



Rare earth elements in conodont apatite: Seawater or pore-water signatures?



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ABSTRACT

Rare earth element (REE) compositions of Lower Palaeozoic conodont microfossils from different sites in Laurentia are presented and compared to modern pore-water REE compositions reported in the literature. These data are modelled to account for matrix-induced fractionation of REEs during uptake by apatite. The apatite-water partition co-efficients (K_d) for adsorption of REEs are applied to a range of modern pore-water compositions (i.e. $\text{Pore-water}_N \times K_d$), the resultant data being similar to Palaeozoic conodont apatite compositions. Similar resemblances to modern pore-water REE compositions are shown by palaeofluids derived from conodonts using the inverse relationship in REE adsorption kinetics (i.e. $\text{Bioapatite}/K_d$), with rare low concentration samples yielding HREE-enriched patterns. These results clearly show the importance of matrix effects and hence the post-mortem physico-chemical processes by which elemental uptake occurs in fossil biogenic minerals, which are crucial to consider when interpreting geochemical signatures. Furthermore, the similarities between apatite REE compositions of conodonts and those derived from modern pore-waters challenge prior hypotheses of seawater REE evolution inferred directly from conodont apatite, and question the reliability of conodont apatite as archives of seawater REE chemistry. These outcomes likely have broader implications for fossil bioapatites in general given the physico-chemical processes occurring within marine sediments and the inherent behaviour of apatite-REE systematics.

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1. Introduction

The rare earth element (REE) compositions of fossil bioapatites, such as ichthyoliths, inarticulate brachiopods, and conodonts, have been reported as reliable archives of 'ancient' seawater compositions (e.g. Wright et al., 1984, 1987; Grandjean et al., 1987; Grandjean and Albarède, 1989; Bertram et al., 1992; Grandjean-Lécuyer et al., 1993; Girard and Albarède, 1996; Holser, 1997; Felitsyn et al., 1998; Lécuyer et al., 1998; Reynard et al., 1999; Armstrong et al., 2001; Girard and Lécuyer, 2002; Picard et al., 2002; Lécuyer et al., 2004; Song et al., 2012; Zhao et al., 2013). This view is predicated on the assumption that fossil bioapatites directly recorded ambient seawater REE compositions at the sediment-water interface during early diagenesis, with little or no fractionation. Such studies have invoked changes in palaeoseawater REE composition, having shifted from reducing (anoxic) to oxidizing conditions at various times during the Phanerozoic (e.g. Devonian, Jurassic, Cretaceous).

Modelling REE abundance and fractionation within fossil bioapatites, however, suggests that diagenetic overprinting is common (e.g. Reynard et al., 1999; Lécuyer et al., 2004; Bright et al., 2009; Zhao et al., 2013; Chen et al., 2015; Zhang et al., 2016). Reynard et al. (1999) presented a model that attempted to differentiate altered from unaltered samples based on the extent of adsorption and substitution of REEs in various bioapatites. This adsorption-substitution model predicts that $(\text{La}/\text{Sm})_N$ ratios < 0.3 and hence strong MREE enrichments were derived from chemical substitution during late diagenetic recrystallization, whereas higher $(\text{La}/\text{Sm})_N$ ratios represent REE uptake by adsorption during early diagenesis, which is assumed to reflect ambient seawater composition. Nevertheless, the latter relatively 'pristine' specimens still show MREE-enriched (albeit weaker) patterns and do not resemble present-day seawater patterns.

Lécuyer et al. (2004) used the adsorption-substitution model to screen apparently late diagenetically altered samples from a large database of marine bioapatites described in earlier studies, to assess potential changes in seawater composition through geological time. They determined a REE seawater evolution curve showing a sudden decrease in $(\text{Sm}/\text{Yb})_N$ ratios during the Cretaceous and a transition from MREE-enriched to modern seawater-like abundance patterns with increasing negative Ce anomalies, implying a switch from reducing to oxidizing

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conditions. This was consistent with earlier propositions that seawater composition, and hence the mechanisms for REE scavenging in the oceans, have changed during the Phanerozoic (e.g. Wright et al., 1987; Grandjean-Lécuyer et al., 1993; Picard et al., 2002).

Notably, REE patterns of ancient marine phosphorite deposits are more diverse, likely due to differences in rock fabric, depositional settings, and diagenetic histories (McArthur and Walsh, 1985; Jarvis et al., 1994; Ilyin, 1998a, 1998b; Shields and Stille, 2001). Some Cambrian deposits have yielded shale-normalised REE abundance patterns very similar to modern seawater, with little or at most only minor HREE depletions implying that diagenetic alteration is insignificant (Shields and Stille, 2001; Shields and Webb, 2004). Similarly, REE patterns of modern and fossil marine microbialites (Devonian) and limestones (Permian), in which REE are relatively immobile, are not only identical but also closely match modern seawater (Kawabe et al., 1991; Webb and Kamber, 2000; Shields and Webb, 2004). The presence of these modern-like REE patterns from such varied Palaeozoic sequences is therefore inconsistent with models of MREE-enriched and HREE-depleted ancient seawater and evolving REE compositions as described above.

The common assumption that bioapatites faithfully record ambient seawater REE signatures has often been challenged. Only trace (ppb) levels of REE are incorporated into living marine bioapatites (Shaw and Wasserburg, 1985), whereas post-mortem uptake increases REE concentrations to $\sim 10^6$ – 10^9 relative to modern seawater and produces varied and fractionated patterns (e.g. Wright et al., 1984; Elderfield and Pagett, 1986; German and Elderfield, 1990; Armstrong et al., 2001; Trueman and Tuross, 2002; Kemp and Trueman, 2003; Lécuyer et al., 2004; Bright et al., 2009; Zhao et al., 2013; Chen et al., 2015). REE uptake can occur both at the sediment-water interface and deeper within the subsea sediment column during early and later diagenesis (Toyoda and Tokonami, 1990; Kemp and Trueman, 2003; Shields and Webb, 2004). Notably, non-seawater REE patterns are often recorded by modern ichthyoliths post-mortem, in nearshore environments especially (Elderfield and Pagett, 1986; German and Elderfield, 1990). Pore-waters have thus been considered a major source of bioapatite REE compositions, not only because the latter adsorb REE post-mortem but also because pore-waters have high REE concentrations relative to seawater (e.g. Elderfield and Pagett, 1986; Sholkovitz et al., 1989; German and Elderfield, 1990; Toyoda and Tokonami, 1990; Trueman et al., 2003; Shields and Webb, 2004; Bright et al., 2009; Chen et al., 2015; Zhang et al., 2016). Studies have revealed significant variability in REE pore-water chemistry, which has been related to different environmental conditions and physico-chemical processes occurring close to the sediment-water interface and further within the subsea sediments, and so are not representative of the overlying seawater composition (e.g. Elderfield and Sholkovitz, 1987; German and Elderfield, 1990; Haley et al., 2004; Abbott et al., 2015 and references therein).

Importantly, the high REE adsorption capacity of bioapatites post-mortem together with the inherent histology, ultrastructure, and permeability of the sample, are key controllers of the rate and extent of REE uptake and resultant REE compositions (e.g. Elderfield and Pagett, 1986; Toyoda and Tokonami, 1990; Trueman and Tuross, 2002; Kemp and Trueman, 2003; Pucéat et al., 2004; Trotter and Eggins, 2006; Tütken et al., 2008; Trueman et al., 2008; Herwartz et al., 2011; Kohn and Moses, 2013). It should also be noted that the mechanism of REE uptake in bioapatites differs from other elements commonly used as environmental proxies, such as the major element of oxygen that is incorporated in-vivo within the apatite lattice, and is strongly bonded to the phosphorus atoms thereby commonly preserving (near) primary isotopic compositions.

Recent studies (Bright et al., 2009; Zhao et al., 2013; Chen et al., 2015; Zhang et al., 2016) have investigated the role of host rock lithologies, their results further questioning the veracity of REE compositions of bioapatite microfossils. Such studies identified conodont REE spectra as diagenetic, hence lacked evidence for a seawater origin with some directly related to siliciclastic and/or volcanogenic sources (Chen et al.,

2015; Zhang et al., 2016). Notably, relationships between bioapatite REE patterns and host rock lithologies had been recognised earlier by Picard et al. (2002), based on fish and reptile samples from carbonates, clays, and sandstones, however these authors concluded that bioapatites from carbonate deposits recorded the composition of the overlying water column. Accordingly, the compositions of ambient waters in contact with bioapatites post-mortem, can be strongly influenced by the local depositional environment and host sediments. Those sources, together with physico-chemical REE recycling at and below the sediment water interface, are important controls on pore-water chemistry and bioapatite REE compositions as outlined above.

Here we report REE compositions of Palaeozoic conodonts, supplemented by a small suite of inarticulate phosphatic brachiopod and ichthyolith specimens, from marine carbonates and compare them with modern pore-water compositions reported in the literature. These REE data are also modelled using a new approach to account for apatite-water REE partitioning and fractionation effects (K_d) that occur during uptake by the apatite matrix. Although apatite-seawater K_d has been discussed previously in REE bioapatite studies (e.g. Reynard et al., 1999; Chen et al., 2015), the implications of the resultant fractionation by an apatite matrix have not been fully appreciated. Our results illustrate the matrix controls and conodont apatite REE systematics, and reconciles apparent large discrepancies between fossil bioapatite and modern marine REE compositions. This study highlights the significance of both pore-water chemistry and matrix-induced fractionation, which have important implications for palaeoseawater studies using REE compositions of conodont microfossils, and potentially other fossil bioapatites.

2. Samples and methods

A thorough account of sample details, preparation, analytical methods, and operating conditions have been previously described in an earlier study (Trotter and Eggins, 2006) that focused on the minor and trace elemental concentrations in different bioapatite histologies. Accordingly, only a brief overview of the methodology is given below.

2.1. Samples

Analyses were undertaken on well-preserved Ordovician and Silurian conodonts together with a small suite of inarticulate brachiopods and ichthyoliths, taken from the existing collections of Barnes and McCracken. The conodonts were mostly thermally unaltered, their Colour Alteration Index (Epstein et al., 1977) values being ~ 1 – 2 (McCracken, 2000; Wright et al., 2002; Trotter et al., 2008, 2016). The samples were extracted from marine carbonate deposits from seven localities across Laurentia: (1) Manitoba, Williston Basin (Upper Ordovician, *Amorphognathodus ordovicicus* Zone); (2) Manitoulin Island, southern Ontario (Upper Ordovician, *Amorphognathodus ordovicicus* Zone); (3) western Newfoundland (Middle Ordovician, *Tripodus laevis* Zone); (4) Anticosti Island, Quebec (Upper Ordovician to Lower Silurian); (5) Cornwallis Island (Lower Silurian, Llandovery); (6) Baffin Island (Middle to Upper Ordovician); and (7) Devon Island (Lower Ordovician to Lower Silurian); the latter three from the Canadian Arctic Islands. The data from Sites 1 to 3 each represent discrete temporal intervals, whereas Sites 4, 5, 6, and 7 incorporate multiple samples from a series of continuous stratigraphic sequences. Thus, the sampled sites span a large geographic area, represent shallow shelf to upper slope carbonate facies, and a time interval covering about 30 Myr (470–430 Ma). For further details see Trotter and Eggins (2006).

2.2. Sample preparation and analysis

Rare earth element compositions were determined in situ using laser ablation inductively coupled mass spectrometry (LA-ICPMS). Analyses were in the form of continuous depth profiles using single

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