

RARE EARTH ELEMENT GEOCHEMISTRY OF PALEOZOIC STROMATOPOROIDS AND EXTANT SPONGE SKELETONS

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Stromatoporoids are widely considered to be the calcified basal skeletons of sponges. However, fundamental questions regarding taxonomy, phylogeny, and even original skeletal mineralogy remain to be answered for many ancient examples. We measured concentrations of rare earth elements and yttrium (REE+Y) in several Late Devonian stromatoporoids from the Canning Basin, Western Australia and in extant sponges with calcified basal skeletons [e.g., *Spirastrella (Acanthochaetetes) wellsi*] and with calcite spicular skeletons (calcareous sponges within the Calcaronea and Calcinea). Differences in stable O and C isotope incorporation in extant calcareous sponge spicules and demosponge basal skeletons suggest important differences in biomineralization processes in the groups. Such differences in biomineralization are expected to have effects on trace element distributions, and trace element distributions are preservable to some degree even in recrystallized fossils. Rare earth elements were analysed because they have predictable behaviour in seawater leading to an easily recognizable, distinctive distribution that can be preserved in skeletal carbonates.

The shale-normalized REE+Y distribution of *Acanthochaetetes* basal skeletons has seawater-like features, including: 1) high REE concentrations (mean $\Sigma\text{REE} = 1.36$ ppm); 2) uniform light REE depletion (mean $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}} = 0.25$) compared to 0.21 for ambient seawater; 3) negative Ce and positive La anomalies; 4) high Y/Ho ratio (mean 49.9); and 5) positive Gd (mean $\text{Gd}/\text{Gd}^* = 1.14$) and Er (mean $\text{Er}/\text{Er}^* = 1.16$) anomalies. Shale-normalized REE+Y patterns of calcareous sponge spicules (Calcaronea and Calcinea) are highly variable, less coherent, and much lower in concentration (mean $\Sigma\text{REE} = 79$ ppb). The specimens have seawater-like LREE depletion ($\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}} = 0.19\text{-}0.33$), positive La and negative Ce anomalies, and superchondritic Y/Ho ratios ($\text{Y}/\text{Ho} > 39.3$), but pronounced positive Nd and negative Gd anomalies are atypical of seawater. Hence, although Calcaronea and Calcinea cannot be distinguished on the basis of REE behaviour, REE geochemistry distinguishes them from *Acanthochaetetes*. We hypothesize that *Acanthochaetetes* skeletons take up cations in equilibrium with ambient seawater, with no active Ca^{2+} transport by the sponge. On the contrary, the REEs in the spicules of *Calcarea* indicate that biomineralization is partially isolated from ambient seawater, which is consistent with intercellular formation in a sheath, and that sclerocytes play some role in providing Ca^{2+} ions to the site of mineralization. The transport mechanism in the *Calcarea* discriminates against REE in a non-uniform way.

Shale-normalized REE+Y distributions of clean, non-dolomitized tabular Devonian reefal stromatoporoids are seawater-like and, hence, are comparable to those of extant *Acanthochaetetes*. The patterns are characterised by 1) high REE concentrations (mean $\Sigma\text{REE} = 4.18$ ppm); 2) light REE depletion (mean $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}} = 0.74$); 3) negative Ce and positive La anomalies; 4) high Y/Ho ratio (mean 40.5); and 5) positive Gd (mean $\text{Gd}/\text{Gd}^* = 1.17$) and Er (mean $\text{Er}/\text{Er}^* = 1.12$) anomalies. The relatively poor LREE depletion results from secondary diagenetic HREE loss. Data are consistent with tested stromatoporoids being calcite basal skeletons of calcified demosponges. REE+Y patterns of branching stromatoporoids differ somewhat, suggesting that trace element geochemistry may help delineate different taxonomic groups within the extinct sponges.