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XPS determination of Mn oxidation states in Mn (hydr)oxides

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ABSTRACT

Hydrous manganese oxides are an important class of minerals that help regulate the geochemical redox cycle in near-surface environments and are also considered to be promising catalysts for energy applications such as the oxidation of water. A complete characterization of these minerals is required to better understand their catalytic and redox activity. In this contribution an empirical methodology using X-ray photoelectron spectroscopy (XPS) is developed to quantify the oxidation state of hydrous multivalent manganese oxides with an emphasis on birnessite, a layered structure that occurs commonly in soils but is also the oxidized endmember in biomimetic water-oxidation catalysts. The Mn$2p_{3/2}$, Mn$3p$, and Mn$3s$ lines of near monovalent Mn(II), Mn(III), and Mn(IV) oxides were fit with component peaks; after the best fit was obtained the relative widths, heights and binding energies of the components were fixed. Unknown multivalent samples were fit such that binding energies, intensities, and peak-widths of each oxidation state, composed of a packet of correlated component peaks, were allowed to vary. Peak-widths were constrained to maintain the difference between the standards. Both average and individual mole fraction oxidation states for all three energy levels were strongly correlated, with close agreement between Mn$3s$ and Mn$3p$ analyses, whereas calculations based on the Mn$2p_{3/2}$ spectra gave systematically more reduced results. Limited stoichiometric analyses were consistent with Mn$3p$ and Mn$3s$. Further, evidence indicates the shape of the Mn$3p$ line was less sensitive to the bonding environment than that for Mn$2p$. Consequently, fitting the Mn$3p$ and Mn$3s$ lines yielded robust quantification of oxidation states over a range of Mn (hydr)oxide phases. In contrast, a common method for determining oxidation states that utilizes the multiplet splitting of the Mn$3s$ line was found to be not appropriate for birnessites.

1. Introduction

Manganese (Mn) oxides occur in a wide variety of soil environments, typically as trace minerals that coat grain surfaces or as fine-grained concretions and nodules [1]. Even when the abundance of Mn oxides is on the order of a few weight percent or less, these phases can exert the primary control on cation exchange [2–6] and on redox activity [7,8]. Mn is known to adopt ten distinct oxidation states (7+ through 3−), but in naturally occurring minerals only three oxidation states (2+, 3+, and 4+) are observed [1]. Mn oxides are the only minerals that are sufficiently oxidative to transform Cr^{3+} to Cr^{6+} [9], and, not surprisingly, the redox activity of a given Mn (hydr)oxide is closely tied to its average Mn oxidation state. Efforts to tease out the relation between valence state and Cr^{3+} oxidation efficiency have targeted the wide range of valence states observed in Mn (hydr)oxides, including:

- monovalent Mn(IV) oxides, such as pyrolusite [$Mn^{4+}O_2$] [10–12];
- monovalent Mn(III) oxides, such as manganite [$Mn^{3+}OOH$] [12] and synthetic $Mn^{3+}{}_2O_3$ [13];
- mixed (MnIII/IV) hydroxides, such as romanechite [$Ba_xMn^{3+}{}_{2x}Mn^{4+}{}_{1-2x}O_2\cdot 2H_2O$], todorokite [$(Ca,Na,K)_x(Mn^{4+},Mn^{3+})_6O_{12}\cdot 3.5H_2O$], cryptomelane [$K_x(Mn^{4+},Mn^{3+})_8O_{16}$], and lithiophorite [$LiAl_2(Mn^{4+}{}_2Mn^{3+})O_6(OH)_6$] [12];
- mixed (MnII/III) oxides, such as hausmannite [$Mn^{3+}(Mn^{2+},Mn^{3+})_2O_4$] [9,12,14]; and
- mixed (MnII/III/IV) oxides, such as birnessite [9,12,14–21].

Comparative investigations reveal that of all Mn oxide phases, birnessite oxidizes Cr^{3+} to Cr^{6+} most rapidly [9,12], but the relationship between Mn oxidation state and the oxidative potential of the mineral is particularly problematic with

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respect to birnessite. Birnessite can exhibit either hexagonal [$Mn^{2+}_{0.05}Mn^{3+}_{0.12}(Mn^{4+}_{0.74}Mn^{3+}_{0.10}\square_{0.17})O_{1.7}(OH)_{0.3}$] or triclinic [$Na_{0.58}(Mn^{4+}_{1.42}Mn^{3+}_{0.58})O_4\cdot 1.5H_2O$] symmetries [22–26], and as indicated by the proposed formulas of these idealized endmembers, the variants of birnessite contain different relative concentrations of Mn^{2+}, Mn^{3+}, and Mn^{4+}. The degree of variation in Mn^{2+}:Mn^{3+}:Mn^{4+} ratios that are observed, or are even structurally allowable, among either hexagonal birnessites or triclinic birnessites, and their relationship to the redox potential is under constrained.

Such concerns are also manifest in the green energy community where, for example, birnessite is a primary phase in biomimetic water-oxidation catalysts [27–31]. In order to understand the efficiency of water oxidation in these systems and the electronic state of the Mn cations in those phases, it is critically important to know the concentrations of Mn(II), Mn(III), and Mn(IV) [32].

Mn K- and L-edge XANES have been used to measure the average oxidation state of Mn by modeling the edge position and the mole fractions of Mn oxidations states by modeling peak shapes, including pre-edge features [33–36]. Nonetheless, XANES is a bulk technique and the near-surface chemistry of the material may be of greater significance as this is where reactions are mediated. Similarly, surface-sensitive information is required to determine the nature and oxidation state of Mn precipitates that form and can undergo redox reactions at mineral surfaces, an important part of the Mn redox cycle in the environment [37,38].

X-ray photoelectron spectroscopy (XPS) is a non-destructive in-house method that has been used since the early 1970s to determine the oxidation states of metals, including manganese, at the near-surface of materials. A common approach takes advantage of the sensitivity of the binding energy (BE) of various electron energy levels (i.e., Mn*2p*, Mn*3p*, and Mn*3s*) to the Mn valence state. This technique can provide an assessment of average Mn oxidation states (e.g. [37]) assuming samples are compared on the same energy scale, not necessarily a trivial task for insulators. Further, it is well known that changes in bonding environment (e.g., variations in ionicity/covalency and the Madelung potential) can affect BEs given the same formal oxidation state. The Auger parameter has also been used to distinguish Mn oxidation states [39].

Much work has focused on correlating the multiplet splitting (MS) in the Mn*3s* line to monovalent Mn oxides such as MnO, Mn_2O_3, MnOOH and MnO_2, where the MS is defined as the energy difference between two prominent peaks that comprise the XPS spectrum; for a compilation of early work see Junta and Hochella [38]. The relevant atomic physics that produces the Mn*3s* MS has been discussed in many previous publications; see for example [40–43]. Typically the relationship for simple oxides is linear, with some studies demonstrating that the MS for the doubly valent (II and III) oxide Mn_3O_4 correctly predicts its oxidation state to be ~2.67+; e.g., Galakhov et al. [44]. This linear relationship for doubly valent compounds is expected on the basis of simple theoretical arguments, as long as the electronegativity of the ligands is similar; for a recent paper see Kosakov et al. [45]. In fact, deviations from linearity have been attributed to certain electronic states [44]. In this regard, it is helpful to note that the Mn*3s* MS for Mn_2O_3 and MnOOH are within error of each other. Obviously, if Mn exhibits three valence states the MS method can at best yield only average oxidation states; it is not clear, however, whether a linear relationship is to be expected.

In only a few cases, Mn*3s* spectra were fit using Mn(II), Mn(III), and Mn(IV) standards to determine the percentage of each oxidation state in potential multivalent aqueous precipitates [46] and synthetic Mn oxides [47]. A number of studies modeled Mn*2p* [45,47–51] and Mn*3p* spectra [52,53]. The papers by co-authors Nesbitt and Banjeree [48–50] are particularly relevant here as they characterized the oxidation state of multivalent K-birnessites. These studies were ambitious because they adapted the atomic multiplet models of Gupta and Sen [54,55] for characterizing the shapes of the Mn(II), Mn(III), and Mn(IV) $2p_{3/2}$ spectral components. Recently, the Mn$2p_{3/2}$ fit parameters from Nesbitt and Banjeree were applied to K-birnessites in a water oxidation catalyst study [32]. The work by Cerrato et al. [52,53] is notable for using the binding energies and shapes of the Mn*3p* lines, along with the Mn*3s* MS to assess the oxidation state of low concentrations of Mn trapped on water filtration media. It is all the more remarkable given that Mn*3s* and *3p* energy levels have low photoionization cross-sections (i.e., low sensitivities).

Despite the technological and environmental importance of layered Mn (hydr)oxides, such as birnessites, and all the structural determinations [22–26], there have been few systematic efforts to determine relative Mn(II), Mn(III), and Mn(IV) concentrations in these multivalent compounds. This knowledge is necessary for a full description of these minerals as well as an understanding of their reactivities. An exception is the work cited above on K-birnessites; however, the XPS characterization of oxidation states was limited to modeling the Mn$2p_{3/2}$ spectrum. In this contribution we present a systematic study comparing and contrasting Mn oxidation states determined by modeling the Mn$2p_{3/2}$, Mn*3p*, and Mn*3s* lines for a broad range of birnessite phases. Additionally, we rigorously tested the efficacy of using the Mn*3s* MS for predicting the average oxidation state of these multivalent Mn (hydr)oxides. Our objective is to develop a purely empirical methodology that is nevertheless robust and easy to implement.

2. Experimental

Near monovalent natural and synthetic minerals were used as standards: MnO (single crystal cleaved in vacuum; data courtesy of Sangeletti et al. [42]), $MnCO_3$ (natural crystals of rhodocrosite from Aldama, Sonora, Mexico and reagent grade powder; no difference detected in Mn peak shapes), MnOOH (manganite; Smithsonian Institution #NMNH 157872), MnO_2 (pyrolusite and rancieite; Smithsonian Institution #NMNH 11478546 and #NMNH 160078, respectively).

Triclinic Na-birnessite was synthesized according to the procedure described in Golden et al. [56]. A 200 ml solution of 0.5 M $MnCl_2$ (Mallinckrodt Baker) was mixed with 250 ml of 5.5 M NaOH (J.T. Baker). The mixture was oxygenated through a glass frit for ~5 h at a rate of 1.5 L/min. The precipitate was divided evenly and centrifuged in 14 centrifuge tubes. The solution was decanted and replaced with fresh deionized (DI) water to rinse. The rinse cycle was repeated five times. Na-birnessite was stored in ~350 ml DI water until experimental use. For experiments, aliquots of Na-birnessite were filtered with a 70 mm, ashless, Grade 40 filter (Whatman), rinsed three times with 100 ml DI water, and left to air-dry. The Na-birnessite was then ground in an agate mortar under acetone to disaggregate clumps. The synthesis of triclinic Na-birnessite with <1 wt% hausmannite was confirmed with a Rigaku II D/MAX-RAPID microdiffractometer (Department of Mineral Sciences, Smithsonian Institution) with a Mo tube source ($\lambda = 0.7093$ Å).

Triclinic K-, Ca-, and Ba-birnessites were created by exchanging interlayer Na in triclinic Na-birnessite with K, Ca, and Ba. A 0.1 M KCl solution was prepared with 1.4951 g KCl (Fluka) diluted to 200 ml. A 0.01 M $CaCl_2$ solution was made from 0.3932 g $CaCl_2\cdot 2H_2O$ (Amresco) diluted to 250 ml with DI water. A 0.1 M $BaCl_2$ solution was mixed using 4.1718 g $BaCl_2$ (J.T. Baker) in 200 ml DI water. All solutions were adjusted to pH 7 using 0.1 M HCl (OmniTrace) and 0.1 M NaOH (J.T. Baker). ~70 to 100 mg of triclinic Na-birnessite was placed in a 250 ml glass beaker with 100 ml of 0.1 M KCl, $CaCl_2$, or