Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37107

Oxygen exposure promotes organic carbon preservation via manganese-driven humification

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Oxygen exposure at the sediment-water interface is typically considered destructive for organic carbon, driving rapid remineralisation during early burial. Yet here we suggest that oxygen can instead promote organic carbon preservation by sustaining manganese redox cycling that abiotically humifies and stabilises organic carbon in marine sediments.

We combine natural sediment observations, laboratory experiments, molecular-scale characterisation and modelling to evaluate the role of oxygen-driven manganese redox cycling in organic carbon humification. In natural sediments from diverse marine settings, reactive manganese shows a strong positive correlation with the fraction of humified organic carbon, condensed aromatic compounds and thermally stable organic carbon, whereas reactive iron correlates primarily with total organic carbon but not with these humification indices, suggesting distinct functional roles for iron and manganese in sedimentary carbon cycling. In experiments adding reduced manganese to natural sediments and synthetic iron organominerals under oxic and abiotic conditions, oxidised manganese is rapidly generated, while organic carbon is oxidatively polymerised into carboxyl-rich intermediates and condensed aromatic structures with enhanced thermal stability. We interpret this to reflect an oxygen-driven manganese-induced humification pathway in sediments, whereby reduced manganese is oxidised by oxygen at iron mineral surfaces, and oxidised manganese forms a redox couple with organic carbon, resulting in reduced manganese for reoxidation and oxidised humified organic carbon. While iron minerals correlate with total organic carbon, consistent with the ‘rusty carbon sink’, we suggest that their surfaces act as mineral platforms facilitating coupled manganese-carbon humification reactions.

We incorporate oxygen-driven manganese-induced humification into a modified organic carbon degradation model for sediments, parameterised using thermal stability indices. Model simulations suggest that, with conservative reactive manganese (300 ppm), the contribution of humified organic carbon to total organic carbon preserved increases with burial time, up to 17%-41% after ten million years. We suggest that this humification pathway during early oxic exposure might stabilise organic carbon over geological timescales. This mechanism links mineral surface catalysis and abiotic transformations to organic carbon burial, advancing mechanistic understanding of burial across marine sedimentary systems.