

Atomic Structure, Defects, and Stacking of Clay Particles by Low-Dose, High Resolution (Cryo)-TEM

Michael L. Whittaker^{1,2}, Christian Kisielowski³, Elizabeth A. Montabana⁴, Benjamin Gilbert¹, and Jillian F. Banfield²

¹. Energy Geoscience Division, Lawrence Berkeley National Laboratory, Berkeley CA

². Department of Earth and Planetary Science, University of California Berkeley, Berkeley CA

³. National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley CA

⁴. Molecular Biophysics and Integrated Bioimaging, Lawrence Berkeley National Laboratory, Berkeley CA

Clay minerals play important roles in myriad natural phenomena and engineered systems, from earthquakes and mudslides to barriers for nuclear waste storage and as caprocks for anthropogenic carbon sequestration. Swelling clays are especially important, with complex behavior that arises from the competing interactions between the layers. These include the electrostatic forces originating from heterovalent substitutions that create permanent negative charge within the layers, and the positively charged cations that intercalate between the layers. Predicting the response of swelling clays to changing environmental conditions, specifically ionic strength, remains a challenge due to the incomplete knowledge of clay layer structures and the roles of substitutions and defects at the single-layer limit. Here, we present new observations of clay layer structure at the atomic scale and new studies of the pathway for expansion or collapse under rapid changes in aqueous chemistry.

Atomic-resolution images of single layers of montmorillonite were obtained using low-dose high-resolution transmission electron microscopy (TEM). The threshold for electron beam-induced damage was found to be dependent on the electron energy. The sensitivity of high resolution information (i.e., small lattice spacing) to beam induced damage was up to ten times higher than the 4.5 Å (110) and 4.6 Å (020). At total electron doses less than $\sim 100 \text{ e}^-/\text{Å}^2$, a maximum resolution of 1.2 Å along the [001] zone axis was achieved. Most layers contain point or line defects that alter the local orientational symmetry in the vicinity of the defect. Edge structures were also clearly resolved. Both the defect and edge structures likely have important implications for the stacking of layers into particle stacks.

Dynamic interactions within stacks of clay layers in aqueous solution were investigated by time-resolved small-, medium- and wide-angle synchrotron X-ray scattering, and corroborated with low-dose cryo-TEM. The exchange of potassium for sodium in the interlayer space was found to occur within seconds, accompanied by collapse of the interlayer water from three to two discrete layers. However, theory predicts that complete exchange should occur within milliseconds. Using cryo-TEM, we directly measure the average interlayer separation and see evidence for rotational interparticle ordering that is dependent on the cation concentration and type and may represent the rate limiting step in the process of collapse.

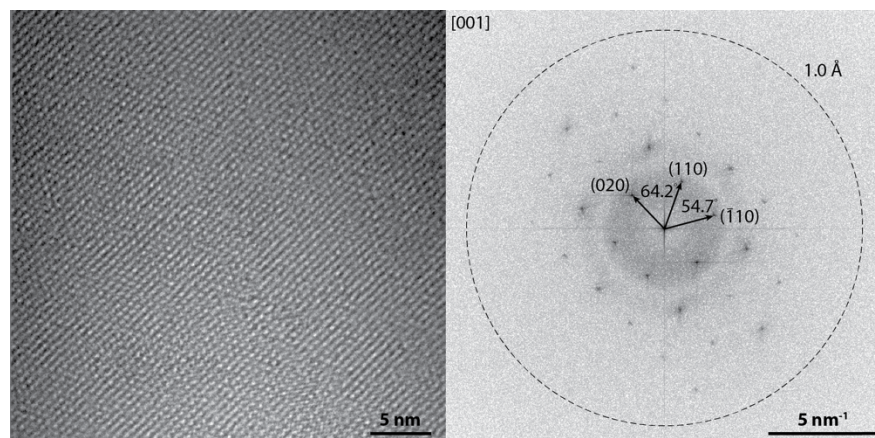


Figure 1. Low-dose, HRTEM image of montmorillonite along the [001] zone axis (left) and associated FFT (right).

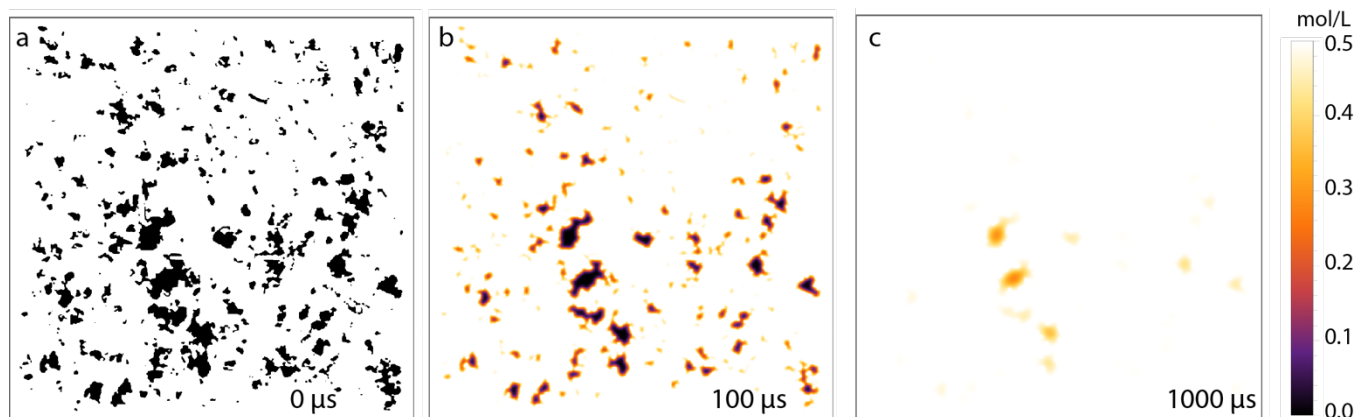


Figure 2. Monte Carlo simulation of the exchange of potassium for sodium in montmorillonite. (a) Before exchange, where black particles represent Na-saturated montmorillonite particles and the exterior solution (white) contains 0.5 M NaCl and 0.5 M KCl. (b) 100 μs and (c) 1000 μs after the initiation of exchange.