

View Abstract

ABSTRACT SYMPOSIUM NAME: Reactivity & Transformation of Manganese Oxides in Natural and Engineering Systems

ABSTRACT SYMPOSIUM PROGRAM AREA NAME: GEOC

CONTROL ID: 3557692

PRESENTATION TYPE: Oral Only : Do not consider for Sci-Mix

TITLE: Effects of reactive halogen species on the formation of photochemically-induced abiotic Mn^{IV} oxides

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ABSTRACT BODY:

Abstract: Manganese (Mn) oxides are strongly oxidative and adsorptive, thus affecting natural geochemical cycling and the fate and transport of pollutants. Because abiotic Mn oxidation kinetics are known to be slow, Mn^{IV} oxides have been assumed to be formed by fast oxidation of Mn²⁺(aq), mediated by fungi or bacteria. Recently, our group discovered that superoxide radicals generated from nitrate photolysis, a simple reaction of nitrate ions and sunlight, can facilitate the oxidation of Mn²⁺(aq) to δ-Mn^{IV}O₂ at a rate comparable to that of biotic processes. This finding motivated us to explore underappreciated oxidants in the environment. Considering the historically unprecedented large quantity of highly saline brine generated from energy and water production, we examined the effects of halide ions (such as Cl⁻ and Br⁻) and their reactive radical species on photochemically-driven Mn²⁺(aq) oxidation and Mn^{IV} oxide formation. Halide ions are abundant in highly saline brine such as seawater and brackish water, as well as in effluent water from desalination and unconventional oil and gas recovery. Under circumneutral pH and ambient temperature, we found that the presence of halide ions increases the oxidation rates of Mn²⁺ and the quantities of formed Mn^{IV} oxides within a few hours. Moreover, because high concentrations of halide ions greatly change the ionic strengths of the systems, they affect the crystallinity of the resulting Mn^{IV} oxide phases. Our findings highlight the unexpected impacts of halogen ions on solid formations in highly saline brine and emphasize the importance of brine photochemistry.

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