

Coupled biotic-abiotic oxidation of organic matter by biogenic MnO₂

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In natural systems MnO₂ typically occurs as a biomineral assemblage consisting of inorganic particles and microbial biomass. Both the inorganic and organic fractions of the assemblage can be powerful oxidants of organic carbon. The latter rely on a set of enzymes to drive specific oxidative transformation of reduced C-substrates. The former are strong, less specific, abiotic oxidants that rely on interfacial interactions between the C-substrate and the mineral. Therefore, organic matter can either be oxidized biotically to fuel microbial activity or abiotically at the mineral surface. We expect that both biotic and abiotic pathways can lead to synergistic transformation of organic matter in biomineral assemblages.

We compared the oxidation of soil reduced-C compounds when added to *Pseudomonas putida*-MnO₂ assemblages, purely abiotic δ-MnO₂ and *P. putida*-only suspensions. To track the reactions, we combined FTIR spectroscopy with time dependent measurements of pH, dissolved oxygen and Mn(II)_{aq} concentration, using reductive dissolution of MnO₂ as a proxy for abiotic oxidation of the organic substrate. We found that glucose added to a δ-MnO₂ suspension at circumneutral pH was not transformed, which indicates that glucose oxidation by MnO₂ may be kinetically hindered due to the poor affinity of aldehydes for MnO₂ surfaces. In biogenic MnO₂, glucose addition promoted the reductive dissolution of the mineral. We explain this observation by extracellular enzymatic oxidation of glucose to gluconate by *Pseudomonas putida*, which generates a carboxylic acid moiety that facilitates MnO₂ reduction.

This mechanism highlights the geosymbiotic nature of biological and chemical oxidation in biomineral assemblages, such that oxidation of the organic molecule by the assemblage occurs to a greater extent than in either component alone. We propose that more complex molecules such as natural organic matter may undergo similar oxidative transformations in soils by the coupled action of biotic and abiotic agents.