

Interactions of short-range ordered aluminosilicates and organic matter: Impact on mineral structure and vice versa

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Weathering of volcanic ejecta typically coincides with accumulation of short-range ordered aluminosilicates (SROAS), including allophane, imogolite, and their precursors. Structural properties of SROAS may be modified by interference of organic matter (OM) in crystallization, and may govern allocation of OM on SROAS surfaces. We thus investigated the mineral structure of SROAS formed in the presence of OM, and OM adsorption on poorly crystalline SROAS with variable chemical composition (Al:Si = 1.4-3.7). We used dissolved OM collected *in situ* from a Dystric Cambisol and by water extraction from litter to clarify effects of OM composition. Structural evolution of SROAS was examined at reaction times of 1-72 h using infrared and solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy. In the absence of OM, amorphous oligation complexes rapidly evolved to polynuclear species with locally ordered imogolite-like domains. Complexation of Al by OM caused partial exclusion of Si and slowed crystallization of the dioctahedral sheet, consequently enhancing abundance of ill-defined Si in SROAS. Particularly aromatic OM originating from lignin degradation may impede assembly of precursors into more crystalline phases. Adsorption of soil OM on pristine SROAS surfaces was studied using synthetic proto-imogolites and Si-rich SROAS. Oxidized aromatic DOM was selectively retained on SROAS as a function of surface accessibility. We studied adsorption of oxalic and salicylic acid to assess structural impacts on surface reactivity towards organic functional groups preferentially interacting with SROAS. Evaluation of fast adsorption kinetics ($t < 30$ s) by a conductivity-based stopped-flow technique allowed us to characterize adsorption mechanisms. Ligand exchange with aluminol groups proceeded at a rate constant of 3.5 s^{-1} (25 °C) with an activation energy up to 34.1 kJ mol^{-1} . Silicon-rich SROAS was less susceptible to ligand exchange than proto-imogolite due to differences in Al speciation. Formation of tetrahedral Al precluded its complexation by carboxyl groups. Hence, SROAS structure affects the abundance of chemical bonds with OM, potentially influencing OM stabilization in soils.