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# Negative cerium anomalies in manganese (hydr)oxide precipitates due to cerium oxidation in the presence of dissolved siderophores

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## Abstract

We present experimental results on the sorption behavior of rare earth elements and yttrium (REY) on precipitating manganese (hydr)oxide in the presence of the biogenic siderophore desferrioxamine B (DFOB). In marked contrast to inorganic systems, where preferential adsorption of HREY and depletion of LREY is commonly observed in manganese (hydr)oxide precipitates, sorption of REY in presence of the DFOB siderophore leads to HREY-depleted and LREY-enriched patterns in the precipitates. Moreover, our data indicate that surface oxidation of Ce(III) to Ce(IV) during sorption onto manganese (hydr)oxides and the resulting development of a positive Ce anomaly, which are commonly observed in inorganic experiments, are prevented in the presence of DFOB. Instead, Ce(III) is oxidized to Ce(IV) but associated with the dissolved desferrioxamine B which forms complexes with Ce(IV), that are at least twenty orders of magnitude more stable than those with Ce(III) and REY(III). The overall result is the formation of a positive Ce anomaly in the solution and a negative Ce anomaly in the Mn (hydr)oxides. The distribution of the strictly trivalent REY and Eu(III) between the manganese (hydr)oxide phase and the remaining ambient solution mimics the distribution of published stability constants for complexes of REY(III) with DFOB, i.e. the heavy REY form more stable complexes with the ligand and hence are better shielded from sorption than the LREY. Surface complexation modeling corroborates our experimental results. Negative Ce anomalies in Mn precipitates have been described from *biogenic* Mn oxides. Our results provide experimental evidence for the development of negative Ce anomalies in *abiogenic* Mn (hydr)oxide precipitates and show that the presence of the widespread siderophore desferrioxamine B during mineral precipitation results in HREY-depleted Mn (hydr)oxides with negative Ce anomalies.

*Keywords:* Rare earth elements; Siderophores; Desferrioxamine B; Manganese oxide; Cerium anomalies; Cerium oxidation

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## 1. INTRODUCTION

The rare earth elements (REE+Y; REY) are a group of chemically coherent elements and consist of the lanthanides La, Ce, Pr, Nd, Pm, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and the pseudolanthanoid Y. The lanthanides are further subdivided into the light REY (LREY; La-Gd) and heavy REY (HREY; Tb-Lu+Y). Rare earth elements are increasingly used in many high-technological applications (Humphries, 2013). Apart from a significantly rising demand and thus a greater need for viable economic deposits and more effective metallurgical (heavy) REY extraction techniques, the extensive use of REY in technological, medicinal and agricultural applications comes along with a significantly enhanced anthropogenic input into the

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environment. Thus, understanding the fate of REY in the supergene realm is of importance for addressing health-related and environmental issues. The REY are also widely used as geochemical proxies for reconstructing the physico-chemical conditions in aqueous and magmatic systems.

In natural systems, the REY are, with the exceptions of Ce and Eu, strictly trivalent and hence show similar behavior for the whole lanthanide series depending on their specific charge and ionic radii. Cerium and Eu are redox-sensitive and may occur in natural systems also as reduced ($Eu^{2+}$) or oxidized species ($Ce^{4+}$). In the latter case, the higher charge and smaller ionic radius of $Ce^{3+}$ compared to $Ce^{4+}$ leads to decoupling of Ce from its strictly trivalent REY neighbors. Cerium(IV) is usually less mobile than REY(III), which may result in the formation of Ce anomalies during partitioning of REY between solutions and solids. While anomalous behavior of Ce is often observed in low-temperature aquatic systems, the development of Eu anomalies is confined to high-temperature reducing systems. Lanthanide tetrad effects have been described in low-temperature aquatic environments (Masuda et al., 1987; Masuda and Akagi, 1989; Bau, 1996, 1999; Minami et al., 1998; Bau et al., 1998; Ohta and Kawabe, 2001; Pourret et al., 2008; Bau and Koschinsky, 2009; Tanaka et al., 2010). Yttrium anomalies or fractionation of Y and Ho are common and typical of aqueous systems and highly evolved magmatic systems (Bau, 1996).

In natural systems, metal (hydr)oxides are very efficient scavengers of particle-reactive elements like the REY and, thus, the removal of REY from seawater by metal (hydr)oxides, for example, is an important geochemical process (e.g., Koeppenkastrop and De Carlo, 1992; Ohta and Kawabe, 2001; Bau and Koschinsky, 2009; Mayanna et al., 2015). The speciation of REY(III) in seawater is dominated by carbonate complexes (Millero, 1992; Schijf et al., 2015). The competition of dissolved carbonate ligands with hydroxyl and/or organic functional groups located on the surface of the metal-(hydr)oxides leads to constant sorption and desorption of trivalent REY at the particle surfaces (Bau and Koschinsky, 2009) even after an exchange equilibrium has been reached. The redox-sensitive lanthanoid Ce is significantly depleted relative to its trivalent LREY neighbors. This fractionation of Ce from its strictly trivalent LREY neighbors is caused by oxidative scavenging of $Ce^{3+}$ as $Ce^{4+}$ during sorption onto Mn and Fe (hydr)oxide compounds in the water column (e.g., Bau and Koschinsky, 2009). Oxidative scavenging occurs in three independent steps: (i) initial sorption of Ce(III) from seawater along with the other REY(III), (ii) partial oxidation of Ce(III) to Ce(IV) on the (hydr)oxide surface, and (iii) limited desorption of Ce(IV) relative to the REY(III) (e.g., Bau, 1999; Bau and Koschinsky, 2009). This oxidative process enriches Ce(IV) on the particle surfaces and may result in the formation of positive Ce anomalies in normalized REY patterns. Manganese and Fe (hydr)oxide particles continuously scavenge particle-reactive trace metals and slowly accumulate Ce from the ambient solution. They may, therefore, develop positive Ce anomalies, whereas the ambient solution (e.g., seawater) is depleted in Ce and may show a negative Ce anomaly. Absence and presence of Ce anomalies are widely used in geochemistry and (paleo-)oceanography as proxies for redox conditions (i.e., German and Elderfield, 1990; Bau and Dulski, 1996; Pattan et al., 2005; Bau and Alexander, 2006; 2009; Frei et al., 2009, 2013; Baldwin et al., 2012), provided that post-depositional processes did not alter the pristine REY signal.

Experimental evidence for preferential sorption and the development of specific REE signatures is given by, amongst others, Bau (1999) for Fe oxyhydroxides and Ohta and Kawabe (2001) for Mn dioxide and Fe oxyhydroxide, respectively. Ce is oxidatively scavenged by metal (hydr)oxides, but $MnO_2$ exhibits a stronger oxidizing potential for $Ce^{3+}$ than Fe (hydr)oxides due to Mn acting as a catalyst for Ce oxidation (Ohta and Kawabe, 2001). Their sorption experiments revealed that REE sorption onto $MnO_2$ leads to the formation of positive Ce anomalies in the oxides even at slightly acidic to circumneutral pH.

The behavior of cerium during particle scavenging was described in a range of scientific publications (e.g., Koeppenkastrop and De Carlo, 1992; De Carlo and Wen, 1998; Davranche et al., 2004, 2008; Quinn et al., 2006b,a; Quinn et al., 2007; Schijf and Marshall, 2011). However, the presence of organic ligands or organic-ligand producing biota may drastically affect REY fractionation during scavenging onto mineral particles. For example, Fig. 1 shows the REY partition coefficients between $MnO_2$ and ambient solution as obtained by Ohta and Kawabe (2001) for inorganic REY sorption and by Davranche et al. (2005) for

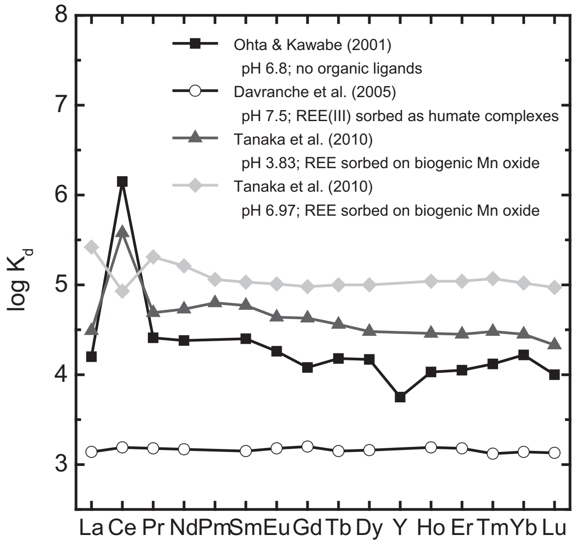

Fig. 1. REY partition coefficients between $MnO_2$ and ambient solution as obtained by sorption experiments conducted by Ohta and Kawabe (2001) without organic ligands, Davranche et al. (2005) with humate ligands and two datasets from Tanaka et al. (2010), where REY were sorbed at different pH on biogenic Mn oxides produced by the *Acremonium sp* strain KR21-2. Note the positive Ce and negative Y anomaly in organic-ligand free experiments, the suppression of Ce oxidation when REY are present as REY(III)-humate complexes and the negative Ce anomaly for REY sorption on biogenic Mn oxide at circumneutral pH.