

Molecular dynamics and spectroscopic insights into iron(III) stabilization of water-soluble polysaccharides

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Aqueous iron ions and iron (oxyhydr)oxides are known to stabilize soil organic matter (SOM) against decomposition and mineralization in terrestrial ecosystems. However, the nature of the stabilizing interactions remains elusive [1]. Previous studies suggest that SOM is protected either due to Fe crosslinking with organic polymeric molecules or OM co-precipitation with/ or sorption to iron (oxyhydr)oxides [1,2,3]. It is also known that the fate of environmental Fe is governed by interactions with organic matter [2].

Here, we combine molecular dynamics (MD) simulations with synchrotron-based spectroscopy and microscopy techniques (STXM/NEXAFS and XAS) to show that the interactions of Fe(III) with SOM depend on the type and number of reactive functional groups present in SOM. Specifically, we examined Fe(III) interaction with two water-soluble polysaccharides, amylose (an only hydroxyl containing polysaccharide) and alginate (a carboxyl group containing polysaccharide), because they represent the most abundant class of organic compounds produced in the biosphere.

EXAFS data show that the local Fe-coordination environments in both amylose and alginate complexes are similar. However, molecular dynamics simulations clearly indicate different modes of coordination of Fe(III) with amylose and alginate. Fe(III) was found to be weakly interacting with amylose forming outer-sphere complexes. However, the reduction in Fe(III) mobility and increase in its local concentration near the amylose chains was sufficient to trigger co-precipitation of Fe minerals within the amylose matrix. On the other hand, the carboxyl groups in alginate coordinate strongly with Fe(III), forming inner-sphere complexes. Additionally, we observe an increased rigidity in the alginate matrix, with 90% of complexed Fe(III) involved in either crosslinking polysaccharide polymers or bridging carboxylic groups of a single polymer.

We show that amylose and alginate, despite having similar effects on iron local bonding patterns, have entirely different modes of interaction with Fe. Our observations are relevant for understanding how interactions with polyvalent ions stabilize OM and emphasize how the OM composition is critical in determining modes of interactions.

[1] M. von Lützow, et al., *European Journal of Soil Science* 57 (2006) 426–445.

[2] Y.K. Henneberry, et al., *Organic Geochemistry* 48 (2012) 81–89.

[3] C. Chen et al. *Environ. Sci. Technol.* 48 (2014) 13751–