INTRODUCTION

Buserite and birnessite are the most common layered hydrous Mn oxides, or phyllomanganates, in natural environments. Birnessite is the main Mn-bearing phase in soils (Taylor et al. 1964; Chukhrov and Gorshkov 1981), and in marine nodules, coatings, and crusts (Burns and Burns 1976; Glover 1977; Chukhrov et al. 1978, 1985, 1989; Drits et al. 1985). Birnessite is also an essential component of some Mn-rich ore deposits (Chukhrov et al. 1987, 1989; Post 1999).

The structures of these minerals consist of layers of edge-sharing Mn-(O,OH) octahedra. Buserite has a 10 Å periodicity along the c* axis with exchangeable cations and two layers of H2O molecules in its interlayer region to compensate for the negative layer charge that arises mostly from the coexistence of heterovalent Mn cations in the octahedral layers (Silvester et al. 1997). Partial dehydration of buserite leads to the formation of 7 Å birnessite with a single layer of H2O molecules and various interlayer cations (Burns and Burns 1977, 1978; Chukhrov et al. 1978, 1989; Cornell and Giovanoli 1982; Stumm 1992; Le Goff et al. 1996), sorption (Gray and Malati 1979; Catts and Langmuir 1986; Paterson et al. 1994; Tu et al. 1994; Appelo and Postma 1999), and redox properties (Oscarson et al. 1983; Stone and Morgan 1984; Stone and Ulrich 1989; Manceau and Charlet 1992; Bidoglio et al. 1993; Silvester et al. 1995; Manceau et al. 1997; Pizzigallo et al. 1998; Daus et al. 2000; Nico and Zasoski 2000; Chorover and Amistadi 2001).

The ability of buserite and birnessite to fix trace elements (Co, Pb, Cd, Cu, Zn, ...) ranks these minerals among the most efficient sorbents of heavy metals (Me) including Pb, Cd, and Zn. MeBi samples were prepared at different surface coverages by equilibrating at pH 4 a Na-rich buserite (NaBu) suspension in the presence of the desired aqueous metal.

Two main types of experimental XRD patterns were obtained as a function of the Me cations sorbed from solution, which exert a strong control on layer stacking sequence, as well as on the location and coordination of Me: (1) CdBi and PbBi samples correspond to a one-layer hexagonal (1H) structure, AbC'a'c'Bc'…, and (2) ZnBi exhibits a one-layer monoclinic (1M) structure in which adjacent layers are shifted by +a/3, AbC'a'Bc'A'b'Ac'B'a'CaBa'C'b'AbC.

Simulated XRD patterns show that octahedral layers contain 0.833 Mn cations (Mn4+ and Mn3+) and 0.167 vacant octahedra; Mninterlayer and adsorbed Mainterlayer compensate for the layer charge deficit. Mninterlayer is octahedrally coordinated in all samples and is located above or below vacant layer octahedra sharing three Olayer with neighboring Mnlayer octahedra to form a triple-corner surface complex (VITC sites). In ZnBi and CdBi samples, Mainterlayer is also located in TC sites; all Cd is octahedrally coordinated whereas about 30% of Zn is tetrahedrally coordinated (IVTC sites). In PbBi samples, all Pb is octahedrally coordinated, most of these cations (~75%) being located in TC sites. Additional Pb is located above or below empty tridentate cavities, sharing three edges with neighboring Mnlayer octahedra (VITE sites).

Structural formulae calculated for each sample show that during the NaBu-to-MeBi structural transformation, interlayer Na+ and Mn2+ are replaced by Me and H+ adsorbed from solution, whereas Mninterlayer resulting from the equilibration of NaBu at low pH is less affected. Sorption of divalent Me above and below vacant layer sites provides optimal conditions for local charge compensation in MeBi.

ABSTRACT

The structure of heavy-metal sorbed synthetic birnessites (MeBi) was studied by powder X-ray diffraction (XRD) using a trial-and-error fitting procedure to improve our understanding of the interactions between buserite/birnessite and environmentally important heavy metals (Me) including Pb, Cd, and Zn. MeBi samples were prepared at different surface coverages by equilibrating at pH 4 a Na-rich buserite (NaBu) suspension in the presence of the desired aqueous metal.

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