

Oxidation of bioavailable carbon substrate by Mn oxides

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The interstitial water in soil is rich in organic molecules, including organic acids and carbohydrates, which are a direct source of nutrients for microorganisms. Nevertheless, organic molecules also interact with soil minerals through adsorption processes and oxidation reactions. Manganese oxides (MnOx) are among the strongest abiotic oxidants in soils with reduction potentials that are high enough to drive the oxidation of a range of organic molecules. From the Mn side, these reactions can induce the accumulation of Mn(III) in the oxide or dissolution to Mn(II). From the carbon side, we hypothesize that the decarboxylation of organic molecules¹ will induce a cascade of multi-electron oxidative transformation, leading to CO₂ production. These reactions may compete with the microbial activity by altering the availability of carbon substrates.

In this study we investigate the kinetics and mechanism of reaction between glucose, a readily available carbon source for bacteria, and δ -MnO₂ under soil-relevant pH conditions (pH=5 to 7). Batch experiments were conducted by adding 5 mM glucose to a 1 mM δ -MnO₂ suspension, in order to have an excess of the electron donor. Samples were collected over 24 hours and reaction products were monitored to compile mass and an electron balances. The extent of reductive dissolution, as measured by Mn(II)_{aq}, increased over time and with decreasing pH. However, independent of pH, a rapid increase in the Mn(III) content in the solid phase, from 4% to almost 40%, was observed within 20 minutes of reaction, provoking a decrease in the Mn oxide average oxidation number from 4.02 to 3.62. Unvaried total organic carbon concentrations exclude sorption or complete oxidation of glucose to CO₂, while formic acid accumulated in solution as the main product of oxidation at all pH values. Further research is on-going to assess the extent to which redox-sensitive minerals can modulate the bioavailability of carbon substrates in natural systems in presence of bacteria.

(1) Wang, Y.; Stone, A. *Geochimica* **2006**, *70*, 4477–4490.