

Molecular-level coupling of iron and carbon cycling and its impact on micronutrient bioavailability

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In oxic soils and sediments ferrous iron is usually oxidised and precipitated in the presence of dissolved organic matter to form nanoparticulate and poorly crystalline iron(III) (hydr)oxides that are coated and coprecipitated with organic carbon (OC). This phenomenon has a profound effect on the eventual mobility and fate of OC and a number of micronutrient trace metals that are also scavenged from solution during iron (hydr)oxide precipitation. In the first instance, the factors that control the fate of OC in soils and sediments are only poorly understood but the sorption of organic molecules by reactive fine-grained minerals is believed to exert a strong influence on OC preservation [1], where at its simplest level by removing dissolved OC from porewaters and sequestering these molecules to solid mineral phases, microbial degradation is severely limited and OC life-times are duly enhanced [2]. In the second instance, the factors that control the fate of micronutrients in soils and sediments are extensively studied for pure iron (hydr)oxides, but the presence of OC as coatings and structural components significantly alters mineral physiochemistry and thus reactivity towards trace metals [3]. Micronutrient concentrations and isotopic compositions in soils and sediments are therefore often difficult to explain and predict. As such the molecular-level interaction of iron and carbon, through often coupled sorption and redox processes, exerts a first order control on OC preservation and micronutrient bioavailability that is still only poorly understood. Here we present new results, including scanning-transmission X-ray microscopy (STXM) and X-ray absorption spectroscopy (XAS), from an on-going study to determine the role of iron (hydr)oxides in the coupled cycling of iron, carbon and micronutrient trace metals. We will focus on the molecular mechanisms of carbon and metal sorption with iron-organic (hydr)oxides, and show that the precise sorption mechanisms are crucial to understanding the behaviour of OC and micronutrient metals during diagenesis.

[1] Keil et al., 1994, *Nature* 370, p549. [2] Keil & Mayer 2014, *Treatise on Geochemistry* v2, V12. [3] Moon & Peacock 2013, *Geochim. Cosmochim. Acta* 104, p148.