

Kinetic structuring: Temporal molecular fractionation of organic matter during mineral adsorption

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While the importance of adsorption onto iron (Fe)-bearing mineral surfaces in organic matter (OM) stabilization has been well-elucidated, our understanding of the structural assembly of OM during adsorption reactions is largely rooted in surface complexation models. Additionally, the spectrum of Fe solid-phase speciation present in many soils may drive the formation of differential structures. This work leverages high-resolution mass spectrometry (FT-ICR-MS) to (1) directly detect the molecular structuring of OM onto contrasting Fe mineral surfaces, and (2) probe the role of mineral solid-phase speciation in temporal molecular fractionation.

Ferrihydrite (Fh), Goethite (Gt) and Hematite (Hm) minerals were subjected to kinetic batch sorption experiments with litter-derived dissolved OM, and sampled at high temporal frequency. Pre- and post-sorption characterization of OM was conducted by FT-ICR-MS and DOC analysis, and specific surface area (SSA) analysis of post-sorption residues.

Results of FT-ICR-MS analysis over five minute intervals during batch sorption reactions reveal detection of kinetic molecular structuring at the Fe mineral interface. Intensity-normalized formulae abundances indicate all minerals experience initial adsorption of carboxyl-containing aromatic and highly-substituted polycyclic compounds, followed by complexation of lignin-like and nitrogenated aliphatic formulae. Only adsorption occurring at or near equilibrium displayed mineral-specific fractionation of distinct compound classes. However, differences in formulae abundance, double bond equivalent (DBE) and thermodynamic indices across adsorption reactions suggest mineral surface properties are driving both the spatiotemporal composition and stability of adsorbed OM.