

Experimental Clay Mineralogy in Electron Microscopy

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Clay minerals are one of the most abundant minerals and widely utilized materials on the earth. However, small particle size and high chemical activity on the particle surface renders the characterization of clay nanoparticles using microscopy approach as difficult and challenging. Recent developments in electron microscopy (EM) and associated technologies have greatly enhanced clay research and made atomic-level visualization feasible. *In-situ* EM experiments at the nano-scale are becoming crucial in understanding the natural processes (interactions and reactions) of clay materials. This paper presents unique applications of *in-situ* heating experiments of clays that reveal microstructural and crystallographic evolution of clay minerals from room to high temperature environments.

Wyoming bentonite (USA) was crushed, dispersed in deionized water, and less than 200 nm nano size smectite was collected using a sedimentation method. A very small drop (~5 μ l) of smectite suspension was pipetted onto a thin holey/Lacey carbon grid and air-dried. The smectite specimen was then placed onto a TEM heating holder/stage (Gatan, Inc) that enabled heating of the sample from room temperature to different temperature settings up to 1,100 °C. The smectite was heated at various temperatures from 100 °C to 1,000 °C in the TEM for different lengths of time. Morphology and electron diffraction (eD) investigation were carried out using JEOL 2100 TEM equipped with Oxford EDS system.

The majority of smectite nanoparticles formed aggregates of different size that composed of thin platy flakes, laths, needle-like fibers without well-defined boundaries and edges, and such morphology appeared quite stable with little change at various temperature before heating to 550 °C for more than 10 hrs. (Figs. 1 to 4). More drastic changes, in both morphology and eD patterns, of smectite were observed after heating at 700 °C. With increased temperature and the duration of heating especially at 550 °C, TEM micrographs showed that edges of the smectite flakes appeared unclear, indistinct, and more homogeneous such that it resembled amorphous materials. A few diffraction rings were enhanced in sharpness and intensity (better crystallinity) after heating at 500 °C for the first hour. The better crystallinity is likely due to the loss of hydroxyl water from the structure. However, with continuous prolonged heating at 550 °C, SAD patterns showed the onset of diffused diffraction rings and HRTEM images also depicted some loss of lattice spacings (Fig. 5). Diffraction patterns quickly weakened after heating at 700 °C, becoming broadly diffused, the size/volume of amorphization increased, and only a few poor lattices remained in a few particles (Fig. 6). After heating at 800 °C the smectite amorphized as shown by both eD pattern and HRTEM images (Fig. 7). This structural disintegration due to rapid dehydroxylation corresponds to results of DTA and TGA analysis. While heating the sample (and thus the Cu grid) to 550 °C or higher, a very small amount Cu vapor from the grid was condensed and adsorbed on the negatively charged surface of the smectite, and the amount increased with the increase of heating temperature (Figs. 6 to 9). This *in-situ* TEM heating experiment illustrated the evolution of smectite microstructure with heating treatment. The formation of Cu nanoparticles on the smectite surface also provided another means to investigate the surface chemistry of smectite at higher temperature.

