Metal Sorption on Soil Manganese Oxides

D. Ross and C. Negra (U. Vermont)
Ross7774
Beamline(s): **X26A**

Introduction: Soil manganese oxides contain reactive sites that affect the behavior of many contaminant metals through sorption and, in some cases, oxidation. These oxides have short-range order and appear more reactive than synthetic Mn oxides. We used XAS techniques and metal adsorption experiments to study the behavior of native soil Mn oxides in high-Mn soils from Vermont's Champlain Valley. Surface reactivity was assessed by the Cr oxidation test (the quantity of Cr(VI) formed from added $Cr(III)Cl_3$). The combination of these techniques provided insights on the nature of the reactive sites.

Methods and Materials: Mn XANES spectra were collected on recently air-dried soils mounted between two layers of prolene. Energy was calibrated to the pre-edge peak of 10% KMnO4 (MnVII) standard with this peak set as 0 eV relative energy. The x-ray microprobe was used to obtain 2-D scans with the monochromator set at 16.5-17.4 keV and a spot size of ~20 x 20 µm. Peaks from individual spectra were fitted and used to estimate point concentrations of metals (SNRLXRF). Soils contained between 0.2 and 1.2% Mn by weight.

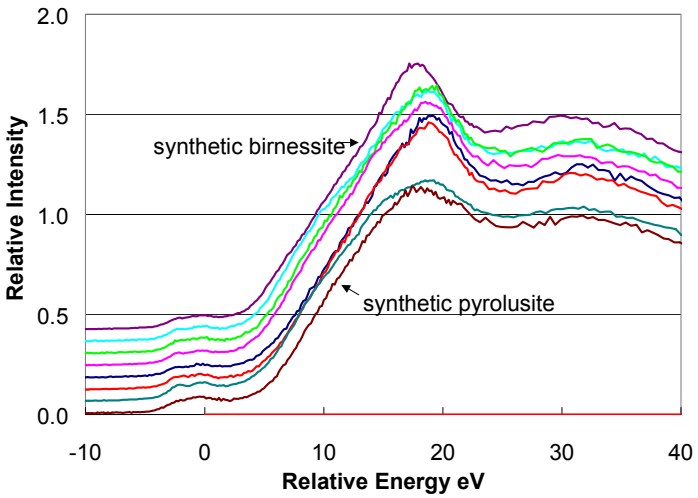

Figure 1. Mn XANES scans for six recently air-dried soils (average of 2 individual scans) and synthetic oxides.

Results: The Mn XANES spectra (Fig. 1) showed similarities to that of synthetic birnessite. In the strongest Cr oxidizing soils, we've always found the main edge position to be at a slightly higher energy than birnessite, suggesting a higher Mn(IV):Mn(III) ratio. There was not a good correlation between Cr oxidizing capacity and edge position but there was a good relationship between pH and edge position. Addition of Mn(II), Co(II), Cu(II), and Pb(II) all significantly decreased the soils ability to oxidize added Cr(III), usually in the order Mn>Co>Pb>Cu. Sorption of these added metals appeared to occur primarily in the region of high Mn oxide concentration (Fig. 2). In some cases, there was a coincidence with concentration of Fe but, in other cases, Mn and the added metal appeared to be separate from the Fe oxides.

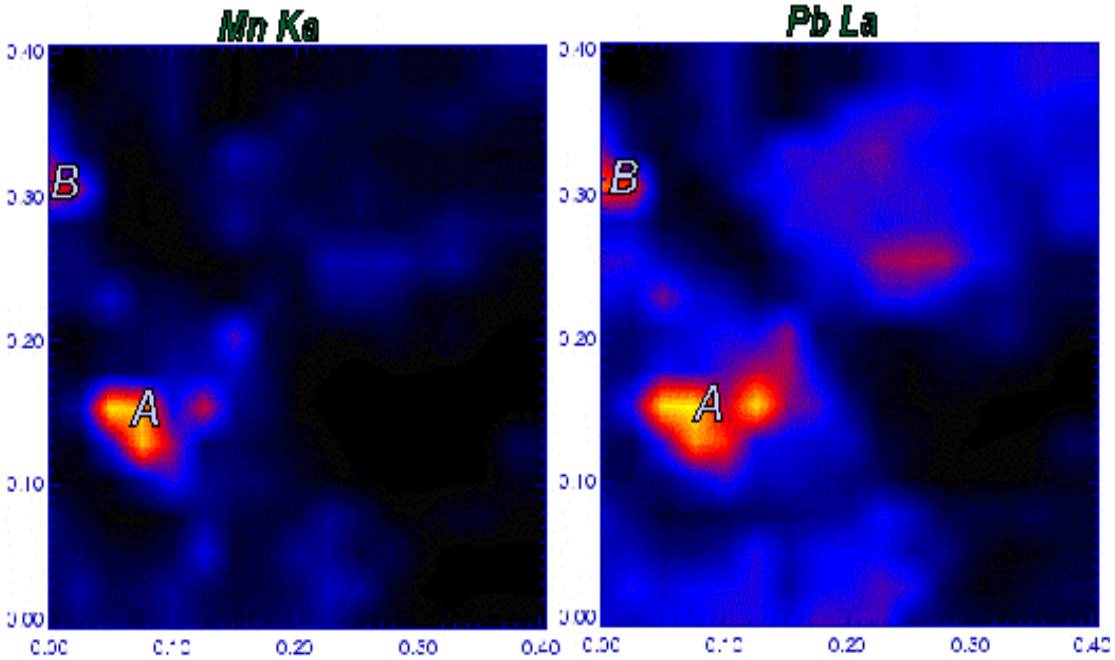

Figure 2. 2-D scans (0.4 x 0.4 mm) of a soil treated with 0.1 mM Pb(NO3)2. Estimated weight percent at (A) Mn = 0.11, Pb=0.07; at (B) Mn=1.07, Pb=0.23.

Conclusions: Metal sorption and oxidation by soil Mn oxides can be observed both by the Cr oxidation test and by XRF mapping. The preponderance of metal associated with native Mn demonstrates the environmental importance of these oxides.