Redox Speciation Of Cerium In The Presence Of Natural Organic Matter

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ABSTRACT

Understanding the interactions between trace metals and natural organic matter (NOM) is crucial due to its 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 complex natural matrices like organic matter remains challenging, especially at environmentally relevant concentrations. X-ray absorption spectroscopy (XAS) at the Ce $M_{4,5}$-edges may offer a robust analytical approach to directly resolve Ce oxidation states under these conditions.

XAS measurements were performed at the DEIMOS beamline, which offers a perfect sample environment for redox sensitive elements, with its Ar-glovebox connected to the end station. Ce redox speciation was investigated across a 5-10 pH range in the presence of NOM under both aerobic and anaerobic conditions. To highlight the role of NOM, parallel experiments were performed without NOM under aerobic conditions. Linear combination fitting with Ce(III) and Ce(IV) references was applied to determine Ce redox speciation.

The results showed a strong pH dependent Ce oxidation in the presence of organic matter under aerobic 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 anaerobic conditions lead to negligible Ce oxidation. At pH 6, in the absence of NOM, ~50% Ce(IV) formed, whereas the Ce-NOM system showed only ~25% Ce(IV). This finding is consistent with preferential complexation of Ce(III) by organic matter, which stabilizes the reduced state and limits the oxidation. At higher pH (8–10), more than 80% Ce(IV) formed, where oxidation is driven by hydrolysis and precipitation as CeO_2 nanoparticles, independent of organic matter.

Overall, this study clarifies the mechanisms controlling Ce redox behavior in the presence of organic matter 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.

REFERENCES

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