# Has the REE composition of seawater changed over geological time?

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The shale-normalised REE pattern of modern seawater is characterised by two main features: negative Ce anomalies and relative enrichment of the heavy REE (Fig. 1c). Positive La anomalies and high Y/Ho ratios could also be added to the list (e.g. Bau and Dulski, 1996). These characteristic features should have been ubiquitous in past oceans, too, were seawater chemistry similar to today. However, one of these features, HREE enrichment (or LREE depletion), is rare in pre-Cenozoic marine phosphate (Jarvis et al., 1994), which has led a series of authors to suggest that pre-Cenozoic seawater had a different REE composition from today (McArthur and Walsh, 1984; Grandjean et al., 1987, 1988; Grandjean-Lécuyer et al., 1993; Ilyin, 1998a,b; Picard et al., 2002). Here we offer a different perspective, one in which seawater REE patterns have hardly changed throughout the Phanerozoic. This contrasting viewpoint is founded on the observation that ancient sedimentary phosphate, especially biogenic phosphate, is an unreliable proxy material for reconstructing seawater REE patterns. We note that other marine authigenic minerals retain REE patterns that do not deviate significantly from those of present-day seawater.

The latest contribution to this debate is presented in a recent article by Picard et al. (2002). That article represents the latest addition to a substantial body of work by researchers at the University of Lyon and we acknowledge their considerable contribution to this field of study. Picard et al. report geochemical data for Jurassic fish and reptile teeth and show them to be depleted in the HREE (Fig. 1b). This means to say that there is a general shale-normalised depletion with increasing atomic number after gadolinium instead of a more typically seawater pattern of progressively increasing HREE enrichment. Although Picard et al. find no theoretical basis for widespread HREE depletion in past ocean water, they nevertheless argue that their data imply a permanent switch in the REE composition of seawater at ∼ 100 Ma. If Picard et al. are correct, then REE scavenging must have been fundamentally different before 100 Ma than today, which might have important implications for carbonate ion availability (and seawater pH) due to the strong control that REE carbonate complexation plays in HREE enrichment in surface waters (Byrne and Kim, 1990).

HREE depletion is clearest in pre-Cenozoic samples showing distinct MREE enrichment, called "bell-

shaped" patterns by Picard et al. Bell-shaped patterns (Fig. 1a) are widely recognised to be secondary features that are wholly unrepresentative of seawater (e.g. German and Elderfield, 1990; Jarvis et al., 1994; Reynard et al., 1999; Shields and Stille, 2002). Picard et al. yield this point but recognise in their data another
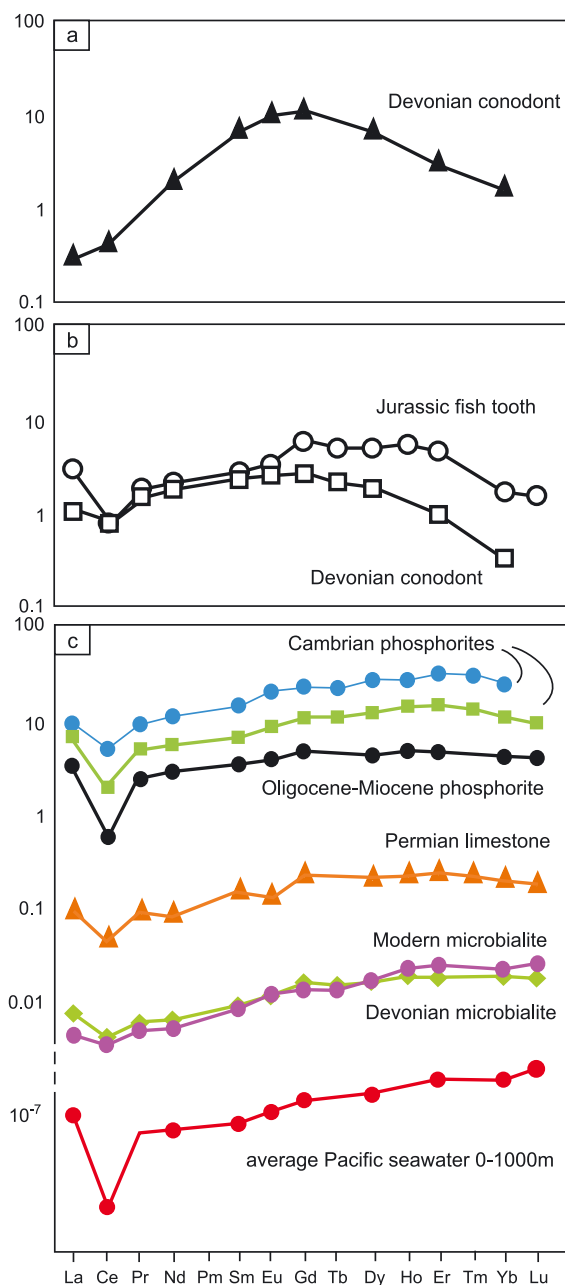
category of REE pattern called "hat-shaped patterns" (Fig. 1b), which are HREE depleted only and are characterised by $(Dy/Yb)_N > 1.8$. It is the last occurrence of a "hat-shaped" pattern in biogenic phosphate that forms the crux of their argument. In their article, Picard et al. remark that the youngest record of a "hat-shaped" REE pattern derives from the Cenomanian of Angola (Grandjean et al., 1987), the total absence of HREE depletion after that time being interpreted to indicate a shift to HREE enrichment in seawater. We would like to point out that there is no sharp temporal divide between HREE-depleted and HREE-enriched biogenic phosphates because hat-shaped patterns of HREE depletion have also been reported from Eocene and Oligocene shark teeth (Grandjean et al., 1987; Grandjean-Lécuyer and Albarède, 1989; Laenen et al., 1997). Indeed even modern phosphatic brachiopods (Lécuyer et al., 1998) and fish teeth (Elderfield and Pagett, 1986; Wright et al., 1987) can be HREE-depleted with $(Dy/Yb)_N$ ratios of 1.7, which is much higher than modern seawater (0.8–1.1), indicating that even present-day fish teeth and inarticulate brachiopods cannot be relied upon to incorporate a seawater REE distribution. Below we outline why biogenic phosphate is such a poor proxy material for seawater REE composition.

Modern biogenic phosphate is enriched in REE by a factor of $10^5$ with respect to ambient seawater. However, in order to reach the high REE concentrations of fossil biogenic phosphate, further post-mortem enrichment of REE by a factor of $10^3$ must take place within the sediment (Toyoda and Toko-



Fig. 1. PAAS-normalised REE patterns (McLennan, 1989) for representative samples of seawater and marine authigenic minerals. Ancient biogenic phosphate (a, b) shows consistently greater MREE arching and HREE depletion than granular phosphorites and microbial limestones of Palaeozoic to Recent age (c), which retain seawater-like $(Dy/Yb)_N$ ratios of between 0.8 and 1.1. REE patterns illustrated are from top to bottom: Cou32A-B (Grandjean-Lécuyer et al., 1993); 93362 (Picard et al., 2002); K25A-4 (Girard and Lécuyer (2002); 992-16-1G (Hein et al., 1999); IX-25 (Shields and Stille, 2001); Blake Plateau-1 (McArthur and Walsh, 1984); EL-1 (Kawabe et al., 1991); average REE pattern from 52 modern microbial limestones (Webb and Kamber, 2000); average REE pattern from 13 microbial limestones of the Lennard Shelf Reef complex, Canning Basin, Australia (Nothdurft, 2001); Piepgras and Jacobsen (1992), where Pr concentrations have been estimated after comparison with other Pacific seawater analyses (e.g. Zhang and Nozaki, 1996).

nami, 1990). Continuing sedimentation ensures that REE scavenging by bones and teeth takes places within the sediment under the generally reducing conditions of diagenesis and organic decay. REE enrichment in biogenic phosphate is best explained by the uptake of non-detrital REE that have been released from oxihydroxide particles within the sediment (Grandjean et al., 1987; Grandjean-Lécuyer and Albarède, 1989), together with the non-quantitative uptake of REE from the host sediment (Lev et al., 1999; Reynard et al., 1999). A study by Palmer (1985) demonstrated that the REE patterns of non-detrital particles in recent foraminifera do not reflect the REE distribution in seawater, but instead are depleted in the HREE with $(Dy/Yb)_N$ of about 1.7. The certainty of post-depositional REE exchange with non-detrital, iron-rich particles and the host sediment should be enough to remove skeletal phosphate from consideration as a proxy material for past seawater REE chemistry (German and Elderfield, 1990). However, the case for a switch in seawater REE composition has been strengthened by other lines of argument outlined below.

Sedimentary pelletal or granular phosphorites constitute a better alternative to biogenic phosphate as a proxy material for seawater REE composition. Such phosphorite forms close to the seawater–sediment interface during periods of hiatus and continual reworking of the top sedimentary layers (Trappe, 1998), which means that early diagenetic exposure to seawater is generally greater than with biogenic phosphate (Ilyin, 1998a). Correspondingly, the REE patterns of granular phosphorites (Fig. 1c) resemble much more closely the modern seawater REE pattern than those of contemporaneous biogenic phosphate (Fig. 1a and b), rarely if ever exhibiting the extreme "bell-shaped" REE patterns typical for conodonts and much skeletal phosphate (Jarvis et al., 1994). However, pre-Cenozoic sedimentary phosphorites are commonly reported to be HREE depleted, too, leading to independent suggestions that there was a switch in seawater REE composition close to the beginning of the Cenozoic (McArthur and Walsh, 1984; Ilyin, 1998a,b).

A closer look at representative HREE-depleted phosphorite patterns (Fig. 1c) reveals an important difference from the "bell-" and "hat-shaped" REE patterns of biogenic phosphate (Fig. 1a and b). While biogenic apatites show a general depletion across all the HREE, phosphorites typically show relatively minor depletion from erbium to lutetium only (Ilyin, 1988a,b; Shields and Stille, 2002). Hence, the parameter used by Picard et al. to illustrate HREE depletion, $(Dy/Yb)_N$, is not anomalously high (>1.8) in many pre-Cenozoic sedimentary phosphorites. For example, Early Cambrian phosphorites of South China yield $(Dy/Yb)_N$ ratios that are typically between 1.1 and 2.0 (Shields and Stille, 2002), and can be as low as 0.8 (Hein et al., 1999; Siegmund, 1995), which is indistinguishable from modern seawater. Because, the precipitation of phosphate results in the preferential removal of MREE from solution (e.g. Byrne et al., 1996), REE uptake by sedimentary apatite is unlikely to be purely quantitative (Reynard et al., 1999), which suggests that the lowest measured $(Dy/Yb)_N$ ratios from any suite of otherwise seawater-like REE patterns, e.g. with a distinct, negative Ce anomaly, will correspond more faithfully to the seawater REE pattern. With that proviso, there appears to be no significant difference between Early Cambrian and modern phosphorite-derived seawater REE patterns.

Due to the tendency of marine phosphate to scavenge REE non-quantitatively from its host sediments (Lev et al., 1999; Reynard et al., 1999), it is unlikely that even granular phosphorite can be considered to be a consistently faithful proxy material for seawater REE composition without the above special pleading or additional constraints. A preferable approach would be to analyse a different marine mineral that does not undergo major REE exchange after deposition. A small step has been made in this direction by analysing the REE compositions of ancient and modern microbial carbonates (Webb and Kamber, 2000). Measured calcites show similar absolute REE concentrations in both ancient and modern examples, which suggests that REE remain relatively immobile in those phases. Fifty two modern examples were analysed yielding identical REE patterns (Fig. 1c) to modern seawater with $(Dy/Yb)_N$ of 0.8 (Webb and Kamber, 2000). By comparison, a Permian open marine limestone analysed by Kawabe et al. (1991) exhibited $(Dy/Yb)_N$ ratios of 1.0 and REE patterns (Fig. 1c), which are identical to modern, near-surface, open Pacific seawater (Zhang and Nozaki, 1996). Late Devonian microbial carbonates from the Lennard Shelf reef complex of the Canning Basin, Western Australia also appear to have retained

REE patterns (Fig. 1c) similar to modern seawater and marine microbialite with a mean $(Dy/Yb)_N$ of 0.9 (Nothdurft, 2001). These carbonate REE patterns contrast markedly with the "bell-" and "hat-shaped" patterns for approximately contemporaneous biogenic phosphate drawn from the literature (Picard et al., Fig. 8, Table 3; Fig. 1a and b).

There appears to be neither empirical evidence nor a theoretical basis for a shift in seawater REE distribution close to the Mesozoic–Cenozoic boundary, while limited data from microbial carbonates and granular phosphorites indicate that seawater REE patterns have remained unchanged throughout the Phanerozoic. Accordingly, HREE depletion and other unseawater-like features in ancient phosphate REE patterns are likely to be derived from post-depositional REE exchange with non-detrital components and non-quantitative uptake of REE from host sediments. Moreover, the striking similarity in REE composition, which has been observed between Recent and Ordovician inarticulate brachiopods (Lécuyer et al., 1998) ,indicates that diagenetic REE scavenging by biogenic phosphate has also not changed greatly over the Phanerozoic. If we cast our gaze even further back, it would appear that HREE enrichment has been a characteristic feature of seawater since at least the late Archaean (Alibert and McCulloch, 1993; Bau and Dulski, 1996; Kamber and Webb, 2001), although far more subtle, but possibly significant changes to HREE fractionation cannot be ruled out (Bau and Möller, 1993). This enigmatically invariant aspect of seawater composition is intriguing and may have important consequences for interpretations of palaeoseawater pH, atmospheric composition (Alibert and McCulloch, 1993), and continental erosion mass balance (Kamber and Webb, 2001).

## Acknowledgements

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