

## ***In situ* x-ray reflectivity study of the mica-fulvic acid interface**

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Mineral-organic interface structures are important in controlling physical and chemical properties of soils. The presence of bridging cations is thought to affect this structure because many soil organics typically show amphoteric behaviour. In this study, in-situ specular X-ray reflectivity measurements of the muscovite-soil fulvic acid interface were obtained with high-brilliance synchrotron radiation (Advanced Photon Source; BESSRC 11-ID) to construct an adsorption model of the fulvic acid on the mica surface with Ångström-scale precision. Experiments were conducted with ASTM-V1 grade muscovite, 100 ppm Elliott Soil Fulvic Acid II (IHSS), and 0.005 m BaCl<sub>2</sub> solution.

It was necessary to choose an adequate structural model for the soil fulvic acid, which is composed of polymeric rather than simple molecules. The model selected was a series of Gaussian peaks whose heights and widths were allowed to be varied arbitrarily. The best-fit model of the derived interfacial electron density profile in a 0.005 m BaCl<sub>2</sub> solution showed two discrete peaks, the first more electron-dense than the second, at  $1.90 \pm 0.04$  Å and  $2.91 \pm 0.08$  Å above the mica surface. These peaks correspond to the positions of barium and/or adsorbed water in ditrigonal and basal oxygen surface sites. The best-fit model of the mica-100 ppm fulvic acid data consisted of a discrete peak  $2.62 \pm 0.09$  Å above the mica surface, with other weaker changes in the electron density extending away from the surface. We interpret these changes as due to the formation of a  $\sim 10$  Å thick fulvic acid layer whose thickness is imprecise because of relatively diffuse film interfaces and poor density contrast with the water layer. In a 0.005 m BaCl<sub>2</sub>-100 ppm fulvic acid solution, the electron density peaks nearest the surface matched those in the BaCl<sub>2</sub> solution. The model also suggests a more compact fulvic acid layer, approximately 7.4 Å thick, with sharper boundaries as compared to the model of the fulvic acid layer alone. The model provides insight into the role that barium plays as a bridging cation which may include causing the adsorbed fulvic acid layer to become more condensed.

## ***In situ* AFM study of vermiculite and hydrobiotite interface reactions**

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*In situ* AFM studies show that the alteration of vermiculite and hydrobiotite in aqueous solutions under acidic conditions comprises of several stages: a) uniform crystalline swelling; b) formation of hillocks and dendritic bulges (Fig.1); c) dissolution via etch pit formation; d) decomposition of bulges; e) depolymerization of silicate layers. While the first step is likely caused by hydration of insufficiently hydrated interlayer cations, the formation of hillocks and bulges may be explained by anisotropic osmotic swelling and delamination of silicate sheets. The formation of bulges is not limited to the surface, but also affects deeper interlayers. The three latter stages of alteration (c-e) are slow under ambient conditions, but can be readily observed at  $T = 50 - 125$  °C.

Comparison to other phyllosilicates shows that under acidic conditions vermiculite and hydrobiotite behave very similar to chlorite, but differ to phlogopite and apophyllite (Aldushin et al., 2004a,b). The results provide new details about the kinetics and mechanisms of swelling as a response of sheet silicates to aqueous solutions and stress the reactivity of basal surfaces of phyllosilicates.

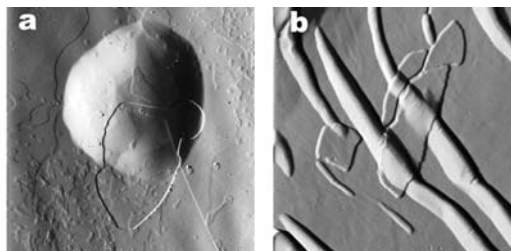


Figure 1. Hillock (a; scan field  $6 \times 6 \mu\text{m}^2$ ) and bulges (b; scan field  $1.5 \times 1.5 \mu\text{m}^2$ ) on the vermiculite surface.

### **References**

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