



Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings



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ABSTRACT

Rare earth elements and yttrium (REY) have a distinct distribution pattern in seawater, and this pattern may be faithfully preserved in carbonate sediments and rocks. Anomalous concentrations of redox-sensitive cerium (Ce) compared with neighbouring REY originate in oxic water column conditions, and as such, Ce anomalies can provide a potentially useful redox proxy in carbonate-dominated marine settings. The methods used to extract REY from carbonates vary widely, and may suffer from widespread leaching of REY from accessory non-carbonate minerals and organic matter, limiting the application of Ce anomalies for palaeo-redox reconstruction. We have systematically compared different methods on 195 carbonate samples with varying purity (% carbonate) from both modern and ancient environments. We used sequential leaching experiments in nitric acid to identify the most 'seawater-like' portion of the carbonate sample where contributions from non-carbonate minerals and organic matter are minimised. We also compared the results of sample dissolution in different types and strengths of acid. Our results confirm that REY concentrations can be inadvertently contaminated by partial leaching of clays and Fe (oxyhydr)oxides during a single-step digestion, and we suggest a pre-leach of 20% of the sample, followed by a partial leach of 40% of the sample to selectively dissolve carbonate. We suggest that REY studies are optimised in carbonates with >85% CaCO₃, and show that dolomites behave differently during the leaching process and must be treated separately. We present REY patterns for modern carbonate-rich sediments from a range of environments, and show that seawater REY are faithfully preserved in some non-skeletal carbonate, but modified leaching procedures are necessary for impure, unlithified or organic rich carbonate sediments. We combine REY with Fe-speciation data to identify how Fe oxides and clays contribute to the REY signal and explore how the two proxies can be used together to provide a complex and high-resolution redox reconstruction in carbonate-dominated marine environments.

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1. Introduction

1.1. The rare earth elements in seawater

The lanthanides, or rare earth elements (REE), consist of fourteen elements that form a series from the lightest (lanthanum, La) to the heaviest (lutetium, Lu). Yttrium (Y) is often included alongside the lanthanides as it has similar chemical properties to Holmium (Ho). Rare earth elements and yttrium (REY) are supplied to the ocean through rivers, Aeolian input and hydrothermal vents, and are removed during sedimentation via particle scavenging (Byrne and Kim, 1990; Douville et al., 1999; Elderfield et al., 1990). Their exceptionally similar chemical properties mean they behave

coherently, resulting in smooth, predictable distribution patterns when normalized to PAAS (post Archean Australian Shale, Pourmand et al., 2012). Normalisation is a common practice as it removes the natural variations in absolute concentrations of REY and allows a comparison with the REY composition of the upper crust, for which shale is a proxy. Hydrothermal input represents a large, but likely secondary flux of REY to the ocean, and carries a flat or heavy rare earth (HREE) depleted REY signal with excess europium (Eu) concentrations (Fig. 1) (Bau and Dulski, 1996; Douville et al., 1999). Rivers are a major source of REY, and carry a flat 'continental type' shale-normalized distribution pattern, but when freshwater interacts with saline waters in estuaries, REY rapidly acquire a typical 'seawater type' pattern with characteristic anomalies (Fig. 1) (Elderfield et al., 1990).

The typical seawater REY profile (Fig. 1) is smooth and coherent with progressive enrichments in heavier REE. REE(III) mono- and di-carbonate ion complexes are the dominant dissolved species in seawater, and the filling of the 4f electron shell across the series results in a systematic increase in

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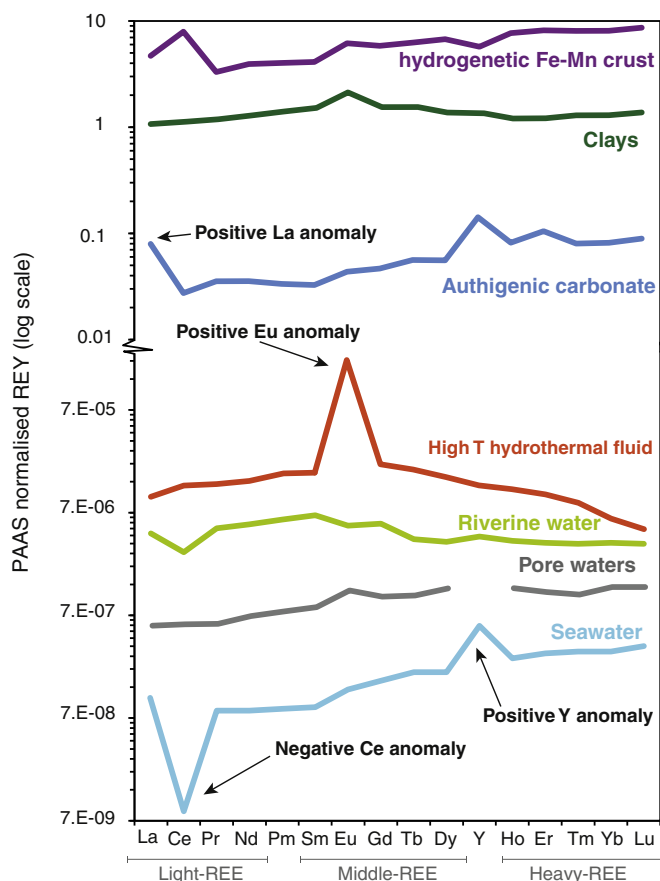


Fig. 1. Shale normalized REY patterns representing key natural environments and minerals, showing typical anomalous features such as Ce, La, Eu and Y anomalies. While some of these distribution patterns are near universal (e.g. seawater), others will vary significantly on a local scale (e.g. pore waters). The rare earth elements are grouped into light (LREE), medium (MREE) and heavy (HREE). Data are based on reported REY, with marine hydrogenetic Fe–Mn crusts and high-temperature hydrothermal (black-smoker) fluids from [Bau and Dulski \(1996\)](#), modern seawater from [James et al. \(1995\)](#), marine pore water from [Haley et al. \(2004\)](#), riverine water from [Soyol-Erdene and Huh \(2013\)](#), and authigenic carbonate and clays from Zebra River (this study).

carbonate complexation from the light to the heavier REE ([Byrne and Kim, 1990](#); [Zhong and Mucci, 1995](#)). This leaves seawater enriched in heavier REE, and the enrichment ratio is often quantified using the shale normalized ytterbium/neodymium (Yb_{SN}/Nd_{SN}) ratio. Deviations from this smooth slope occur where an element in the series has a unique chemical property that affects its solubility and removal via scavenging onto Fe–Mn (oxyhydr)oxides, organic matter and clay particles. In modern seawater this results in positive Y, La, Eu, gadolinium (Gd) and Lu anomalies, and negative Ce anomalies.

Modern seawater contains a large positive Y anomaly (mass ratio of Y to Ho), with larger Y anomalies (40–80) occurring in open marine settings and smaller Y anomalies (33–40) in near shore or restricted settings ([Bau et al., 1997](#); [De Baar et al., 1985a, 1985b](#); [Nozaki and Zhang, 1995](#)). Y/Ho also varies with salinity, phosphate mineral solubility, and fractionation during chemical weathering, biological processes and redox cycling ([Hill et al., 2000](#); [Liu and Byrne, 1997](#)). Our understanding of Y anomalies is somewhat limited, as many earlier studies did not include Y measurements alongside REEs (e.g. [De Baar et al., 1985a](#)). Small relative enrichments in La, Gd and Lu are possibly a consequence of their respective empty, half-filled and full 4f electron shells, which increase their relative stability in solution ([Byrne and Kim, 1990](#); [Byrne et al., 1996](#); [De Baar et al., 1985b](#); [Bolhar et al., 2004](#)). Gd anomalies are generally small, and where great, may be an analytical artifact due to interferences with other ions of similar mass/charge ratio. The presence of these anomalies, particularly Y/Ho > 36, is often used to support the preservation of unaltered seawater REY patterns in the marine rock record.

REY are typically in the +3 oxidation state, but Eu can occur in the +2 oxidation state in strongly reducing environments. Seawater shows variable but small positive Eu anomalies (around 1.5). Eu anomalies can be calculated by comparison with neighbouring REE:

$$Eu_{SN}/Eu_{SN}^* = \frac{2 * [Eu]_{SN}}{[Sm]_{SN} + [Gd]_{SN}} \quad (1)$$

Larger positive Eu anomalies may be present where seawater has mixed with hydrothermal fluids ([Meyer et al., 2012](#)). Apparent Eu anomalies may result from interference with barium oxides formed during analysis, and this can be evaluated through measurement of Ba concentrations ([Jarvis et al., 1989](#)).

REY patterns may also contain redox sensitive Ce anomalies ([Bodin et al., 2013](#); [Meyer et al., 2012](#); [Schroder and Grotzinger, 2007](#)). Ce is unique among the REY because it can exist in both the +3 and +4 oxidation state. In the presence of oxygen, Ce(III) is partially oxidised to Ce(IV) on the surface of Mn (oxyhydr)oxides, where it no longer participates in solid-solution exchange reactions, leaving residual seawater depleted in Ce relative to other trivalent REE ([German and Elderfield, 1990](#)). This fractionation of Ce only occurs under oxic conditions ([German et al., 1991](#)). Ce anomalies (Ce_{SN}/Ce_{SN}^*) are traditionally calculated by comparing the normalized concentration of Ce ($[Ce]_{SN}$) with its neighbouring REE:

$$Ce_{SN}/Ce_{SN}^* = \frac{2 * [Ce]_{SN}}{[La]_{SN} + [Pr]_{SN}} \quad (2)$$

The anomalous behaviour of La can artificially exaggerate the Ce anomaly. A more appropriate way to calculate Ce anomalies, avoiding comparison with La, was proposed by [Lawrence et al. \(2006\)](#), and has been used throughout this study:

$$Ce_{SN}/Ce_{SN}^* = \frac{[Ce]_{SN}}{([Pr]_{SN})^2 / [Nd]_{SN}} \quad (3)$$

Negative Ce anomalies are ubiquitous in the modern, well-oxygenated ocean, but their magnitude varies within and between ocean basins ([De Baar et al. 1985a](#), [De Baar, 1991](#)), and can respond to changes in water column redox on a meter scale (e.g. [De Carlo and Green, 2002](#)). The relative importance of Fe and Mn (oxyhydr)oxides in the oxidation and scavenging of Ce is debated (see [Bau et al., 2014](#)), but Mn is generally considered to be the main carrier phase for excess Ce ([Edmonds and German, 2004](#); [De Baar et al., 1988](#); [De Carlo and Green, 2002](#); [Sholkovitz et al., 1994](#); [De Carlo, 2000](#); [Bau, 1999](#); [Ohta and Kawabe, 2001](#)). Since both Ce and Mn have a high reduction potential, the formation of Ce-enriched Mn oxides requires elevated oxygen concentrations compared with oxic signals from redox proxies based on Fe–C–S and trace element systematics. In modern stratified water columns, negative Ce anomalies develop in the oxic surface waters and are eroded in intermediate conditions, with Ce anomalies absent in deeper fully anoxic waters ([German et al., 1991](#)). In some modern manganese waters, local positive Ce anomalies develop beneath the Mn (IV/II) redoxcline ([Bau et al., 1997](#); [De Baar et al., 1988](#); [De Carlo and Green, 2002](#)). These positive Ce anomalies have also been documented in carbonates from the late Ediacaran ([Mazumdar et al., 2003](#)) and Fe formations and cherts from the Palaeoproterozoic ([Planavsky et al., 2010](#); [Slack et al., 2007](#)). Ce anomaly formation may be disrupted under strongly alkaline conditions ([Möller and Bau, 1993](#); [Pourret et al., 2008](#)), in the presence of siderophores ([Kraemer et al., 2015](#)), as well as in surface waters due to photo-reduction of Mn oxides ([Sunda and Huntsman, 1988](#)).

The preservation of characteristic seawater anomalies in the REY distribution pattern in authigenic minerals can verify that the sample was deposited in open marine conditions and has not been secondarily altered, increasing confidence in other geochemical data and chemostratigraphy ([Bolhar and Van Kranendonk, 2007](#); [Frimmel, 2010](#)). REY can also yield information about relative water depth and proximity to hydrothermal vents. These indicators must be interpreted with caution,

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