



Diagenetic uptake of rare earth elements by bioapatite, with an example from Lower Triassic conodonts of South China



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ABSTRACT

The distribution patterns of rare earth elements (REEs) are frequently used as proxies for ancient seawater chemistry or paleomarine environmental conditions. However, recent work has shown that diagenesis can lead to remobilization and inter-elemental fractionation of REEs, and that these effects often occur in conjunction with redox reactions in sediment porewaters. Here, we review existing literature on the diagenetic fluxes of REEs in marine sediments and porewaters in order to systematize existing knowledge on this subject. REEs undergo significant redistribution among sediment phases during both early and late diagenesis as a consequence of adsorption and desorption processes. Remobilization of REEs commonly leads to inter-elemental fractionation, variously leading to enrichment or depletion of the light, middle, or heavy REE fractions. Further, REE remobilization can be facilitated by redox changes, e.g., through reductive dissolution of host phases in suboxic and anoxic porewaters. Characteristic REE distribution patterns develop through these processes: (1) a ‘flat distribution’ signifying predominantly terrigenous siliciclastic influence, (2) a ‘middle-REE bulge’ probably due to adsorption of light and heavy REEs to Mn- and Fe-oxyhydroxides, respectively, and (3) ‘heavy-REE enrichment’ indicative of hydrogenous (seawater) influence (note: all patterns in this paper are normalized to the REE composition of average upper continental crust, or UCC).

In the second part of this study, we undertake an analysis of the REE distributions in conodonts and whole-rock samples from West Pingdingshan, a Permian–Triassic boundary section in South China. Using $\Sigma\text{REE}/\text{Th}$ and Y/Ho ratios, we show that almost all of the conodont samples have a strong diagenetic overprint, and that the hydrogenous REE fraction is small and not isolatable. Furthermore, the conodonts contain two diagenetic REE components, one characterized by low ΣREE (100–300 ppm), high $\Sigma\text{REE}/\text{Th}$ ratios (>1000), strong middle REE enrichment, and Eu/Eu^* ratios of ~1.5–2.0, and the second by high ΣREE (300–2000 ppm), low $\Sigma\text{REE}/\text{Th}$ ratios (~20–30), little or no middle REE enrichment, and Eu/Eu^* ratios of ~1.0. The first component exhibits a pronounced middle-REE bulge that represents an early diagenetic signature associated with suboxic conditions, possibly related to adsorption of REEs onto Fe–Mn oxyhydroxides in the shallow subsurface environment. The second component shows a flat REE distribution that is similar to both our whole-rock samples and average UCC, indicating derivation from REEs released from detrital siliciclastics (e.g., clay minerals), probably at a range of burial depths from shallow to deep. Failure of the conodont samples to yield an isolatable hydrogenous component demonstrates that bioapatite does not always preserve a primary marine REE signature. Given that bioapatite REEs have been widely used for this purpose, often on the assumption of minimal or no diagenetic influence, our findings are likely to necessitate a re-evaluation of the results of many earlier studies. In general, we counsel caution in inferring a hydrogenous origin for REEs in bioapatite owing to frequent diagenetic alteration of REE distributions.

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Contents

1. Introduction	182
2. Rare earth elements.	182
2.1. General background	182

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2.2.	The REE cycle – sources and sinks to seawater	183
2.3.	Adsorption/desorption processes	184
2.4.	Redox influences on sediment REEs	185
3.	REE distributions in modern and ancient marine systems	185
3.1.	Modern marine systems	185
3.2.	Ancient marine systems	189
3.3.	Generalized REE distributions in sediment porewaters	190
3.4.	Cerium and europium anomalies	191
4.	Case study: diagenesis of REEs in Lower Triassic conodonts	192
4.1.	Geologic background	192
4.2.	Methods	193
4.3.	REE profiles and distributions	194
4.4.	Recognition of REE components	194
4.5.	Cerium and europium anomalies	196
4.6.	Evaluation of REE enrichment mechanisms	197
5.	Broader implications of bioapatite REE signals	198
6.	Conclusions	199
	Acknowledgments	199
	Appendix A. Supplementary data	200
	References	200

1. Introduction

The rare earth element (REE) composition of bioapatite has been used in many studies as a proxy for ancient seawater chemistry and a tool for reconstruction of paleomarine environmental conditions (e.g., Grandjean et al., 1987; Wright et al., 1987; Girard and Albarède, 1996; Lécuyer et al., 2004; Trotter and Eggins, 2006; Song et al., 2012; Zhao et al., 2013). However, REE assimilation in the phosphatic skeletons of living organisms is quite limited (Kohn et al., 1999), and bioapatite commonly becomes enriched in REEs by a factor of $>10^6$ through post-mortem uptake (Toyoda and Tokonami, 1990). Bioapatite may faithfully reflect the chemistry of contemporaneous seawater if (1) uptake of REEs proceeds mainly at or near the sediment-water interface from porewaters having a composition similar to that of seawater, and (2) absorption/desorption processes lead to minimal REE fractionation. However, evidence is accumulating that the REE composition of sedimentary porewaters can differ radically from that of overlying seawater as a consequence of diagenetic processes (Sholkovitz et al., 1989; Sholkovitz et al., 1992; Haley et al., 2004; Himmeler et al., 2013; Soyol-Erdene and Huh, 2013). For this reason, it is essential to evaluate possible diagenetic controls on the concentration and distribution of REEs in sediments prior to attempting to reconstruct ancient seawater chemistry or paleomarine environmental conditions.

Sediment porewater chemistry is highly sensitive to a wide range of diagenetic processes. REEs are adsorbed and desorbed from solid phases in the sediment, such as clay minerals, Fe- and Mn-oxyhydroxides, and colloids (Elderfield and Sholkovitz, 1987; Kidder et al., 2003; Pattan et al., 2005). In many systems, (re)mobilization of REEs is a consequence of redox-dependent reactions associated with the transition from an oxic near-surface environment to a deeper sulfidic or methanogenic environment (Haley et al., 2004; Kim et al., 2012). These processes can lead to inter-elemental fractionations among REEs, resulting in distribution patterns that differ from the HREE-enriched pattern typical of modern seawater, and that, in some cases, are characteristic of a specific diagenetic process. With increasing burial, REE concentrations in porewaters tend to become much higher than those in seawater.

The present review documents REE distribution patterns in the sediment and sediment porewaters of various modern marine systems. We examine the relationship of REE patterns to specific diagenetic zones and processes, and we consider the influence on REEs of spatial variation in early diagenetic processes as a function of water depth, organic loading, and other variables. Identifying the processes responsible for REE fractionation is important because of the potential utility of REEs as paleo-environmental and paleoceanographic proxies. Our goal

is to achieve an improved understanding of (1) the controls on REE uptake by bioapatite in marine sediments, and (2) the circumstances under which REEs in bioapatite can serve as a reliable proxy for ancient seawater chemistry and paleoenvironmental conditions.

2. Rare earth elements

2.1. General background

The REEs are a set of 17 elements that comprise the 15-element lanthanide series (La to Lu, $Z = 57$ to 71) plus the chemically similar scandium (Sc; $Z = 21$) and yttrium (Y; $Z = 39$), although promethium ($Z = 61$) does not naturally occur. They are exclusively trivalent except as noted below. The REEs are subdivided by atomic number into three fractions: (1) light REEs (LREE), consisting of La, Ce, Pr, and Nd, (2) middle REEs (MREE), consisting of Sm, Eu, Gd, Tb, Dy, and Ho, and (3) heavy REEs (HREE), consisting of Er, Tm, Yb, and Lu (Table 1). With increasing atomic number, the 4f electron shell of the REEs becomes progressively filled and their ionic radius gradually decreases

Table 1
REE atomic and concentration data.

	Element	Atomic number	Ionic radius ^a (10^{-10} m)		Orbital configuration	Main valence state	Upper continental crust (ppm) ^b
			CN = 6	CN = 8			
LREE	La	57	1.032	1.160	[Xe]5d ¹ 6s ²	+3	30
	Ce	58	1.010	1.143	[Xe]4f ¹ 5d ¹ 6s ²	+3, +4	64
	Pr	59	0.990	1.126	[Xe]4f ³ 6s ²	+3	7.1
	Nd	60	0.983	1.109	[Xe]4f ⁴ 6s ²	+3	26
MREE	Sm	62	0.958	1.079	[Xe]4f ⁶ 6s ²	+3	4.5
	Eu	63	0.947	1.066	[Xe]4f ⁷ 6s ²	+3, +2	0.88
	Gd	64	0.938	1.053	[Xe]4f ⁷ 5d ¹ 6s ²	+3	3.8
	Tb	65	0.923	1.040	[Xe]4f ⁹ 6s ²	+3	0.64
	Dy	66	0.912	1.027	[Xe]4f ¹⁰ 6s ²	+3	3.5
	Ho	67	0.901	1.015	[Xe]4f ¹¹ 6s ²	+3	0.80
HREE	Er	68	0.890	1.004	[Xe]4f ¹² 6s ²	+3	2.3
	Tm	69	0.880	0.994	[Xe]4f ¹³ 6s ²	+3	0.33
	Yb	70	0.868	0.985	[Xe]4f ¹⁴ 6s ²	+3	2.2
	Lu	71	0.861	0.977	[Xe]4f ¹⁴ 5d ¹ 6s ²	+3	0.32

^a From Taylor and McLennan (1985) for trivalent cations; CN = coordination number.

^b From McLennan (2001).

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