Cryo-TEM-EELS study of the impact of organics on $Cr(OH)_3$ oxidation by δ-MnO_2

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The biogeochemical cycling of chromium (Cr) in the environment interconnects closely with that of manganese (Mn), where primarily the latter oxidizes Cr(III) to the mobile and toxic Cr(VI) state. Under most environmental conditions, Cr(III) and Mn(IV) occur as poorly-crystalline Cr(III) hydroxides and Mn(IV) oxides, with their formation often mediated by the action of Cr-reducing or Mn-oxidizing bacteria respectively. While the oxidation of aqueous Cr(III) by Mn(IV) oxides has been widely studied, the reaction between the poorly-crystalline Cr(III) hydroxides and Mn(IV) oxides, and the effects of redox active and complexing organic compounds, remain poorly understood.

To investigate interactions between poorly-crystalline Cr(III) and Mn(IV) phases, δ-MnO_2 and $Cr(OH)_3$ were synthesized and reacted in the presence and absence of selected organic species, including low molecular weight organic acids and humic acids. Throughout the reaction, solution chemistry was monitored, and cryo-TEM imaging and EELS analysis were used to investigate nano-scale changes in phase and redox state.

Despite the poor solubility of the Mn and Cr phases at pH 7, significant amounts of aqueous Cr(VI) were measured over a period of days at concentrations dependent upon the initial Mn to Cr ratio. The presence of humic acid was generally found to increase Cr(VI) production, while the low molecular weight acids exhibited both promotion and inhibition of Cr(VI) production, depending upon their concentration in relation to the solid phases. During TEM-EELS analysis at room temperature, the δ-MnO_2, and to a lesser extent $Cr(OH)_3$, were found to be highly susceptable to beam-damage. However, when cooled to cryogenic temperatures, minimal beam-damage was noted and the distributions of Mn and Cr redox states could be mapped with nano-scale resolution.