
Transformation of Birnessite to Buserite, Todorokite, and Manganite under Mild Hydrothermal Treatment

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Abstract: Investigations were conducted to determine the hydrothermal transformations of synthetic birnessite exchanged with different metal ions. Autoclaving in a Teflon-lined stainless steel pressure vessel at 155° C for 24 hr of Mg-, Ca-, La-, and Co-saturated birnessite yielded manganese minerals having 10- Å X-ray powder diffraction (XRD) spacings. The autoclaved Mg-birnessite yielded a mineral identical to natural todorokite in its infrared (IR) spectrum and XRD patterns. High-resolution transmission electron microscopy (HRTEM) provided images having 10-, 12.5-, 15-, and 20 Å wide fringes indicating heterogeneous channel widths in the crystallographic *a* direction, and IR spectroscopy produced bands at 757, 635, 552, 515, 460, and 435 cm⁻¹, confirming the product obtained by autoclaving Mg-birnessite to be todorokite. Prolonged autoclaving of Mg-birnessite yielded manganite (γ -MnOOH) as a by-product; manganite did not form when the autoclaving time was shortened to 8 hr. Also, when Ca-saturated samples were autoclaved, the product gave *d*-values of 10 Å, but the XRD lines were broad and heterogeneity of the channel sizes was evident from HRTEM observations. The Ca-derivative had an IR spectrum similar to that of natural todorokite. Images showing 10- Å lattice fringes were observed by HRTEM for the Ni-saturated sample, which also produced an XRD pattern similar to that of the Mg-saturated sample. Co- and La-saturated samples did not form todorokite, although HRTEM of La-saturated samples indicated some 10- Å lattice fringes that were unstable in the electron beam. Birnessite saturated with Na, K, NH₄, Cs, Ba, or Mn(II) gave products having 7- Å spacings upon autoclaving.

Key Words: Birnessite • Buserite • High-resolution transmission electron microscopy • Hydrothermal • Manganite • Todorokite

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