

Divalent Cations Influence the Composition of Adsorbed Organic Carbon on Mineral Surfaces: A Comparative Study of Clay Minerals and Metal Oxides

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Soils are critical to the global carbon cycle and contain an estimated 2500 Pg of C, about half of which exists as soil organic carbon (SOC). Through chemical associations (e.g., sorption) with organic molecules, soil minerals play an important role in facilitating SOC retention by enabling protection of SOC from microbial degradation. Such organo–mineral interactions are important in deep mineral soil, where SOC retention is regulated by abundant soil minerals, mineral–water interfacial chemistry, and soluble base cations (Ca^{2+} , Mg^{2+}). To better understand the environmentally-relevant mineralogical and cation controls on these organo–mineral interactions, we investigated the reactions between dissolved organic matter (DOM; pinelands stream water, USA), and clay minerals (kaolinite and montmorillonite), and oxides (allophane and $\delta\text{-MnO}_2$) for up to 30 days in the presence of Ca^{2+} and Mg^{2+} .

We found salient differences across both mineralogy and cation conditions. Whereas clays removed OM (up to 50–60%) in both the absence and presence of Ca^{2+} and Mg^{2+} , the cations exhibited greater control on OM adsorption onto oxides. Without cations, oxides adsorbed little OM, which increased dramatically with Ca^{2+} or Mg^{2+} (up to 70%). Evaluated on a per mass basis, oxides retained substantially more OM (by an order of magnitude) than clays. Cations also accelerated OM adsorption onto minerals.

The composition of adsorbed OM varied by mineralogy and reaction time. Clay minerals showed a 2-step adsorption process: rapid uptake of highly unsaturated aromatics followed by continuous removal of aromatics and carboxyl-rich aliphatic molecules. With cations, oxides showed a 3-step adsorption that includes strong preferential uptakes of aromatics at the initial (<30 min) and late (>50 h) stages with a period without preferential aromatic adsorption in between. Partitioning of aliphatics and carboxyls onto oxide surfaces varied and depended on the extent of sorption, type of cations, and mineralogy.

Our results demonstrate strong mineralogical and cation controls on the magnitude and composition of OM retained by different minerals. We will discuss potential molecular mechanisms responsible for these differences in relation to mineral structure and surface chemistry, and OM composition.