WHAT DETERMINES THE COORDINATION CHEMISTRY OF Zn SORBED ON
PHYLLOMANGANATE? A. Manceau, B. Lanson, V.A. Drits, LGIT, Maison des Geosciences, Univ. J. Fourier and CNRS, BP53, 38041 Grenoble Cedex 9, France. manceau@ujf-grenoble.fr, Academy of Science, Moscow, Russia.

Recent studies on the speciation of zinc in soils showed that this element is generally partitioned between clay minerals, Fe oxhydroxides and Mn oxides, and specifically in the phyllomanganate birnessite [1]. The uptake mechanism of trace elements on birnessite is poorly understood and has been systematically described as being similar to that of Zn in chalcophanite (ZnMn$_3$O$_7$.3H$_2$O). In this mineral, the charge deficiency of the MnO$_2$ octahedral layer, arising from Mn$^{4+}$ octahedral vacancies, is perfectly compensated by the bonding in the interlayer region of two octahedrally coordinated Zn$^{2+}$ on either side of each vacant site (Fig. 1a). Successive Mn layers are translated by +a/3 (monoclinic stack), and interlayer water molecules bonded to Zn form weak H-bonds with the next layer. Zn K-edge micro-EXAFS analysis of natural Zn-containing birnessite showed that Zn is effectively capped above octahedral holes of the Mn layer as in chalcophanite but, in contrast, that it is tetrahedrally coordinated (Fig. 1b, [1]). To understand the reasons for this difference, the sorption mechanism of Zn on well-crystallized synthetic hexagonal birnessite (H$_{0.333}$Mn$_{0.123}$Mn$_{0.045}$Mn$_{0.722}$Mn$_{0.111}$□$_{0.167}$)(OH)$_{0.013}$O$_2$.48H$_2$O) has been investigated experimentally by X-ray and electron diffraction, and powder and polarized EXAFS, and empirically by bond valence calculations of the interlayer structure.

It will be argued that one of the clues to the distinctive structural features between birnessite and chalcophanite is the replacement of about 13% of Mn$^{4+}$ by Mn$^{3+}$ in octahedral layers of birnessite, this charge deficit (0.11 charge per Mn) adding to the already important deficit originating from Mn$^{4+}$ vacancies (0.67 charge per Mn). This additional negative layer charge is compensated by the formation of strong H-bonds between water molecules, coordinated to Zn, and oxygen atoms, coordinated to Mn$^{3+}$ in the next Mn layer. Fig. 2 shows that, in the case of a +a/3 monoclinic stack of layer, the formation of strong H-bonds is only feasible when Zn is 4-fold coordinated. Therefore, both the coordination of the interlayer cation and the stacking mode of layers appear to be controlled by the deficit of positive charge in the Mn octahedral layer, and aim at optimizing the amount of positive charges transferred from the interlayer to the Mn layers by covalent and H-bonds. Owing to the non-stoichiometry of natural birnessites, this sorption mechanism, already identified in a natural sample, is believed to be common in nature.


Fig. 1: Polyhedral representation of the structure of chalcophanite (a) and Zn-sorbed birnessite at low surface coverage (b) [1].

Fig. 2: Idealized interlayer structure of phyllosmanganate with an +a/3 stacking mode of Mn layers. a) Octahedral coordination of interlayer Zn. b) Tetrahedral coordination of Zn.