Conversion of Ferruginous Allophanes to Ferruginous Beidellites at 95 °C Under Alkaline Conditions with Alternating Oxidation and Reduction

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Abstract: Ferruginous beidellites with Al:Fe atomic ratios up to 2.36 were obtained when solutions containing Al, Fe^{2+} and H_4SiO_4 were adjusted to pH 8.5 with $Ca(OH)_2$ and incubated at 95 °C in the presence of $CaCO_3$ as a pH buffer. Incubation took place under cyclic reducing and oxidizing conditions achieved by adding 2 m*M* hydrazine at 14–15-d intervals over a period of 10–13 weeks. During the 14–15-d cycle, atmospheric oxygen slowly diffused through the high-density polyethylene bottles used, causing a slow oxidation of Fe(II) to Fe(III). The infrared (IR) spectra of the products approached that of natural beidellite, but indicated little change in octahedral Al:Fe ratio in the products for starting Al:Fe ratios from 2.5 up to 3.5, which was the highest Al:Fe ratio at which a well-crystallized product was obtained. Chemical analysis showed the presence of more Al+Fe in the products than could be incorporated into a dioctahedral formula. After the excess was assigned to a hydroxy-aluminium interlayer, the formula of the most Al-rich beidellite was calculated to be $0.575Ca(Si_{6.85}Al_{1.15})(Al_{2.47}Fe_{1.53})O_{20}(OH)_4$. This composition lay within the range recorded for the ferruginous beidellites that form in Vertisols.

Key Words: Allophane • Beidellite • Infrared Spectra • Nontronite • Vertisols • X-ray Diffraction (XRD)

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