

Two-Stage Adsorption of Dissolved Organic Matter at Mineral–Water Interfaces

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Dissolved organic matter (DOM) is an important component of the global carbon cycle and impacts the (bio)geochemistry of nutrients and contaminants. In terrestrial and aquatic environments, DOM can be protected from microbial respiration through surface reactions with soil minerals, which slows its mineralization and the release of CO₂ to the atmosphere. However, the mechanisms of mineral–organic reactions are not well understood and remain one of the major uncertainties in current climate models. In this study, we report time-dependent (minutes to months) mineral–organic reactions using six common soil minerals representative of diverse climates, including Fe (goethite) and Al (boehmite) oxides, 1:1 (kaolinite) and 2:1 (montmorillonite) clays, quartz, and carbonates (calcite). Using complementary spectroscopy and mass spectrometry methods, we examined compositional changes of DOM. The adsorption and molecular fractionation of DOM were strongest in metal oxide reactions, followed by clays and carbonates, whereas quartz exhibited little reactivity. Results from short-term reactions (<1 day) agree with known mineral properties. Goethite and boehmite preferentially sorbed highly unsaturated aromatic compounds and removed 60–80% DOM. In contrast, clay minerals sorbed less than 15% DOM within 24 h but selectively preserved less conjugated aromatics and unsaturated aliphatics. Although calcite had a low adsorption capacity, it preferentially retained aliphatic carboxylic acids and O-rich, unsaturated compounds. Long-term mineral reactions deviated from the traditional sorption model, during which all minerals, except quartz, continued to remove aromatics from water with extremely slow kinetics. In oxide and calcite reactions, the adsorption of aromatics was accompanied by minor changes in DOM concentrations. On the other hand, 20–30% additional DOM was removed by clay minerals. This work demonstrates that mineral–organic reactions are highly dynamic. We conceptualize these interactions as two distinct stages: The first stage proceeds quickly and reaches an apparent equilibrium in less than a day, during which DOM molecular fractionation is dictated by mineral surface chemistry; the second stage is characterized by a slow, preferential removal of aromatics, which can be accompanied by surface rearrangements and breakdown of sorbed organic molecules, and mineral dissolution and reprecipitation. This two-stage model can help in the prediction of the fate of DOM in the environment.