XPS study of reductive dissolution of birnessite by H$_2$SeO$_3$ with constraints on reaction mechanism

**D. Banerjee** and H.W. Nesbitt

Department of Earth Sciences, University of Western Ontario, London, Ontario, N6A 5B7 Canada

**ABSTRACT**

Reductive dissolution of 7 Å birnessite [Mn$_{2+0.05}$Mn$_{3+0.25}$Mn$_{4+0.7}$O$_{1.75}$(OH)$_{0.25}$] by selenious acid (H$_2$SeO$_3$) produces Mn$^{2+}$ and Mn$^{3+}$ surface reaction products (here represented as S-MnOOH and S-MnO, respectively) and Mn$_{2+3+}$-selenite surface complexes at the solution-mineral interface.

Mn$_{2p_{3/2}}$, Se$_{3d}$, and O$_{1s}$ X-ray photoelectron spectra of reacted surfaces reveal that Mn$^{4+}$ of birnessite is reduced simultaneously to Mn$^{3+}$ and Mn$^{2+}$ while Se$^{6+}$ is oxidized to Se$^{4+}$ according to the probable stoichiometric reactions:

$$2\text{MnO}_2 + \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} \rightarrow 2\text{S-MnOOH} + \text{H}_2\text{SeO}_4$$

$$\text{MnO}_2 + \text{H}_2\text{SeO}_3 \rightarrow \text{S-MnO} + \text{H}_2\text{SeO}_4$$

There is no XPS evidence for reduction of surface Mn$^{3+}$ to Mn$^{2+}$ in the presence of selenite. Whereas this reaction proceeds in the presence of arsenite, selenite apparently inhibits reduction of Mn$^{3+}$, perhaps through formation of a strong Mn-selenite surface complex.

The rate of release of Mn$^{2+}$ to dilute selenious acid ($1.5 \times 10^{-3}$ M) is considerably lower than the rate of release to aerated, distilled water at similar pH. This behavior suggests that adsorbed selenite complexes impede the proton promoted dissolution of the soluble Mn$^{2+}$ component of birnessite.

**INTRODUCTION**

The redox cycling of selenium in natural aquatic environments is significant because Se is both an essential and a toxic element (Lakin 1973; Mayland et al. 1989). Previous studies have shown that adsorption and redox reactions of selenium on various mineral surfaces (e.g., Al-, Fe-, Mn-oxides, clays, calcite) are very important processes controlling the mobility and availability of selenium in the environment (Frost and Griffin 1977; Singh et al. 1981; Neal et al. 1987a, 1987b; Balistrieri and Chao 1987, 1990; Goldberg and Glaubig 1988; Sposito et al. 1988; Cowan et al. 1990; Spackman et al. 1990; Velinsky and Cutter 1991; Glasauer et al. 1996; Papelis et al. 1995a, 1995b; Pickering et al. 1995). Although most of the spectroscopic studies have observed the adsorption behavior of selenium at various pH conditions, a few studies have investigated the effect of selenite on dissolution rate of oxides (Sposito et al. 1988; Bondietti et al. 1993). These studies have suggested that at pH $< 5$ selenite enhances dissolution via formation of mononuclear complexes whereas at near-neutral pH selenite greatly inhibits dissolution through formation of strong binuclear surface complexes.

**Birnessite** [Mn$_{1.75}$(OH)$_{0.25}$] is a commonly occurring layer-structured, nonstoichiometric manganese oxyhydroxide in soils and sediments (Giovanoli 1980; Dixon et al. 1986). Several studies using XPS have shown that birnessite is capable of oxidizing a wide range of natural inorganic and organic cationic and anionic species like Co$^{2+}$ (Murray and Dillard 1979; Dillard et al. 1982), Cr$^{3+}$ (Banerjee and Nesbitt 1999a), AsO$_4^{3–}$ (Nesbitt et al. 1998) and oxalate (Banerjee and Nesbitt 1999b) via surface redox reactions. Most of these redox reactions occur at and are restricted to the upper 30 Å of the mineral surface.

The first objective of this paper is to determine the chemi-