REY scavenging in the presence of siderophores produces negative Ce anomalies in manganese oxides

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We conducted scavenging experiments with Rare Earths and Yttrium (REY) on Mn (hydr)oxide in presence of the siderophore desferrioxamine B (DFOB). Siderophores are a group of biogenic complexing agents excreted by a wide range of plants and bacteria. 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 or other organic ligands, trivalent Ce is surface-oxidized to Ce(IV) during sorption onto Mn (hydr)oxides. Such Mn precipitates, therefore, often show positive Ce anomalies, whereas the ambient solutions display negative ones (e.g., Fe-Mn crusts and seawater).

However, REY scavenging in the presence of DFOB produces negative Ce anomalies in the Mn (hydr)oxides and a distinct and characteristic positive Ce anomaly in the siderophore-bearing solution. Furthermore, the heavy REY (Sm-Lu incl. Y) also remain in solution, creating strongly Ce- and HREY-enriched residual solutions during scavenging of REY onto Mn (hydr)oxides. This process efficiently separates light REY (excl. Ce) from middle REY and heavy REY.

Such preferential partitioning of Ce into the residual aqueous phase has been described in the literature for natural Mn (hydr)oxides [1], but the mechanism for this is still unclear. Our experimental results demonstrate that biogenic organic ligands such as siderophores that form very strong aqueous complexes with Ce^{4+}, may produce solutions with positive Ce anomalies and Mn (hydr)oxide minerals with negative Ce anomalies, complicating the use of Ce anomalies as paleo-redox proxies.

[1] Loges *et al*. (2012) *Geochim. Cosmochim. Acta* **86**, 296-317.