Redox speciation of cerium in the presence of colloids

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ABSTRACT

Understanding the interactions between trace metals and colloids is crucial due to their significant influence on metal speciation, mobility, toxicity, and bioavailability. Cerium (Ce), a lanthanide element, is of particular interest because of its abundance and unique redox properties, since it exists in both Ce(III) and Ce(IV) oxidation states. This redox flexibility makes Ce a powerful proxy for paleo-environmental reconstructions.[1] However, distinguishing between Ce(III) and Ce(IV) in colloids like organic matter (OM) and Manganese dioxide (MnO_2) remains challenging, especially at environmentally relevant concentrations. X-ray absorption spectroscopy (XAS) at either Ce K-, L_3- and $M_{4,5}$-edges offer powerful tools to directly resolve Ce oxidation states under these conditions.

In this study, Ce $M_{4,5}$-edge XAS was performed at the SOLEIL DEIMOS beamline for the Ce-OM system (pH 5-10) under both aerobic and anaerobic conditions. DEIMOS beamline offers a perfect sample environment for redox-sensitive elements with its Ar-glovebox connected to the end station. Potential formation of CeO_2 nanoparticle and their structure was determined at Ce K-edge EXAFS on SNBL BM31 beamline. Ce L_3-edge XANES for the Ce-MnO_2 and Ce-OM-MnO_2 systems (pH 6.5) were conducted at the SOLEIL LUCIA beamline.

In the Ce-OM system, the results showed a strong pH dependent Ce oxidation in the presence of OM under ambient atmospheric conditions, with negligible Ce(IV) at pH 5 and nearly complete oxidation (~94%) at pH 10. Dissolved oxygen (O_2) was identified as the primary oxidant, as anoxic conditions lead to negligible Ce oxidation. Results show a preferential complexation of Ce(III) by OM, which stabilizes it over Ce(IV). Ce K-edge EXAFS and transmission electron microscopy showed that oxidation of Ce(III) to Ce(IV) is driven by hydrolysis and precipitation of ~2 nm CeO_2 nanoparticles. In both Ce-MnO_2 and Ce-OM-MnO_2 systems, Ce L_3-edge XANES demonstrated the formation of Ce(IV), indicating that MnO_2 effectively promotes Ce(III) oxidation and facilitates the accumulation of surface-bound Ce(IV) on MnO_2 even in the presence of OM.

Overall, this study clarifies the mechanisms controlling Ce redox behavior in the presence of OM and MnO_2 across different pH conditions. These findings can be directly used in developing risk assessment and management strategies for Ce in aquatic environments. Longer term, they can also be incorporated into predictive models of Ce redox speciation, improving our ability to evaluate and manage Ce contamination in natural systems.

1. Liu, Y.-G.; Miah, M. R. U.; Schmitt, R. A. Cerium: A Chemical Tracer for Paleo-Oceanic Redox Conditions. *Geochim. Cosmochim. Acta* **1988**, *52* (6), 1361–1371. https://doi.org/10.1016/0016-7037(88)90207-4.