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Surface Structural Control of Trace Element Partitioning in Natural Mn Oxides

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The surface of Mn oxide minerals can be highly reactive and capable of mediating geochemical transformations of other elements. In particular, minerals of the phyllomanganate group, of which birnessite is one of the predominant members, play a pivotal role in sorption and redox processes of dissolved inorganic and organic constituents which occur in soil, groundwater, oceanic and aquatic systems. An understanding of such processes is crucial to the successful prediction of potential contaminant transport in the environment. Until recently, the relatively poor structural characterization of birnessites remained a principal limitation in understanding these reactions at the atomic level. A significant advance towards this goal has been achieved owing to the successful synthesis of the high and low pH forms of birnessite, and synthetic birnessites are becoming benchmark model materials for laboratory studies of natural processes aimed at simplifying the inherent complexity and heterogeneity of natural materials.

An overview of main results obtained on the structure and surface reactivity of birnessites by the complementary use of solution chemistry, X-ray diffraction (XRD), selected area electron diffraction (SAED), and powder and polarized extended X-ray absorption fine structure (EXAFS) spectroscopy will be presented first. It will be shown subsequently how the fundamental knowledge gained on synthetic materials provides key information about the structural chemistry of Mn oxides in natural systems. In particular, hexagonal birnessite was positively identified, and the uptake mechanism of various trace elements determined, by combining, for the first time, spatially resolved micro-X-ray fluorescence (µXRF), µEXAFS and µXRD on third generation synchrotron sources. For instance, zinc was shown to be sorbed in the interlayer space above and below vacant sites with either four- or six-fold coordination.

All-in-all, the following ideas will be highlighted. First, the necessity of coupling synchrotron-based and laboratory structural techniques, such as electron diffraction. Second, the uppermost importance of studying, in parallel to natural samples, carefully synthesized and relevant model compounds. Third, the importance of giving proper quantitative account to the key role of mineral defects in the uptake of trace elements. Fourth, the importance of performing *in-situ* chemical and structural microscopic investigations to determine the partitioning of trace elements among co-existing mineral phases (µSXRF), the nature of elements-bearing phases (µXRD), and the mechanism of metal uptake at the molecular scale (µXAFS) in heterogeneous Earth's surface materials. Only recently, with the advent of high-brilliance synchrotron radiation sources, has it become possible to combine µSXRF, µXRD and µXAFS, and they offer unprecedented scientific opportunities to understand the structural control of trace element partitioning in natural systems.

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