Chemical Geology 416 (2015) 36–50

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

A new sample processing protocol for procuring seawater REE signatures in biogenic and abiogenic carbonates

Amir H. Zaky [a],*, Uwe Brand [b], Karem Azmy [a]

[a] Department of Earth Sciences, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada
[b] Department of Earth Sciences, Brock University, St. Catharines, ON L2S 3A1, Canada

ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form 2 October 2015
Accepted 6 October 2015
Available online 9 October 2015

Keywords:
Processing protocol
REEs
Biogenic and abiogenic archives
Robust REE signatures

ABSTRACT

Rare Earth Elements are important proxies for tracing the evolution and redox history of the Earth's hydrosphere. Many biogenic and abiogenic archives have been analyzed for their REE contents with qualified success, which may be due to depositional and post-depositional alteration effects. Review of the database reveals a lack of a rigorous sample processing protocol and probably the leading cause for the spurious REE results reported in the literature.

We propose a 'sample cleaning protocol' that should satisfy the most stringent demands for procuring reliable and robust REEs from marine materials. Without cleaning, the results may represent REE compositions not only of the shell's structure but also of lattice-bound oxides, detritus, particulates and organic remnants. Thus, cleaning of material is a fundamental step that should be conducted with care and attention to detail prior to analyzing their REE contents. To achieve this goal, valves from recently dead *Liothyrella neozelanica* recovered from deep water of the South Pacific Ocean (north of New Zealand) were subjected to five different cleaning procedures. In Procedure-1 (P-1) valve fragments were only washed and rinsed with distilled water. In Procedure-2 (P-2) a set of fragments was immersed in 2.5% hydrogen peroxide (H_2O_2) for three continuous days and then water washed. In Procedure-3 (P-3) valve fragments were physically cleaned using a sharp stainless-steel blade and then water washed. In Procedure-4 (P-4) a set of fragments was physically cleaned then immersed briefly in 10% hydrochloric acid (HCl) until they were deemed clean, and then water washed. In Procedure-5 (P-5) the last set of fragments was processed using all cleaning protocols such as physical scraping, H_2O_2, HCl leaches and water washing.

Detritus and nano-particulates adsorbed on the calcitic structure of brachiopod shells including the proteinaceous periostracum may lead to elevated $\sum$REE content, anomalous Ce/Ce* and elevated Mn, Fe and U concentrations as documented by the P-1 protocol results. Hydrogen peroxide immersion (P-2) eliminates primarily the organic tissue, which leads to an invariant Ce/Ce* anomaly. Physical cleaning (P-3) removes adsorptive nano-particulates and the periostracum, and leads to depleted $\sum$REE and lower Mn, Fe, and U concentrations with a slight Ce/Ce* anomaly. Physical cleaning followed by chemical cleaning (P-4 and P-5) removes adsorptive particulates, organic remnants, the periostracum and the primary layer. These last two procedures produce drastic reductions in $\sum$REE, Mn, Fe, and U concentrations and normal Ce/Ce* anomalies with typical seawater REE signatures in brachiopod calcite.

Procedure P-4 was tested on Silurian, Pennsylvanian and Permian brachiopods and enclosing whole rock as well as conodonts and fish debris to assess the reliability of REE contents in Deep-Time fossils and carbonates. The brachiopod shells contain $\sum$REEs, Mn, Fe, and U concentrations and Ce/Ce* values comparable to their modern counterparts, while in the coeval micritic whole rock they are slightly to significantly enriched. Those with elevated Fe and Mn (by more than 300 and 100 ppm, respectively) their Ce/Ce* values should be adjusted by −13% if they are to be considered in paleoredox investigations. In contrast, REE contents of conodonts give the typical 'bell shape' trend for the lanthanides indicative of post-depositional alteration coupled with extraneous Ce/Ce* anomaly values. Strict adherence to the proposed sample processing protocol is critical if we want reliable and robust 'seawater' REE signatures from brachiopods and whole rocks, and potentially other archives.

1. Introduction

Rare earth elements (REEs) are powerful tools for modeling the hydrosphere, reconstructing paleoenvironmental settings and investigating

---

* Corresponding author.
E-mail address: ahb485@mun.ca (A.H. Zaky).

http://dx.doi.org/10.1016/j.chemgeo.2015.10.015
0009-2541/

mass extinction events (cf. Wright et al. 1984, 1987; Lécuyer et al. 1998, 2003, 2004; Reynard et al. 1999; Webb and Kamber 2000; Kemp and Trueman 2003; Trueman et al. 2006; Anderson et al. 2007; Garbelli et al. 2015). The naturally occurring fourteen lanthanides, constituting the REE group, occur in the trivalent state in seawater. However, redox changes the oxidation state of certain elements to either tetravalent or divalent. In highly oxygenated seawater, oxidation reaction of Ce^{3+} to Ce^{4+} takes place through bacterial mediation. The CeO_2 product of this reaction is highly insoluble and rapidly removed due to scavenging by sinking organic particulates and ferromanganese nodules causing Ce depletion in the corresponding dissolved concentrations (Elderfield and Greaves 1982; Sholkovitz and Schneider 1991; Piepgras and Jacobsen 1992; German et al. 1995; Byrne and Sholkovitz 1996; Nozaki 2001). Therefore, well oxygenated seas and open-oceans are depleted in Ce whereas anoxic water is enriched in it (Elderfield and Sholkovitz 1987; de Baar et al. 1988; Sholkovitz et al. 1989, 1992; German et al. 1991; Haley et al. 2004). On the other hand, reduction of Eu^{3+} to Eu^{2+} is mostly restricted to magmatic processes and high-temperature systems (Dubinin 2004). Thus, Eu concentrations do not vary significantly in seawater except in areas of hydrothermal and mid-oceanic ridge activity, where Eu enrichment has been reported in deposited material (Michard et al. 1983; Sverjensky 1984; Bau 1991; Bau and Möller 1992; Bau and Dulski 1999; Nozaki 2001; Bau et al. 2010).

The gradual diminution of the REE radii with increasing atomic number, the lanthanide contraction, is the result of the progressive filling of their shielded 4f-orbital (de Baar et al. 1985a; Nozaki 2001; Kim et al. 2012). It causes a gradual increase in the stability constant of the free ion in solution across the series from La to Lu (Turner et al. 1981; Bright et al. 2009). The consequently small, but systematic change in their chemical properties leads to slight fractionation in marine water driven by the preferential scavenging of the light elements from the water by sinking particulates relative to the heavy ones (de Baar et al. 1985a; German and Elderfield 1989; German et al. 1991; Bright et al. 2009). Lanthanum, Gd and Lu, with empty-, half- and completely-filled 4f electron shells, respectively, are particularly stable, and thus, have lower tendencies to complex with sinking particulates than the other rare earth elements (de Baar et al. 1985a). The common shale normalized (SN) REE distribution pattern of modern oxygenated seawater results from the gradual enrichment with increasing atomic number punctuated by a negative Ce excursion relative to adjacent La and Pr, with occasionally small positive La, Gd and Lu excursions (de Baar et al. 1985a, 1985b; Elderfield et al. 1988; Bau et al. 1996, 2010; Nozaki 2001; Shields and Webb 2004; Bright et al. 2009). In a deviation from that trend, slightly to extensively positive Ce_{SN} and Eu_{SN} anomalies have been reported from anoxic seawater and hydrothermal vent sites, respectively (de Baar et al. 1988; German and Elderfield 1989; de Baar 1991; German et al. 1991; Hongo and Nozaki 2001; Craddock et al. 2010; Schmidt et al. 2010).

Under anoxic conditions, insoluble cerium oxide, adsorbed on sinking particulates experiences reductive dissolution (de Baar et al. 1988). Such dissolution restores the Ce concentration to its original value and subsequently shifts the Ce excursion of the corresponding seawater REE_{SN} pattern from negative to near unity (German and Elderfield 1989; German et al. 1991). The magnitude and direction of the Ce excursion are quantified by calculating the Ce_{SN} anomaly (Ce/Ce^*), which represents the ratio of the shale-normalized concentration of Ce versus that of neighboring elements La, Pr, Nd or Sm (e.g., de Baar et al. 1985b; Bau and Dulski, 1996). The corresponding value of the Ce_{SN} anomaly is 1 (no anomaly) or more (positive) in anoxic seawater, and less than 1 (negative) when oxygen exists (de Baar et al. 1988). In open seawater, the Ce/Ce^* anomaly gets more pronounced with depth due to a decrease in the amount of dissolved Ce with concomitant enrichments in La, Pr, Nd or Sm (de Baar et al. 1985a, 1985b; German and Elderfield 1989).

REE concentrations, behavior, distribution and redox cycling in modern seas and oceans have been investigated in the last few decades, but its composition in Phanerozoic oceans is still unresolved (Azmy et al. 2011). The biggest difficulty complicating our understanding is the sparse information about the REE signal acquired by modern and fossil carbonate and apatite archives. Biogenic apatite deemed to be the most reliable material for REE studies has been investigated thoroughly in the last few decades (e.g., McArthur and Walsh 1984; Wright et al. 1984, 1987; Elderfield and Pagett 1986; Lécuyer et al. 1998, 2003, 2004; Girard and Lécuyer 2002; Picard et al. 2002; Kemp and Trueman 2003). It has been noted, that modern marine phosphatic brachiopods and ichthyoliths have $\sum$REE contents of less than 1 ppm and display seawater-like REE_{SN} patterns including negative Ce anomalies (Zhang and Nozaki 1996; Wright, 1985, Elderfield and Pagett 1986; Grandjean et al. 1987; Toyoda and Tokonami 1990; Lécuyer et al. 1998, 2004). In contrast, REE signals from fossil marine phosphorites exhibit elevated $\sum$REE contents, middle REE enrichment (bell shape) and/or heavy REE depletion (e.g., Elderfield and Pagett 1986; Trueman and Palmer 1997; Reynard et al. 1999; Trueman and Tuross 2002; Martin and Scher 2004; Bright et al. 2009; Kocsis et al. 2010). In order to explain the enigmatic REE signals, two main hypotheses have been suggested in the literature. First, the composition of the primary carrier responsible for REE removal from the water column has changed (e.g., Roth 1986; Grandjean-Lécuyer et al. 1993), and second, the REE composition of paleo-seawater has evolved with geologic time (McArthur and Walsh 1984; Grandjean et al. 1987, 1988; Ilyin 1998; Picard et al. 2002).

Recrystallization occurs spontaneously during fossilization of biogenic apatite (Trueman and Tuross 2002; Kohn 2008; Kocsis et al. 2010). Modern bones are composed of extremely small nonstoichiometric carbonate-hydroxyapatite crystallites and are intimately associated with the collagenous matrix (Weiner and Price 1986; Moradian-Oldak et al. 1991; Elliott 2002; Rubin et al. 2003). Fossil phosphorite, on the other hand, is made up of large-sized apatite crystals and is nonporous in the region of the collagen (Trueman et al. 2002, 2008a, 2008b). It has been argued that soon after death and upon exposure of the apatite to pore-water, new apatite crystals grow to replace the highly adsorptive metastable carbonate-hydroxyapatite and continue to fill the porosity that was originally occupied by the collagen (Tuross et al. 1989; Reynard et al. 1999; Roberts et al., 2002; Smith et al. 2005). In addition to that, REEs released from labile phases due to changes in pore-water redox conditions in the diagenetic environment may be incorporated into the biogenic apatite crystal lattice (Trueman and Tuross 2002; Trueman et al. 2006). Because of that and the mineralogical dissimilarities between the initial and the final apatite products of the recrystallization process, several authors characterize the bell-shape, absence of negative Ce anomalies and the extremely elevated $\sum$REE concentrations of phosphatic archives synonymous to diagenetic alteration (McArthur and Walsh 1984; Elderfield and Pagett 1986; Trueman and Tuross 2002; Trueman et al. 2002, 2004, 2006, 2008a, 2008b; Bright et al. 2009; Kocsis et al. 2010). Late phase diagenesis may also enhance the REE concentrations of biogenic apatite by up to 50% of the total content depending on REE-uptake conditions (Kocsis et al. 2010).

The REE contents of archives such as foraminifers, corals and reefal microbialites have received some attention (e.g., Palmer 1985; Sholkovitz and Shen 1995; Webb and Kamber 2000; Kamber and Webb 2001; Nothdurft et al. 2004; Olivier and Boyet 2006; Roberts et al. 2012; Loope et al. 2013; Johannesson et al. 2014). Sholkovitz and Shen (1995) argued that modern corals do not fractionate REEs significantly during uptake. However, the measurements of Akagi et al. (2004) show substantial REE differences in distribution coefficient among different coral species suggesting a species-dependent uptake. Although REEs are not involved in the metabolic process, modern foraminiferal tests are enriched in REEs and display a depleted heavy REE_{SN} pattern relative to the ambient seawater that suggests a biological (vital) effect controlling their uptake (Palmer 1985). In addition to that, their REE compositions increase by up to 1 order of magnitude at the sediment–water interface due to the interaction with pore-water (Roberts et al. 2012). Fossils of reefal microbialites exhibit REE_{SN} similar to modern