Ion Exchange, Thermal Transformations, and Oxidizing Properties of Birnessite

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Abstract: Synthetic sodium birnessite, having a cation-exchange capacity (CEC) of 240 meq/100 g (cmol/kg) was transformed into Li, K, Mg, Ca, Sr, Ni, and Mn^{2+} cationic forms by ion exchange in an aqueous medium. Competitive adsorption studies of Ni and Ba vs. Mg showed a strong preference for Ni and Ba by birnessite. The product of Mg^{2+}-exchange was buserite, which showed a basal spacing of 9.6 Å (22 ° C, relative humidity (RH) = 54%), which on drying at 105 ° C under vacuum collapsed to 7 Å. Of the cation-saturated birnessites with 7- Å basal spacing, only Li-, Na-, Mg-, and Ca-birnessites showed cation exchange.

Heating birnessite saturated with cations other than K produced a disordered phase between 200 ° and 400 ° C, which transformed to well-crystallized phases at 600 ° C. K-exchanged birnessite did not transform to a disordered phase; rather a topotactic transformation to cryptomelane was observed. Generally the larger cations, K, Ba, and Sr, gave rise to hollandite-type structures. Mn- and Ni-birnessite transformed to bixbyite-type products, and Mg-birnessite (buserite) transformed to a hausmannite-type product. Li-birnessite transformed to cryptomelane and at higher temperature converted to hausmannite. The hollandite-type products retained the morphology of the parent birnessite. The mineralogy of final products were controlled by the saturating cation. Products obtained by heating natural birnessite were similar to those obtained by heating birnessite saturated with transition elements.

Key Words: Birnessite • Bixbyite • Buserite • Cation exchange • Cryptomelane • Hausmannite • Hollandite • Oxidation • Thermal treatment

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