

Rare earth elements in biogenic carbonate as proxies for the marine carbonate system?

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The marine geochemical behaviour of rare earth elements (REE) shows a strong carbonate ion ($[CO_3^{2-}]$) dependence [1]. In seawater (S=35, T=25°C), the contribution of the two carbonate species ($LnCO_3^+$ vs. $Ln(CO_3)_2^-$) is equal at a different pH for each REE, from 8.47 for La to 7.42 for Lu (free pH scale) [2]. If the aqueous complexation of seawater REE exerts a dominant and predictable effect on the uptake of REE during biogenic carbonate precipitation, it hints at the potential for marine calcifiers to preserve a record in their skeletons of the status of the marine carbonate system [3]. However, to accurately interpret REE concentrations in biogenic archives requires knowledge of carbonate/seawater REE partitioning (K_d^{REE}), together with “vital effects”.

To quantify the effect of the marine carbonate system on K_d^{REE} , we adopted an empirical approach by culturing serpulid worms (*Serpula vermicularis*) under three seawater pH treatments for 13 weeks. *Serpula vermicularis* are coastal filter feeders that extrude a mainly calcitic tube. After the experiment, we harvested new tube growth, measured the REE and Ca concentrations, and calculated the K_d^{REE} at four pH values across the range of pH_{NBS} 8.1 to 7.5.

Our results show that differences between the pH treatments are expressed by lower REE concentrations in the serpulid tubes and a flattening of the K_d^{REE} with decreasing pH, while the total dissolved REE concentrations in the experimental tanks remain identical. We use the results to test firstly that a predictable and systematic relationship between K_d^{REE} and pH exists. Secondly, we construct a calibration line using the REE concentration ratios in the serpulid tubes and parameters of the marine carbonate system to identify if this approach to reconstructing change in the marine carbonate system has potential application in fossil biogenic carbonate samples.

[1] Cantrell, K.J. and R.H. Byrne (1987) GCA 51: 597-605. [2] Byrne, R.H. (2002) Geochem. Trans. 3: 11-16. [3] Ponnurangam, A., et al. (2016) Biogeosciences 13: 751-760.