

Characterization of smectite to NH₄-illite conversion series in the fossil hydrothermal system of Harghita Băi, East Carpathians, Romania

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ABSTRACT

Ammonium-illite (NH₄-I) is one of the alteration products present in a breccia structure in the fossil hydrothermal system from Harghita Băi (East Carpathians), Romania. A series from smectite (S) via ordered interstratified structures to NH₄-I (40 to 5%S) was characterized by X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), scanning and transmission electron microscopy (SEM and TEM), and chemical analyses. Calculation of one-dimensional X-ray patterns was simulated with the NEWMOD code. Transition from two- to one-water smectite interlayer was identified by XRD. Selected samples were saturated with K⁺-, Mg²⁺-, and Li⁺-cations to differentiate low- to high-charge smectite or beidelite layers. X-ray patterns of random powders of K⁺-saturated samples, heated at 300 °C show a transition from *1Md* to *cis*- and *trans*-vacant *1M* polytype. The cell parameters of the *cis*-vacant and *trans*-vacant *1M* polytype were calculated by oblique texture electron diffraction. The vibration frequencies at 1430 cm⁻¹ of the N-H bond were identified in the samples analyzed. Scanning and transmission electron microscopy images show morphological changes from flaky to lath-like shapes. The mean shape ratio of lath crystals ranges from 6 to 5.42 nm and the mean area from 7.8 to 24 × 10⁴ nm². The mean thickness of the NH₄-I layers ranges from 4.62 to 7.89 nm. The calculated structural formula of end-member NH₄-I (5%S) is: [(NH₄)_{0.66}K_{0.10}Na_{0.01}Sr_{0.02}]_{0.81}(Al_{1.85}Fe_{0.01}Fe_{0.15}Mg_{0.15})_{2.01}(Si_{3.30}Al_{0.70})_{4.00}O₁₀(OH)₂. The fixed NH₄⁺ content quantified ranges from 0.39 to 0.66 atoms per half unit cell [O₁₀(OH)₂]. Tetrahedral and octahedral substitutions took place as the %S decreases. The NH₄-I-S series formed via direct precipitation from solution at different temperatures.

Keywords: Ammonium-illite, chemistry, electron microscopy, Harghita Băi, infrared spectroscopy, polytypes, cell parameters, two- to one-water smectite interlayer, X-ray diffraction