Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.13321

Complexity of synergistic and competing reactions involved in setting manganese oxide distributions within surface waters - Berner Lecture

COLLEEN M HANSEL

Woods Hole Oceanographic Institution

Presenting Author: chansel@whoi.edu

The distribution of manganese (Mn) oxide deposits is variable throughout the geologic record and in modern environments. Manganese oxides are potent oxidants and adsorbents impacting the speciation, cycling, and (bio)availability of numerous metals, nutrients, and carbon. The cycling and mineralization of Mn occurs via a broad diversity of abiotic and biotic reactions, including both light-dependent and -independent processes. Yet, despite the importance of Mn oxides on the biogeochemistry of terrestrial and aquatic environments, the operative pathways controlling their formation within natural systems are poorly constrained. Historically, photoinhibition of Mn-oxidizing microbes and/or photoreduction of Mn oxides were believed to be responsible for a lack of Mn oxides within surface sun-lit marine waters. This explanation is complicated, however, by recent laboratory-based discoveries of a suite of light-dependent Mn oxide formation pathways, including Mn oxidation by phototrophic organisms and reaction with reactive oxygen species (ROS), both of biotic and abiotic origin. Further, more recent coastal investigations have revealed accumulation of Mn oxides within surface sunlit waters. This presentation will report the presence of Mn oxides in the surface waters of Siders Pond, a meromictic pond on Cape Cod, Massachusetts. Synchrotron-based analyses confirmed that particulate Mn in Siders Pond was composed of Mn oxides, predominantly as the hexagonal birnessite phase ∂-MnO_2. Manganese oxide concentrations varied spatially and temporally, with maximum Mn oxide concentrations occuring within the surface mixed layer during mid-summer. The concentration and distribution of Mn oxides were not well-correlated with any other measured variables, including pH and chlorophyll. A suite of incubation experiments using site water indicated that steady-state Mn oxide levels represented a balance of synergistic and competing Mn redox reactions. These reactions included light-independent mineral catalyzed oxidation, light-dependent microbial oxidation, and photoreduction. This study highlights the importance of concurrent biotic and abiotic reactions in setting Mn oxide concentrations within surface waters, where reaction kinetics of opposing reactions is a key control on the presence and persistence of Mn oxides within surface environments.