

Carbon preservation in sedimentary deposits: Beyond mineral protection

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The deposition and preservation of organic carbon (OC) in sedimentary environments (including soils and sediments) play major roles in mediating the global carbon cycle. More than 90% of OC burial in the ocean occurs in continental margin sediments, which contributes to the evolution of the Earth's atmosphere, such as oxygen content, over geological timescales.¹ However, how OC escapes mineralization and persists in such sedimentary deposits has long been a puzzle. Mineral protection through physicochemical associations of organic matter with minerals and cations is considered to be one of the primary mechanisms contributing to the environmental persistence of sedimentary OC. A recent study published in *Nature* by Moore et al.² has presented novel evidence supporting mineral enhancement of OC preservation (Figure 1).

Using abiotic incubation experiments mimicking marine sedimentary settings, specifically the reduction zones of iron (Fe) and manganese (Mn) oxides, Moore et al. demonstrated that both Fe and Mn cations and minerals catalyzed the transformation of simple organic molecules (i.e., glucose and glycine) into

recalcitrant forms, such as complex aromatics, via the Maillard reaction (i.e., polycondensation). The above processes are also referred to as Fe- and Mn-catalyzed geopolymerization. Employing nanoparticle tracking analysis, they showed that these reactive forms of Fe and Mn may catalyze the Maillard reaction by up to two orders of magnitude compared to a catalyst-free control, thereby enabling geopolymerization to effectively compete with mineralization. Although the Maillard reaction has been previously proven to occur at soil temperatures (25°C–45°C), the potential of Fe and Mn to catalyze organics transformation in natural marine sediments at relatively low temperatures (10°C) has not been determined. The study hence provides the first evidence of its kind to prove that geopolymerization could occur in marine surface sediments on a global scale.

Moreover, using fingerprinting techniques by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, Moore et al. showed that the products of the Fe- and Mn-catalyzed Maillard reaction were somewhat consistent with

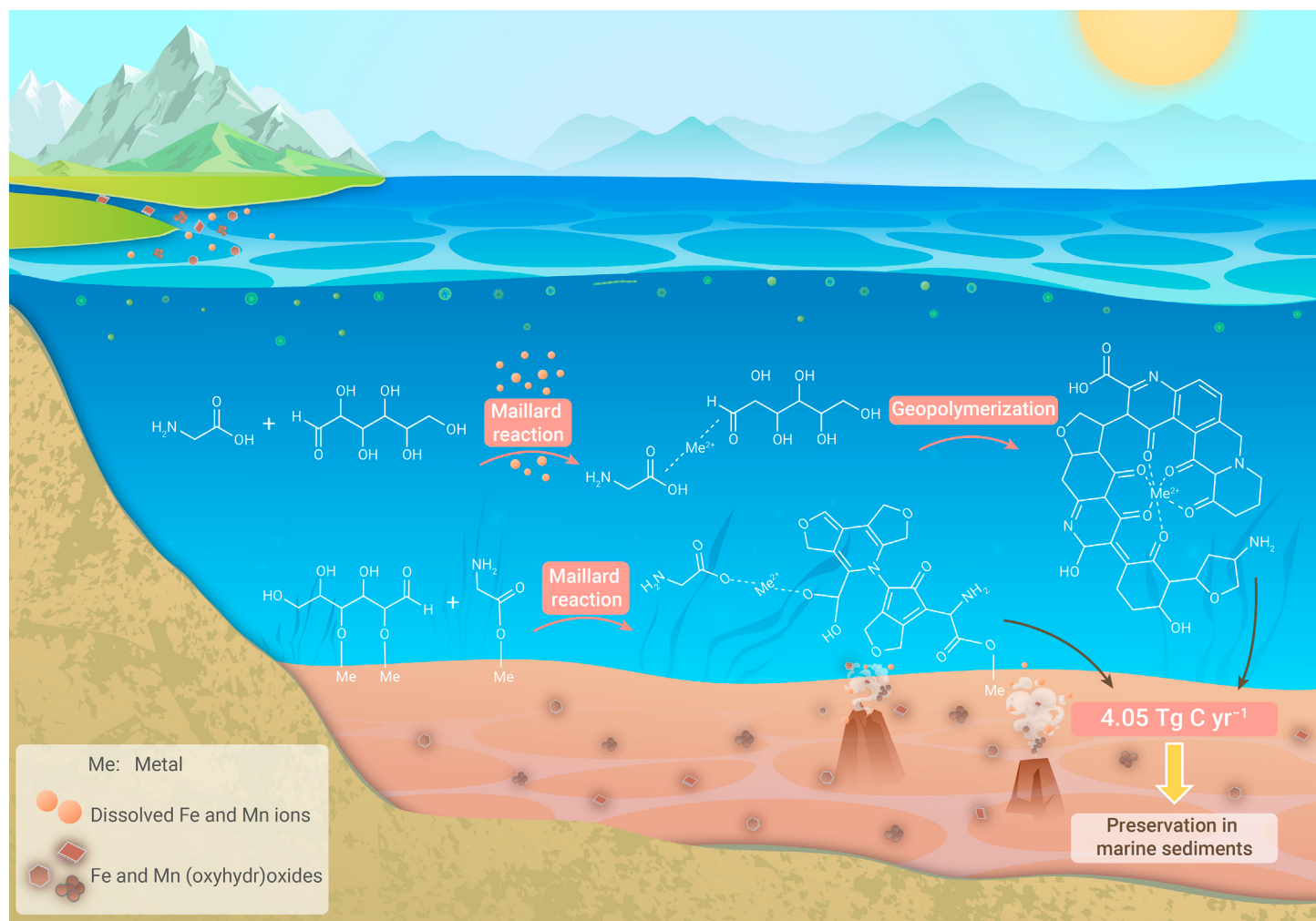


Figure 1. Iron (Fe) and manganese (Mn) catalysis of organic carbon geopolymerization and preservation in continental margin sediments

the chemical signature of dissolved OC and total OC present in continental margin sediments from a spatially and temporally diverse sample set. These results imply that geopolymerization catalyzed by reactive minerals or cations may play a more important role in OC preservation in global marine sediments than previously thought, leaving a chemical signature therein. With the aid of a pore-water model, Moore et al. further estimated that Fe- and Mn-catalyzed geopolymerization may generate and thus preserve $4.05 \pm 0.55 \text{ Tg C year}^{-1}$ in continental margin sediments under optimal conditions. This magnitude of OC preservation could substantially affect the trajectory of Earth's atmosphere over geological timescales.

The study represents an attempt to highlight the potential importance of geopolymerization in OC preservation in the surface sediments on continental margins. The result is thought-provoking, given that the global relevance between sedimentary OC preservation and mineral-catalyzed reactions is difficult to discern and is conventionally considered to be negligible in the ambient marine environment. These findings are also inspiring to soil scientists because the Maillard reaction, involving the polycondensation of carbohydrates and amino acids, has long been proposed as a significant abiotic pathway for the formation of soil humic substances. However, the importance of humic substances has been challenged in soil carbon studies due to limited evidence that soil carbon storage or persistence is controlled by "humification," the process that biopolymers break down into individual monomers that then polymerize to form amorphous, humic materials.³ The emergent view considers that soil organic matter is a continuum of progressively decomposing organic compounds⁴ without a clear dominating sign of polycondensation. The use of a humic substance is more often than not frowned upon in the soil science community nowadays. The study by Moore et al. definitely provides some food for thought on this topic. Proving the existence of geopolymerized humic substances in soils may be more difficult than in marine sediments due to the complexity and high abundance of both plant- and microbe-derived biopolymers in soils. However, soils provide abundant supplies of reactive Fe and Mn minerals as well as simple organic molecules. It is hence a matter of how geopolymerization may compete with mineralization (i.e., before the organic reactants are consumed by soil microbes and abiotic decay) and how stable the geopolymers are in decomposer-replete soil environments. The existence of geopolymerized humic substances remains an open question.

Nonetheless, some limitations and uncertainties of the study still deserve to be noted. The laboratory simulation experiment conducted by the authors employed relatively simplified and optimal conditions (e.g., reagent selection), likely boosting reaction rates relative to those observed in natural marine sediments. Marginal seawater and sediments are replete with both algae- and plant-derived OC. Microbial-mediated transformation of these materials may yield recalcitrant molecules. Therefore, the organic molecules chosen for the simulation experiments may not accurately represent the starting material for Fe- and Mn-catalyzed reactions occurring in continental margin sediments due to substantial degradation processes caused by biological and photochemical reactions throughout the water column. Apart from Fe and Mn oxides, clay minerals such as montmorillonite are also potential catalysts for the polymerization of simple organic molecules. Hence, further experimental endeavors should use

diverse organic matter and different forms of Fe and Mn oxides as well as clay minerals as catalysts at different concentrations to confirm the importance of geopolymerization in OC preservation in continental margin sediments. Given that both OC supply and mineral distribution are highly variable spatially and temporally in sediments, such explorations may help to identify hotspots and hot moments for mineral-catalyzed OC preservation in the ocean. Furthermore, deep-going analysis on the organic molecule composition of geopolymerized substances through fingerprinting techniques is imperative for obtaining additional insights into the processes involving Fe- and Mn-catalyzed OC geopolymerization.

Future research should consider the following aspects. First, salinity may affect Fe- and Mn-catalyzed Maillard reaction kinetics as well as the subsequent sorption of geopolymers on minerals. Therefore, the effects of seawater salinity should be accounted for to constrain the rate of geopolymerization in margin sediments. Second, microbes play a key role in both OC mineralization and mineral transformation, such as the reduction of Fe and Mn oxides. Microbial processes can also catalyze OC transformation via electron transfer among mineral surfaces. Exploring microbial-mediated Fe and Mn catalysis of OC preservation is a direction to further understand OC-mineral-microbe interactions in deposition environments along with the competition between geopolymerization and microbial degradation. Future experiments should investigate the role of microbes in mineral-catalyzed OC preservation. Third, apart from catalyzing the Maillard reaction, redox-active Fe and Mn minerals can catalyze the production of radicals (e.g., via Fenton-like reactions), inducing nonspecific decomposition of organics, which is unfavorable for OC preservation,⁵ especially in oxic environments. The dual effect of Fe and Mn minerals on OC preservation and decomposition hence requires further evaluation.

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DECLARATION OF INTERESTS

The authors declare no competing interests.