# How minerals impact the storage of organic carbon in our oceans

**Prof. Caroline Peacock**

> Working with the MinOrg team and our collaborators has been hugely enjoyable and opened up new research avenues exploring the role of iron and manganese in the global Earth system.
>
> **Professor Caroline Peacock**

*Image: Dr Oliver Moore preparing laboratory experiments to test the formation of geopolymerised substances at ocean temperatures.*

**The oceanic carbon cycle is pivotal to our understanding of how Earth's climate and surface conditions have evolved and how they might change in the future. However, a gap in knowledge surrounding the storage of organic carbon poses a considerable challenge. Project MinOrg has now made a major contribution to help close that gap with insight into the role minerals play in oceanic carbon storage.**

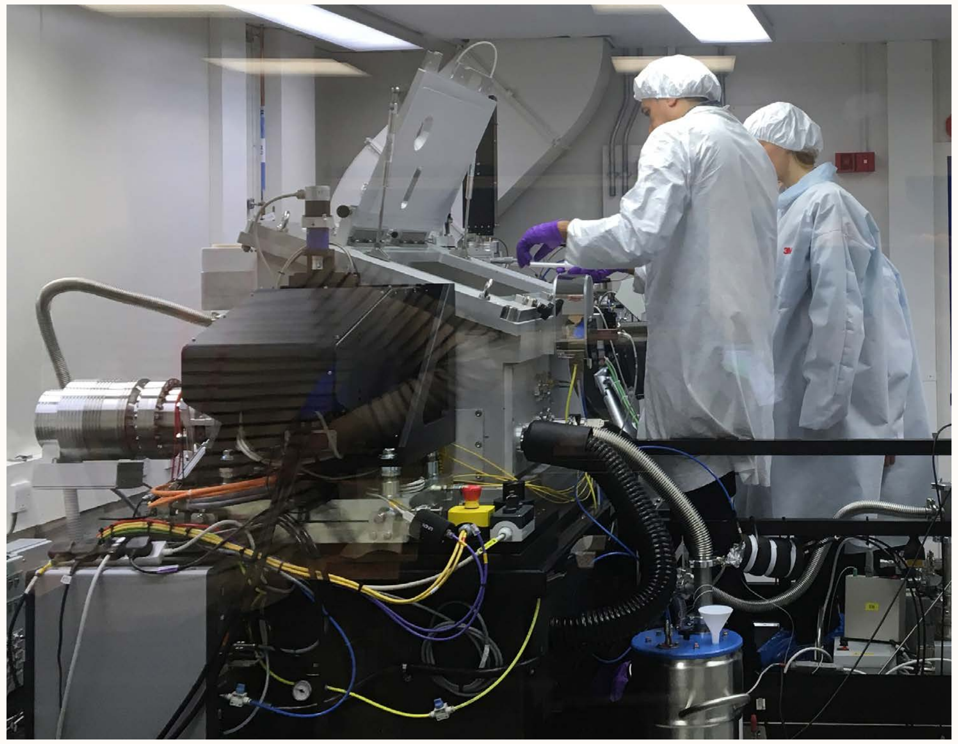


*Image: Dr Lisa Curti with beamline scientist Dr Majid Kazemian preparing to analyse laboratory samples using NEXAFS spectroscopy on Beamline I08 at Diamond Light Source.*

## Oceans and carbon storage

Our oceans and ocean sediments act as a carbon sink, i.e. a natural environment that can store carbon and lock it away from the atmosphere. Since the Industrial Revolution, the storage of carbon in seawater has helped offset rising emissions. Over geological time, the storage of carbon in ocean sediments has helped regulate climate and create the stable conditions required for complex life to evolve. As we face unprecedented human climate change, it is now more important than ever to understand how our oceans perform regarding carbon storage and release.

Within our oceans and ocean sediments are processes that break down organic carbon (OC) and processes that store it. The balance between the two affects our atmosphere's carbon dioxide ($CO_2$) and oxygen ($O_2$) levels. On the short timescales relevant to human climate change, a relatively recently discovered form of dissolved OC in seawater that is resistant to decomposition might be critical to OC storage, while on longer timescales, sediments can preserve and store OC over millions of years. Project MinOrg hypothesised that minerals found in our oceans and ocean sediments are integral to the preservation of OC in seawater and sediments and set about investigating this with laboratory experiments and computer modelling.

Understanding how OC is stored in seawater and sediments could revolutionise how we think about carbon cycling and might offer new ways to maximise carbon storage and mitigate climate change. The problem is that the extent to which minerals preserve OC in seawater and sediments remains uncertain. The contributing mechanisms behind how OC interacts with minerals are largely uncharted.

## Minerals and the Maillard reaction

The MinOrg project, led by Professor Caroline Peacock at the University of Leeds, set out to quantify the role of minerals in preserving OC. MinOrg showed that the Maillard reaction occurs in ocean sediments and potentially seawater and might lock away millions of tonnes of carbon in the seabed each year. The Maillard reaction is more commonly known in the art of cuisine, as it gives us the enjoyable scent, flavour and appearance of foods such as roast potatoes and crusty bread. The reaction takes place between amino acids (from proteins) and sugars (like glucose or fructose) under heat. As the reaction progresses, these amino acids and sugars chemically bond together to form larger, more complex carbon-rich molecules. This process of forming larger molecules from smaller building blocks is a type of polymerisation.

In the context of the Maillard reaction, the resulting polymers, called 'geopolymerised substances' (GPS), are too large to be easily broken down by microorganisms. This makes them more resistant to degradation and allows them to persist in the environment for longer periods.

At the bottom of the ocean, however, the reaction lacks the high temperatures of an oven to act as a catalyst. Sediment temperatures are around a mere 10°C. The Maillard reaction was considered so slow at this temperature that it was largely discounted as an OC preservation mechanism and assumed to be of minor significance for OC burial in ocean sediments.

## Exploring iron and manganese as catalysts

The MinOrg project sought to understand how the Maillard reaction operates in the cold, dark depths of the oceans. Recent discoveries suggested (Hardie *et al.*, 2010; Johnson *et al.*, 2015; Jokic *et al.*, 2001) that manganese minerals can catalyse the Maillard reaction. So, the team incubated common organic molecules with dissolved and mineral forms of Fe (ferrihydrite) and Mn (birnessite). This mixture was then incubated at a temperature of 10°C, akin to the seabed's conditions along continental edges. The experiments were conducted in both oxic (contains dissolved oxygen) and anoxic (no dissolved oxygen) conditions.

Results from the experiments closely matched the chemical composition of OC found in continental margin sediments across a wide range of locations and time periods. The crucial discovery was that the Maillard reaction was significantly accelerated in the presence of Fe and Mn minerals—up to 100 times faster than in mixtures lacking these catalysts. This finding indicates that reactive forms of Fe and Mn could play a vital role in catalysing the Maillard reaction within continental margin sediments, with the potential to promote OC preservation on a globally significant scale.

To compare and analyse the outcomes of the MinOrg experiments, the team turned to near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. In the most basic terms, NEXAFS spectroscopy acts as an intensely powerful microscope, enabling the MinOrg team to compare the atomic arrangement and chemical composition of the substances produced in their experiments with real ocean sediment samples.

The team found strong evidence for the compatibility of their experimental outcomes with real-world ocean sediment compositions.

The MinOrg team then used a nanoparticle tracking instrument to measure the amount of GPS produced in the Maillard reaction to understand the impact of Fe and Mn as catalysts. With no Fe or Mn, only a tiny amount of GPS was made (0.2 nanomoles per litre per year).

Under anoxic conditions, greater dissolved Fe and Mn concentrations produced increased polymerisation. Up to ten times more GPS was created compared to experiments without Fe and Mn. Specifically, with Fe, they created about 7 nanomoles of GPS per litre per year, and with Mn, they made about 5 nanomoles of GPS per litre per year. This was achieved using a catalyst concentration of 400 micromoles per litre.

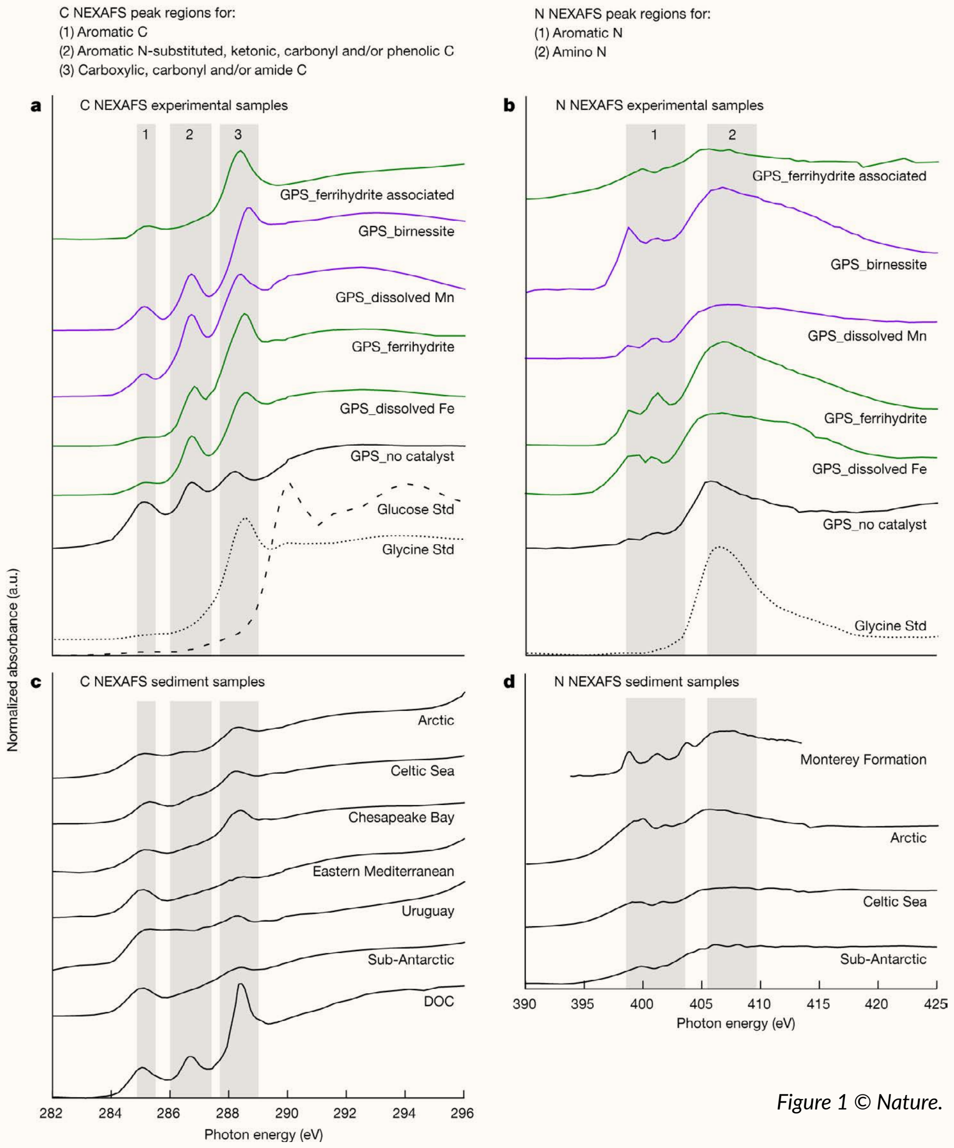


*Figure 1 © Nature.*

> To discover that iron and manganese play such a pivotal role in the preservation and burial of carbon, and ultimately the global carbon cycle and climate is immensely exciting.
>
> **Dr Oliver Moore**

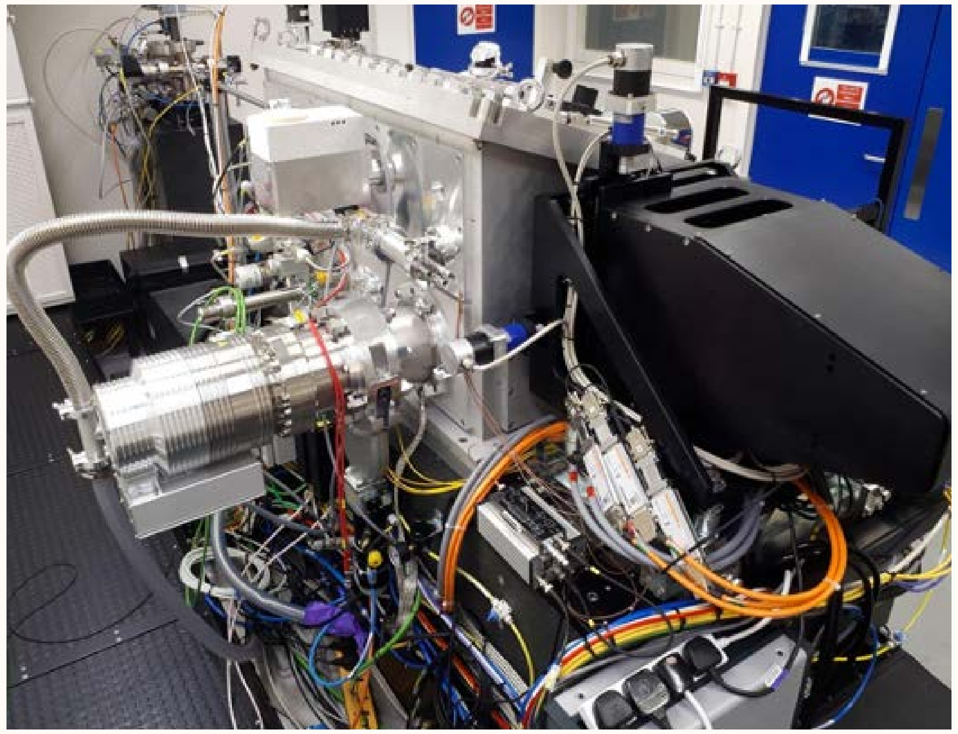


*Image: The combined microscopy and spectroscopy instrumentation on Beamline I08 at Diamond Light Source.*

> Our discoveries might also be used to help lock away carbon in sediments and soils, which may help combat climate change.
>
> **Dr Oliver Moore**

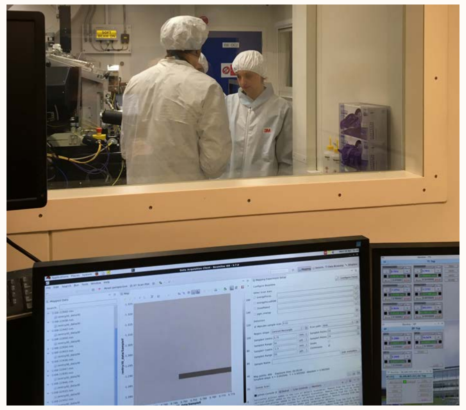


*Image: Dr Lisa Curti with beamline scientist Dr Majid Kazemian preparing to exit the beamline hutch and set up remote analyses using the beamline control computer stations on Beamline I08 at Diamond Light Source.*

Under oxic conditions, ferrihydrite and birnessite produced substantially increased polymerisation at all catalyst concentrations tested, which was up to ten times greater than that of dissolved Fe and Mn and one hundred times greater than that of the catalyst-free control.

The scientists at MinOrg propose that the enhanced reactivity observed when dissolved Fe and Mn were introduced happened because these ions bonded with OC to help polymerise the OC molecules together while using ferrihydrite and birnessite provided a surface upon which the polymerisation reaction could occur.

## Modelling real-world impact

After measuring the catalytic effect of Fe and Mn on the Maillard reaction, the MinOrg project utilised a series of evidence-based constraints to estimate the potential scale and importance of GPS production in oxygenated surface sediments along continental edges. They aimed to understand how this process might contribute to OC preservation in these environments.

The team employed a computational method known as the Monte Carlo technique. This approach allowed them to simulate how the production rates of GPS, derived from their experimental data, were distributed across the Earth's surface.

With a 95 per cent confidence level, the final estimations indicated that the geopolymerisation of OC, catalysed by Fe and Mn minerals in continental margin sediments, could yield and preserve approximately 4.05 teragrams of carbon per year.

The potential influence of Fe and Mn availability on preserving OC at this scale could significantly impact our understanding of the global carbon cycle, as long-term carbon storage estimates do not usually consider these elements.

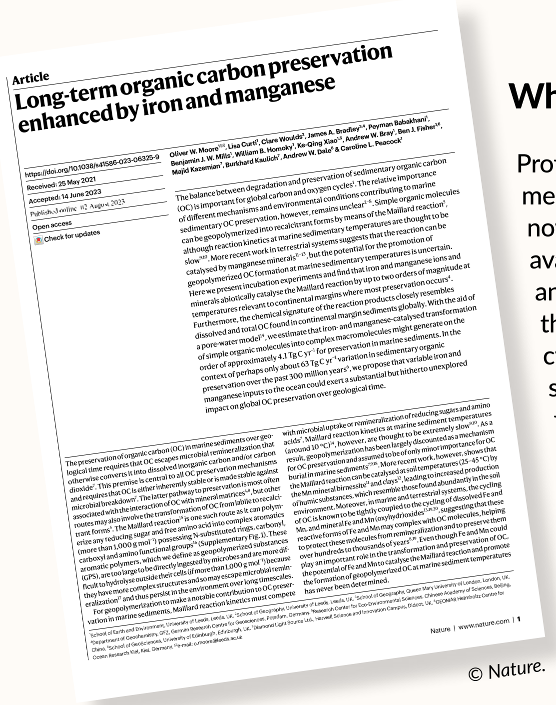
To assess the potential impact of sedimentary GPS formation on Earth's surface chemistry, the team used a specialist model to simulate scenarios over approximately the last 541 million years. Using their data from their work thus far, they observed that changes in OC preservation due to the formation of GPS were able to shift global average surface temperature by approximately 5°C. Such an impact on temperature emphasised the importance of MinOrg's work in helping to understand what controls climate and demonstrates that promoting carbon storage in the oceans might be a viable way to tackle climate change.

## Conclusion

MinOrg's findings evidence the catalytic influence of Fe and Mn in the Maillard reaction; a significant implication for our previous understanding of the oceanic carbon cycle. We now know that these elements play a pivotal role in the preservation of OC, potentially preventing its release into the atmosphere. Such findings urge the reevaluation of conventional climate prediction models and highlight the need to consider Fe and Mn as critical factors in future studies concerning carbon burial and climate change.

## Team overview

Project MinOrg was led by Prof Caroline Peacock and comprised biogeochemists Dr Lisa Curti, Dr Oliver Moore and Prof Clare Woulds, geomicrobiologst Prof Ke-Qing Xiao, and biogeochemical modellers Dr Peyman Babakhani and Dr Mingyu Zhao. On the work reported here, the MinOrg team collaborated with colleagues Prof Ben Mills, Dr Will Homoky, Dr Andy Bray and Dr Ben Fisher at University of Leeds, Dr James Bradley at Queen Mary Univeristy of London, Dr Andy Dale at GEOMAR Helmholtz Centre for Ocean Research Kiel, and Dr Majid Kazemian and Dr Burkhard Kaulich at Diamond Light Source Synchrotron.



Article

Long-term organic carbon preservation enhanced by iron and manganese

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The balance between degradation and preservation of sedimentary organic carbon (OC) is important for global carbon and oxygen cycles[1]. The relative importance of different mechanisms and environmental conditions contributing to marine sedimentary OC preservation, however, remains unclear[2–8]. Simple organic molecules can be geopolymerized into recalcitrant forms by means of the Maillard reaction[5], although reaction kinetics at marine sedimentary temperatures are thought to be slow[9,10]. More recent work in terrestrial systems suggests that the reaction can be catalysed by manganese minerals[11–13], but the potential for the promotion of geopolymerized OC formation at marine sedimentary temperatures is uncertain. Here we present incubation experiments and find that iron and manganese ions and minerals abiotically catalyse the Maillard reaction by up to two orders of magnitude at temperatures relevant to continental margins where most preservation occurs[4]. Furthermore, the chemical signature of the reaction products closely resembles dissolved and total OC found in continental margin sediments globally. With the aid of a pore-water model[14], we estimate that iron- and manganese-catalysed transformation of simple organic molecules into complex macromolecules might generate on the order of approximately 4.1 Tg C yr$^{-1}$ for preservation in marine sediments. In the context of perhaps only about 63 Tg C yr$^{-1}$ variation in sedimentary organic preservation over the past 300 million years[6], we propose that variable iron and manganese inputs to the ocean could exert a substantial but hitherto unexplored impact on global OC preservation over geological time.

The preservation of organic carbon (OC) in marine sediments over geological time requires that OC escapes microbial remineralization that otherwise converts it into dissolved inorganic carbon and/or carbon dioxide[7]. This premise is central to all OC preservation mechanisms and requires that OC is either inherently stable or is made stable against microbial breakdown[7]. The latter pathway to preservation is most often associated with the interaction of OC with mineral matrices[4,8], but other routes may also involve the transformation of OC from labile to recalcitrant forms[5]. The Maillard reaction[15] is one such route as it can polymerize any reducing sugar and free amino acid into complex aromatics (more than 1,000 g mol$^{-1}$) possessing N-substituted rings, carbonyl, carboxyl and amino functional groups[16] (Supplementary Fig. 1). These aromatic polymers, which we define as geopolymerized substances (GPS), are too large to be directly ingested by microbes and are more difficult to hydrolyse outside their cells (if more than 1,000 g mol$^{-1}$) because they have more complex structures and so may escape microbial remineralization[17] and thus persist in the environment over long timescales.

For geopolymerization to make a notable contribution to OC preservation in marine sediments, Maillard reaction kinetics must compete with microbial uptake or remineralization of reducing sugars and amino acids[7]. Maillard reaction kinetics at marine sediment temperatures (around 10 °C)[14], however, are thought to be extremely slow[9,10]. As a result, geopolymerization has been largely discounted as a mechanism for OC preservation and assumed to be of only minor importance for OC burial in marine sediments[7,9,18]. More recent work, however, shows that the Maillard reaction can be catalysed at soil temperatures (25–45 °C) by the Mn mineral birnessite[11] and clays[12], leading to increased production of humic substances, which resemble those found abundantly in the soil environment. Moreover, in marine and terrestrial systems, the cycling of OC is known to be tightly coupled to the cycling of dissolved Fe and Mn, and mineral Fe and Mn (oxyhydr)oxides[13,19,20], suggesting that these reactive forms of Fe and Mn may complex with OC molecules, helping to protect these molecules from remineralization and to preserve them over hundreds to thousands of years[8,19]. Even though Fe and Mn could play an important role in the transformation and preservation of OC, the potential of Fe and Mn to catalyse the Maillard reaction and promote the formation of geopolymerized OC at marine sediment temperatures has never been determined.

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## What's next?

Prof Caroline Peacock and members of the MinOrg team will now more widely explore how the availability and distribution of iron and manganese may help shape the global carbon and oxygen cycles and hence the Earth system over past, present and future timescales.

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# MinOrg: The role of minerals in the oceanic carbon cycle

## PROJECT SUMMARY

MinOrg set out to increase our understanding of the oceanic carbon cycle, aiding understanding of how Earth's climate and surface conditions have evolved over time, and pointing to ways that might improve climate change predictions.

The project explored why and how OC is preserved in seawater and sediments, testing its hypothesis: OC and minerals interaction promotes carbon preservation in seawater and sediments to an extent that impacts the global carbon cycle and climate.

## PROJECT PARTNERS

GEOMAR Helmholtz Centre for Ocean Research Kiel

## PROJECT LEAD PROFILE

Caroline Peacock is a Professor of Biogeochemistry and Royal Society Wolfson Research Merit Award Holder at the University of Leeds. She researches how minerals control the cycling of elements critical to life, including carbon and nutrients. Her team uses experiments, advanced analytical and computational techniques to quantify how minerals impact global elemental cycles and the past, present and future Earth.

## PROJECT CONTACTS

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