

Molecular fractionation and sub-nano scale distribution of dissolved organic matter on allophane

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Allophane is widely distributed in volcanic ash soils and also occurs in forests, sediments, and soils derived from igneous and sedimentary rock sandstones. The molecular fractionation and sequestration of dissolved organic matter (DOM) within allophane nano structures is a key soil process that may affect the carbon (C) cycling in soil environments, but the underlying mechanisms are poorly understood.

In this study, we investigated the adsorptive fractionation of DOM at the allophane-water interface using the Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and double spherical-aberration-corrected scanning transmission electron microscopy (Cs-STEM) to provide direct information of the molecular fractionation and sub-nano scale distribution of DOM on allophane. Copper titration experiments and WHAM 7 model were used to assess the role of carboxylic groups in the fractionation of DOM on allophane. Cs-STEM results revealed that, within allophane aggregates, C mainly distributed on the edges of the pore spaces between allophane aggregates while some DOM molecules localized at some small pore spaces. Moreover, Cs-STEM results suggested that DOM molecules were able to enter the interior spaces within tiny allophane nanoparticles/aggregates. FT-ICR-MS analysis indicated that molecules with high aromaticity, oxygen number and COO groups were preferentially adsorbed. The results of Cu titration and WHAM 7 calculations indicated that carboxylic functional groups of DOM were selectively removed from solutions during adsorption. Overall, both chemical adsorption and physical sequestration may be responsible for the observed strong fractionation of DOM molecules on allophane. Our results shed light on the spatial heterogeneity of mineral aggregates as a critical driver of the chemical fractionation of DOM, highlighting an underappreciated mechanism in carbon cycling models. We expect our results will significantly improve our understanding on DOM-mineral interactions and contribute to predicting C cycling in the environment.