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Birnessite polytype systematics and identification by powder X-ray diffraction

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ABSTRACT

The polytypes of birnessite with a periodic stacking along the **c*** axis of one-, two-, and three-layers are derived in terms of an anion close-packing formalism. Birnessite layers may be stacked so as to build two types of interlayers: P-type in which basal O atoms from adjacent layers coincide in projection along the **c*** axis, thus forming interlayer prisms; and, O-type in which these O atoms form interlayer octahedra. The polytypes can be categorized into three groups that depend on the type of interlayers: polytypes consisting of homogeneous interlayers of O- or P-type, and polytypes in which both interlayer types alternate. Ideal birnessite layers can be described by a hexagonal unit cell (a_h = $b_h \approx 2.85$ Å and $\gamma = 120°$) or by an orthogonal C-centered cell ($a = \sqrt{3}\ b$, $b_h \approx 2.85$ Å, and $\gamma = 90°$); and, hexagonal birnessite polytypes ($1H$, $2H_1$, $2H_2$, $3R_1$, $3R_2$, $3H_1$, and $3H_2$) have orthogonal analogs ($1O$, $2O_1$, $2O_2$, $1M_1$, $1M_2$, $3O_1$, and $3O_2$).

X-ray diffraction (XRD) patterns from different polytypes having the same layer symmetry and the same number of layers per unit cell exhibit *hkl* reflections at identical 2θ positions. XRD patterns corresponding to such polytypes differ only by their *hkl* intensity distributions, thus leading to possible ambiguities in polytype identification. In addition, the characteristics of the birnessite XRD patterns depend not only on the layer stacking but also on the presence of vacant layer sites, and on the type, location, and local environment of interlayer cations.

Several structure models are described for birnessite consisting of orthogonal vacancy-free or of hexagonal vacancy-bearing layers. These models differ by their stacking modes and by their interlayer structures, which contain mono-, di-, or trivalent cations. Calculated XRD patterns for these models show that the *hkl* intensity distributions are determined by the polytype, with limited influence of the interlayer structure. Actual structures of phyllomanganates can thus be approximated by idealized models for polytype identification purpose. General rules for this identification are formulated. Finally, the occurrence of the different polytypes among natural and synthetic birnessite described in the literature is considered with special attention given to poorly understood structural and crystal-chemical features.

Keywords: Birnessite, polytype, phyllomanganate, Mn oxide