



Siderophore-mediated oxidation of Ce and fractionation of HREE by Mn (hydr)oxide-coprecipitation and sorption on MnO₂: Experimental evidence for negative Ce-anomalies in abiogenic manganese precipitates

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We conducted experiments with Rare Earths and Yttrium (REY), where the REY were sorbed on synthetic manganese dioxide as well as on coprecipitating manganese (hydr)oxide in the presence and absence of the siderophore desferrioxamine-B (DFOB). Siderophores are a group of globally abundant biogenic complexing agents which are excreted by plants and bacteria to enhance the bioavailability of Fe in oxic environments. The model siderophore used in this study, DFOB, is a hydroxamate siderophore occurring in almost all environmental settings with concentrations in the nanomolar to millimolar range and is one of the most thoroughly studied siderophores.

In the absence of siderophores and other organic ligands, trivalent Ce is usually surface-oxidized to tetravalent Ce during sorption onto manganese (hydr)oxides. Such Mn precipitates, therefore, often show positive Ce anomalies, whereas the ambient solutions exhibit negative Ce anomalies (Ohta and Kawabe, 2001).

In marked contrast, however, REY sorption in the presence of DFOB produces negative Ce anomalies in the Mn precipitates and a distinct and characteristic positive Ce anomaly in the residual siderophore-bearing solution. Furthermore, the heavy REY with ionic radii larger than the radius of Sm are also almost completely prevented from sorption onto the Mn solid phases. Sorption of REY onto Mn (hydr)oxides in the presence of DFOB creates a distinct and pronounced fractionation of Ce and the heavy REY from the light and middle REY. Apart from Ce, which is oxidized in solution by the siderophore, the distribution of the other REY mimics the stability constants for multi-dentate complexes of REY with DFOB, as determined by Christenson & Schijf (2011). Heavier REY are forming stronger complexes (and are hence better “protected” from sorption) than light REY, excluding Ce. Preferential partitioning of Ce into the liquid phase during the precipitation of Mn (hydr)oxides has only rarely been described for natural Mn (hydr)oxides (e.g., Tanaka et al., 2010, Loges et al., 2012). Our experimental results demonstrate that biogenic organic ligands such as hydroxamate siderophores, may produce solutions with positive Ce anomaly (Bau et al., 2013) and may even counteract the surface oxidation of Ce on Mn (hydr)oxides.

References

Bau, M., Tepe, N., Mohwinkel, D., 2013. Siderophore-promoted transfer of rare earth elements and iron from volcanic ash into glacial meltwater, river and ocean water. *Earth Planet. Sci. Lett.* 364, 30–36.

Christenson E. A. and Schijf J. (2011) Stability of YREE complexes with the trihydroxamate siderophore desferrioxamine B at seawater ionic strength. *Geochim. Cosmochim. Acta* 75, 7047–7062.

Loges, A., Wagner, T., Barth, M., Bau, M., Göb, S., and Markl, G. 2012. Negative Ce anomalies in Mn oxides: The role of Ce⁴⁺ mobility during water–mineral interaction. *Geochimica and Cosmochimica Acta* 86, 296–317

Ohta A. and Kawabe I. (2001) REE (III) adsorption onto Mn dioxide (δ -MnO₂) and Fe oxyhydroxide: Ce(III) oxidation by δ -MnO₂. *Geochim. Cosmochim. Acta* 65, 695–703.

Tanaka K., Tani Y., Takahashi Y., Tanimizu M., Suzuki Y., Kozai N. and Ohnuki T. (2010) A specific Ce oxidation process during sorption of rare earth elements on biogenic Mn oxide produced by *Acremonium* sp. strain KR21-2. *Geochim. Cosmochim. Acta* 74, 5463–5477.