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Iron (oxyhydr)oxide minerals protect carboxyl-rich organic carbon from microbial remineralisation in the marine environment

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Organic carbon (OC) preservation plays a pivotal role in the global carbon cycle and regulates both atmospheric CO_2 and O_2 concentrations over geological time. The interaction between OC and iron minerals plays an important role in both soils and sediments, where a significant proportion of OC that avoids degradation is thought to be sequestered and stabilized by reactive iron minerals. To avoid degradation and become preserved, OC must escape microbial remineralisation but the controls on OC sequestration and stabilization against microbial remineralization however, are only poorly understood. Recent work indicates that mineral protection involving ligand exchange between OC functional groups and iron (oxyhydr)oxide minerals might control global OC preservation and burial over 1000 – 100,000 year timescales[1]. Whether ligand exchange between OC and iron (oxyhydr)oxides can protect OC from remineralisation however, is unknown. Here we determine whether carboxyl ligand exchange between OC and iron (oxyhydr)oxides[2] can protect OC from remineralisation as a function of carboxyl-richness. We test whether carboxyl ligand exchange inhibits remineralisation and whether increasing carboxyl-richness provides enhanced protection from microbial attack. We take a direct mechanistic approach, adsorbing carboxylic acids to ferrihydrite in experiments applicable to marine sediments. We perform adsorption modelling and STXM NEXAFS, and then microbial incubation experiments to measure the remineralisation of uniformly ^{13}C-labelled carboxylic acids in the absence and presence of ferrihydrite, by following the evolution of ^{13}C dissolved inorganic carbon over time. We show that carboxyl ligand exchange with ferrihydrite protects OC from remineralisation, by slowing down remineralisation and reducing the final amount of OC remineralised[3]. We also show that carboxyl-richness provides a first order control on OC remineralisation in the presence of ferrihydrite, where increasing carboxyl-richness decreases remineralisation[3]. Our work indicates that the protection of OC in marine sediments is strongly coupled to carboxyl-richness.

[1]Hemingway et al., 2019, *Nature*, 570, 228-231

[2]Curti et al., 2021, *Comms. Earth Environ*., doi: 10.1038/s43247-021-00301-9

[3]Curti et al., 2023, *Comms. Earth Environ*., submitted.