** since the dawn of photosynthesis some 3 billion years ago, and is of paramount importance today as we seek to understand and mitigate the CO_2-driven greenhouse effect.

A key question around organic matter burial in seafloor sediments is: What controls the capability of sediments to **accumulate and stabilise organic matter**? Over the last few years several ground-breaking studies have highlighted the importance of highly reactive iron (hydr)oxide minerals in the sediments, suggesting that these particles might be able to bind organic matter, and possibly even transform organic carbon, rendering it resistant to degradation and thus promoting its preservation and burial. This potential process for the accumulation and stabilisation of organic matter has come to be known as the **"rusty carbon sink"**. However, our understanding of the coupling between reactive iron and organic matter is currently limited by a number of important questions: How much organic matter is bound to exactly which iron (hydr)oxide minerals? Are different organic compounds more susceptible to binding to iron (hydr)oxides? Do iron (hydr)oxides stabilise organic matter against microbial oxidation, and does organc matter protect iron (hydr)oxides from microbial reduction? How stable is the iron-organic matter coupling during burial into deeper sediments? And last but not least, do current methods to quantify iron-bound organic matter produce reliable data? To answer these questions Drs März, Faust and Prof Peacock are investigating exactly how iron (hydr)oxides bind and stabilise organic matter and thus protect it from degradationin the frame of several ongoing research projects at the University of Leeds (The Changing Arctic Ocean Seafloor, ChAOS, http://www.changing-arctic-ocean.ac.uk/?page_id=199; The Role of Minerals in the Oceanic Carbon Cycle, MINORG).

This PhD project will provide a **vital new component to these ongoing research efforts by investigating the iron-organic matter coupling from a fundamental point of view, and specifically in Arctic Ocean sediments**. The Arctic is one of the most rapidly changing environments on the planet as globalwarming takes hold, and a better understanding of the reactivity and cycling of organic matter, and specifically organic carbon, in this ecosystem is urgently required. As an integral part of two ongoing research projects the successful PhD student will be embedded in a vibrant and active research community, and will have the opportunity to present their research at national and international meetings, and help develop and lead a number of peer-reviewed publications.

Objectives:

1) Testing, calibrating, and potentially modifying the typically used methods for measuring the amount of iron-bound organic carbon in sediments, using specifically prepared reference materials.
2) Determining the amount of iron-bound organic carbon in Arctic Ocean surface sediments (Barents Sea, Arctic fjords), and relating the distribution of this carbon to environmental parameters such as water masses, sea ice, primary productivity, proximity to land.
3) Determining the amount of iron-bound organic carbon in deeper Arctic Ocean sediments to test the potential for long-term carbon storage and study the effects of diagenetic processes on the stability of the iron-carbon coupling.
4) Establishing iron-bound organic carbon budgets for the Barents Sea and Arctic fjords in comporison to worldwide estimates, and predicting changes to iron-carbon coupling with ongoing climate change and associated changes in carbon input, iron and carbon speciation, and burial rates.

Approach & training:

As a first step, the PhD student will **test and improve existing methods** to quantify iron-bound organic carbon by preparing reference materials containing varying amounts of different types of iron (hydr)oxides and organic compounds, and extracting them using the typically used method for iron-bound organic matter extraction. Following this fundamental approach to evaluate and improve the extraction method, the PhD student will apply the (potentially revised) extraction method to **surface sediments from the Arctic Ocean** to better understand how the association of iron with organic matter is controlled by variable environmental parameters (e.g., primary productivity, sea ice cover, proximity to land). Subsequently, in an attempt to quantify how stable the iron-organic coupling

Megacorer tubes filled with ~35 cm of sediment from the Barents Sea, with brown iron-rich surface sediment and a rather unfortunate sponge in the left tube (courtesy of J Faust) is in Arctic marine sediments over longer timescales (1,000s of years), the PhD student will analyse **sediment samples that have been buried beneath the seafloor** and have experienced early diagenetic processes. In addition, all extracted samples will be analysed for their stable carbon and nitrogen isotope composition (before and after removing iron-bound carbon and nitrogen) to better characterise the type of organic material that is associated with iron minerals.

All analyses will be conducted in the Cohen Geochemistry labs at the University of Leeds and the student will have the opportunity to look at the iron-organic matter coupling in very fine detail using an especially powerful type of microscopy and spectroscopy available at the world-leading Diamond Light Source synchrotron facility near Oxford. Preparation of iron-organic matter reference materials is currently being developed as part of the MINORG project, so the PhD student will benefit from world-leading expertise available at Leeds. A unique set of Arctic Ocean sediment samples and relevant background data has also been gathered by Drs März, Faust and collaborators in the frame of the ongoing ChAOS project, and these samples are available for investigation. For key sites, complementary data on the inorganic and organic geochemical sediment composition and macro- to microbiology can be obtained from collaborators on the ChAOS project, providing the student with a unique set of multi-disciplinary background data. To study the effect of the proximity to land, sediment samples from fjords in Svalbard and northern Norway are available for this PhD project from earlier research cruises. In addition, this PhD project offers the unique opportunity to **join a research expedition** onboard the RRS *James Clark Ross* to the Barents Sea in summer 2019 to collect additional samples and data. Due to our very close collaboration with Norwegian scientists, there might be further opportunities to join research expedition to the Arctic Ocean onboard the Norwegian icebreaker *Kronprins Haakon*. Finally, this project is in collaboration with Iso-Analytical (http://www.iso-analytical.co.uk/), who will provide **additional financial support** to the project as well as a **paid three month internship**.

This project will include analyses of prepared reference materials, bulk sediment samples, and sequential leaching methods to extract different metal phases and the associated carbon fractions (led by Drs März and Faust). Selected samples, and analogue samples created in the laboratory, will be analysed at very high spatial and chemical resolution using the latest synchrotron nanoprobes, to further investigate the mineral-organic couplings and how these might promote carbon stabilization and burial (led by Prof Peacock). Carbon and nitrogen isotopes will be analysed at Iso-Analytical to characterise the nature of iron-bound organic matter.

The student will be trained in geochemical procedures and analyses by Drs März, Faust and Prof Peacock (Leeds) and Dr Steve Brookes (Iso-Analytical) who have substantial experience in extracting different metal phases from sediment samples and total acid digestions, analysis of dissolved phases using AAS, ICP-OES and ICP-MS and of solid samples using XRD, CN combustion analysis and IRMS, synchrotron-based spectroscopy, and C/N isotope analysis. Hands-on training and support will further be provided by highly qualified technicians in the Cohen Geochemistry labs and at Iso-Analytical. The successful candidate will have access to a wide range of training workshops (scientific writing and presentation skills, statistics, science communication and outreach), and will be supported by the supervisors in preparing conference presentations and peer-reviewed publications. Additional perks of this project include the close links to several larger, multi-disciplinary and multi-institutional projects that involve shipboard expeditions to the polar oceans, providing the student with a unique opportunity for networking and seagoing experience, as well as experience of working with an industry partner.

Student qualification:

The successful candidate should have an excellent degree in an Earth Science or closely related subject, or Environmental Sciences discipline, and have a keen interest in, and some experience of lab work, fieldwork, analytical methods and interdisciplinary research. Ideally the successful candidate will have experience in conducting a research project and presenting research results to a scientific audience.

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