Charge Heterogeneity and Nanostructure of 2:1 Layer Silicates by High-Resolution Transmission Electron Microscopy

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Abstract: Several soil and reference smectites and vermiculites and one reference illite were examined by high-resolution transmission electron microscopy (HRTEM) to decipher the nanostructure and layer charge heterogeneity in these minerals. HRTEM results were compared with those obtained from powder X-ray diffraction (XRD) analysis. Samples were either exchanged with Na^+ ions followed by equilibration with a very dilute solution of NaCl in a pressure membrane apparatus at 316 hPa (pF = 2.5) to see the effect of hydration and applied pressure on layer organization, or exchanged with dodecylammonium ions to see the expansion behavior. Oriented samples were embedded in a low viscosity resin and cut approximately 500 Å thick perpendicular to d(001) using an ultramicrotome fitted with a diamond knife. In general, Na-saturated soil clays possessed crystallites that were thinner (c-direction) and shorter (ab-direction) as compared with reference clays. In all cases, samples treated with dodecylammonium chloride exhibited nanostructures that were more disintegrated as compared with Na-saturated samples. In a soil vermiculite, dodecylammonium ion exchange showed frayed edges indicating the initiation of mica transformation to vermiculite from edge toward core. In a reference vermiculite (Transvaal) treated with dodecylammonium ions, in addition to completely expanded crystallites, a regular interstratification between expanded vermiculite and mica (phlogopite) layers was clearly observed in some crystallites. Such nanostructural details were not detected by XRD. HRTEM of the Na-treated illite showed thick crystallites having 10 Å layer separations, whereas the dodecylammonium-exchanged illite showed three types of layers with different degrees of expansion indicating charge heterogeneity in illite: 1) unexpanded (10 Å, highest charge) crystallites; 2) expanded high-charge vermiculite-like (24 Å) crystallites; and 3) occasionally expanded high-charge vermiculite-like (24 Å) layers interspersed in the matrix of 10 Å crystallites.

Key Words: Charge heterogeneity • Clays • High-resolution transmission electron microscopy • Illite • Montmorillonite • Nanostructure • Smectite • Vermiculite

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