

Structural Fe promotes allophane reactivity towards model organic compounds

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Short-range ordered aluminosilicates (SROAS) play a key role in stabilizing soil organic carbon (OC), particularly in volcanic soils. Allophane minerals are porous, amorphous aluminosilicates with nanospherical structure, formed from volcanic ash weathering. Owing to their affinity for organic molecules, they promote soil OC accrual. In Fe rich environments, Fe substitutes for Al or forms surface clusters during allophane precipitation. While previous studies investigated the allophane adsorption capacity towards organic molecules [1], little is known about how structural-Fe impacts the mineral reactivity.

In this work, we synthesized allophanes with (Al+Fe)/Si molar ratio of 2 and Fe/Al ratios of 0, 0.05 and 0.1. The nanoparticle structure was characterized by XRD, Fe K-edge XAS and Electron Microscopy, the ζ potential was determined and the specific surface area was calculated with BET method. Sorption isotherms were performed with model organic molecules: citric, glucuronic, vanillic acids and phenylalanine. The mineral/solution ratio was fixed at 5 g·L⁻¹, the organic molecule concentrations varied from 0.1 to 0.5 mM and pH value was adjusted to 5 or 6.5. After 24 h, the suspensions were filtered to 0.22 μ m and the aqueous OC measured.

The results show that phenylalanine is not retained by allophane in any of the studied conditions. Adsorption of vanillic acid is mainly pH dependent with up to 50 % adsorbed at pH 5, suggesting the saturation of the mineral surface. Conversely, up to 93 % of citric acid is adsorbed by Fe-free allophane, increasing to 100 % in presence of Fe, regardless of pH value. Both lower pH and the Fe presence promote glucuronic acid adsorption, which increased from 30 to 50 % at pH 6.5 and 5, respectively, in Fe-free allophane, and from 50 to 75 % at pH 6.5 and 5, respectively, in presence of Fe.

This study highlights the role of Fe as driver of soil C dynamics. While allophane type minerals are known to adsorb OC, our results show that the presence of structural-Fe may enhance the SROAS organic C stabilization capacity, depending on organic compound structure.

[1] Lenhardt, Stein & Rennert (2023), *Clays and Clay Minerals*. 71, 416-429