

**INVESTIGATING ORGANIC MATTER-MINERAL INTERACTIONS AT
THE MOLECULAR SCALE: AN INTEGRATED FIELD AND LABORATORY
STUDY**

by

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ABSTRACT

Intimate association of organic matter (OM) with soil mineral phases has been acknowledged as a fundamental mechanism for stabilizing organic compounds against biological degradation, controlling the long-term sequestration of organic matter in terrestrial ecosystems. However, the fundamental nature of the interactions between OM and soil mineral components is not well understood. Since both the organic and mineral phases of soils are involved, the extent to which OM interacts with minerals depends on both mineralogical properties as well as the composition of OM involved. Landscape topographic positions have important impacts on biogeochemical C and mineral cycling processes, and thus affect OM-mineral interaction.

We applied NEXAFS spectroscopy and Py-FIMS to characterize organic matter in soils obtained from a pasture hillslope. Results showed that the recalcitrant aromatic C and lignin was enriched in the subsoils and poorly-drained footslope locations. In addition, organic compounds had a greater thermal stability in the subsoils and poorly-drained footslope locations. STXM coupled with NEXAFS spectroscopy was used to investigate C associations with Ca, Fe, Al and Si species in pasture soils at the nanometer scale. Good C-Ca spatial correlations were found for soil clay fractions with no CaCO₃, suggesting a strong role of Ca in organo-mineral assemblage formation. C showed similar correlation with Fe to Al & Si, implying a

similar association of Fe oxides and aluminosilicates in organo-mineral assemblages. Iron oxides are important for OM-mineral interactions because of their abundance and reactivity. Iron is susceptible to redox variations along landscape gradients over a wide range of spatial scales. We applied Fe K-edge EXAFS and Mössbauer spectroscopy to characterize Fe mineral phases in a floodplain soil profile with spatially sharp redox gradients. Results showed that the permanent reducing conditions led to a strong reduction in the structural Fe(III) in the phyllosilicates, in addition to a complete reductive dissolution of Fe(III) oxides. Therefore the importance of Fe oxides in OM-mineral interaction should be expected to decrease in the low-redox conditions.

Poorly-crystalline Fe oxy-hydroxide ferrihydrite, because of its high surface area, is of particular importance in OM retention. Organic matter-ferrihydrite complexes can be formed by either adsorption or coprecipitation. We compared these interactions by preparing OM-ferrihydrite complexes at varying C:Fe ratios using dissolved organic matter extracted from a forest litter layer. Our study clearly demonstrated that coprecipitation could result in greater C retention capacity and C stability than adsorption. Iron EXAFS measurements revealed that coprecipitation of OM with Fe led to the formation of OM-Fe(III) cation complexes in the solid phase by suppressing ferrihydrite formation, which might be related to a significantly greater organic carbon retention for coprecipitation than adsorption. Formation of strong complexes between carboxyl C functional groups and ferrihydrite via a ligand exchange mechanism was evidenced by FTIR and C (1s) NEXAFS analysis for both adsorption and coprecipitation.

The ripening of ferrihydrite to more stable and hence less reactive phases such as goethite is catalyzed by surface reaction with aqueous Fe(II). While ferrihydrite within most natural environments contains high concentrations of co-precipitated organic matter, little is known regarding the impact of this OM on the reactivity of ferrihydrite. We explored the extent, pathways and products of Fe(II)-induced secondary mineralization of OM-Fe coprecipitates by reacting aqueous Fe(II) (0.2 and 2.0 mM) with ferrihydrite containing a range of coprecipitated OM loadings (0-21% C). Results demonstrated that OM coprecipitated with ferrihydrite resulted in diminished secondary mineralization and preservation of ferrihydrite. Goethite formation and magnetite nucleation were inhibited by the coprecipitated OM.