On the Atomic Structure of Montmorillonite Edges

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Smectites are natural nanominerals abundant in soils and sediments. The swelling behavior and reactivity of montmorillonite (MMT), a smectite mineral with a low layer charge that originates from an excess of isomorphic substitutions in the octahedral sheet relative to the tetrahedral sheet, have found widespread application in engineered barriers and nanocomposite materials. Although the edges of MMT represent a small fraction of the total surface area relative to the basal surfaces, the edges are highly-reactive and contribute to cation and anion retention, soil organic matter stabilization, and the colloidal properties of clay minerals [1]. Despite the importance of the MMT edge in many geological and geochemical processes, the structure remains poorly characterized due to the experimental difficulties of isolating the edge. Atomistic simulations have proven invaluable for the investigation of the edge structure of 2:1 phyllosilicates but, in general, have been limited to quantum mechanical methods due to the absence of a validated forcefield for classical mechanical simulations of the phyllosilicate edge. The CLAYFF forcefield has recently been used in classical MD simulations of the pyrophyllite edge [2]. In this presentation, we extend previous work on the 2:1 clay edge by considering the effects of isomorphic substitutions of Mg for Al in the octahedral sheet on the edge structure. DFT geometry optimizations were also performed to validate and interpret the MD simulation results. Through a combination of classical MD simulations and DFT calculations, we explored the role of substitution location and layer charge on the edge structure of octahedrally substituted MMT. Consistent with the anisotropy of the edges, our results predict a range of disordered structures in the octahedral sheet. The extent and morphology of the disorder was dependent upon the edge face considered but also appears related to the local charge deficit.

[1] Bergaya & Lagaly (2013), Handbook of Clay Science, In *Developments in clay science* 5, 2nd edition. ed. Elsevier, Amsterdam, Oxford, p 1752.
[2] Newton & Sposito (2015), *Clays and Clay Minerals* **65**, 278-290.
This research supported by the National Research Foundation of Korea (NRF-2015R1A4A1041105).