GEOC 37: Synergistic effect of calcium on organic carbon sequestration to ferrihydrite: Potential for Fe-Ca-OC ternary complexes

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Sequestration of organic carbon (OC) in environmental systems is critical to mitigating climate change. Organo-mineral associations, especially those with iron (Fe) oxides, drive the chemistry of OC sequestration and stability in soils. In the past 20 years, research exploring the sequestration of OC to Fe oxides has intensified. Poorly crystalline Fe oxides, such as ferrihydrite, demonstrate a high affinity for OC in binary systems. Calcium commonly co-associates with OC and Fe oxides in soils, though the bonding mechanism (e.g., cation bridging) and implications of the co-association for OC sequestration remain unresolved. In an effort to gain a more environmentally comprehensive understanding of C cycling in chemically heterogeneous systems, we explored the effect of calcium (Ca^{2+}) on the sorption of dissolved OC to 2-line ferrihydrite. Sorption experiments conducted at pH 4 to 9 at varying initial C/Fe molar ratios and Ca^{2+} concentrations were completed to determine the effects of Ca^{2+} on leaf litter-extractable OC sequestration to ferrihydrite. OC sorption extent to ferrihydrite in the presence of Ca^{2+} increased across all tested pH values, especially at pH >7. Sorbed OC concentration at pH 9 increased from 8.72 to 13.30 mmol OC g^{-1} ferrihydrite between treatments of no added Ca^{2+} and 30 mM Ca^{2+} addition. Desorption experiments were performed on synthesized complexes to determine complex stability. Batch experiments were paired with spectroscopic studies to probe sorbed OC speciation and mechanism of sorption complexes. ATR-FTIR spectroscopy analysis revealed that carboxylic functional moieties were the primary sorbed OC species and

suggested an increase in Fe-carboxylate ligand exchange in the presence of Ca at pH 9. Soft and hard X-ray absorption spectroscopy was performed in conjunction with ATR-FTIR to further probe OC chemical composition and OC sorption mechanism(s) to ferrihydrite. Results from batch and spectroscopic experiments provide significant evidence for the enhancement of dissolved OC sequestration to 2-line ferrihydrite and suggest the formation of Fe-Ca-OC ternary complexes. Findings of this research will improve modeling of environmental C cycling and have the potential to improve OM stabilization management strategies.

Sessions

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Sunday, Mar 18 2:50 PM
Room 338, Ernest N. Morial Convention Center
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