



What's af(Fe)cting OC-Fe interactions? An experimental approach to understanding iron bound organic carbon in sediments.

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Drawdown of atmospheric CO₂ over geologic timescales is largely controlled by imbalances in the carbonate-silicate cycles and the preservation of Organic Carbon (OC) in marine sediments. Up to 85% of this OC is buried in continental shelf sediments of which ~20% is associated with reactive iron (Fe) (hydr)oxides. Association with Fe (hydr)oxides may enhance OC preservation yet despite the importance of this, little is known about which Fe (hydr)oxide phase(s) is involved in OC uptake or the binding mechanism of OC to these reactive iron minerals.

To estimate the importance of this OC-Fe association, a citrate-dithionite-bicarbonate (CDB) extraction method is commonly used to dissolve an operationally defined 'easily reducible iron oxide' fraction and release the associated OC from the sediment. However, natural samples often contain a range of Fe (hydr)oxide phases extractable by CDB, and the Fe phases extracted are defined entirely on the susceptibility of their pure forms to chemical reduction. This suggests that factors affecting mineral stability, including association with OC, could lead to incomplete or excessive phase extraction, which would affect estimates of OC bound to these Fe phases.

To address these issues, we simplified the geochemical system by synthesising OC-iron (hydr)oxide composites with known Fe (hydr)oxide phases and OC moieties with differing chemical structures, added them to OC-free sediment, and then applied the CDB extraction method to determine i) the precise Fe phases extracted; ii) the impact of OC moiety on Fe release and iii) the optimal experimental conditions for the extraction.

We show that reduction of our composites by CDB results in only partial dissolution of the most easily reduced Fe phase (ferrihydrite) and a recovery of only ~20% of total Fe. We also find that the recovery is likely controlled by the functional groups present in the OC and the handling/storage/preparation of samples prior to analysis. These factors could lead to misidentification of the mineral phases extracted and an underestimation of the amount of OC associated with Fe. A change in the estimates for OC associated with Fe would have widespread implications for our understanding of the role of OC-Fe interactions in global carbon cycling.

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