Manganese Oxide Associations and Interactions with Organic Carbon

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Manganese (Mn) oxides are widely distributed throughout the geologic record and within modern marine sediments and soils. Concentrated Mn veneers reminiscent of rock varnish were also recently observed on Mars. Yet, despite a diversity of abiotic and biotic processes that oxidize Mn(II) to Mn oxide minerals, the operative reaction pathways within modern and ancient environments remain poorly understood. Here we explore the association of organic carbon (OC) with Mn oxides formed in a range of natural deposits and by a diversity of axenic Mn(II)-oxidizing microbes that oxidize Mn(II) to Mn oxides via both direct and indirect (via extracellular superoxide) enzymatic pathways. Organic carbon rapidly associates with Mn oxides during mineralization, leading to considerable levels of mineral-hosted carbon (4 to 17 mol OC/kg mineral). The Mn oxide associated carbon is dominated by proteinaceous and lipopolysaccharide-like material that is stable despite mineral ripening over time to less reactive Mn oxide phases. Organic carbon is both adsorbed on and co-precipitated within the Mn oxides, suggesting that Mn oxides may play a key role in OC burial and preservation within sediments. Further, a dominance of metal-binding and Mn(II)-oxidizing proteins within the biogenic Mn oxides point to a role for these enzymes in the Mn oxide nucleation and/or precipitation processes. In fact, Mn oxide colloids formed by way of abiotic simulations of superoxide mediated Mn oxide formation do not undergo aggregation or crystallization to particulate phases in the absence of OC. This presence and in some cases dominance of proteinaceous carbon within the biogenic and natural oxides may contribute to preferential preservation of proteins in sediments, and thereby provide an explanation for the dominance of protein-dependent metabolisms within the subsurface biosphere.