Elemental fractionation in biogenic calcium carbonates

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Biogenic calcium carbonates (e.g. coral skeleton, foraminifera and bivalve shell) have been widely used as proxies for past changes in sea water temperature because elemental composition (Sr/Ca and Mg/Ca ratio) of their skeletons are believed to vary quantitatively as a function of the ambient seawater temperature. However, recent studies using micro-analytical technique have revealed that there is a large chemical heterogeneity in their skeleton, which cannot be explained by the temperature variation [1]. To reconstruct the past climate accurately, it is essential to understand the mechanism of elemental fractionation in biogenic calcium carbonate.

In this study, micro-analytical techniques were applied to find significant features of elemental distributions in several different types of biogenic calcium carbonates, including *Caryophyllia ambrosia ambrosia* (deep-sea coral), *Porites sp.* (reef coral), *Bathymodiolus platifrons* (deep-sea mussel), *Hippopus hippopus* (giant clam), *Pulleniatina obliquiloculata*, and *Globigerinoides sacculifer* (planktonic foraminifera). Sr/Ca, Mg/Ca, and Ba/Ca ratios are analyzed by using Nano-SIMS [2]. Mg, Sr, and S distributions are measured by using EPMA. Skeletal structures are observed by using SEM to find the information of biological process recorded as a skeletal structure.

All analyzed samples show large elemental variations related to the skeletal structure. Variations are too large to be explained by the temperature change. Foraminifera and bivalve show strong positive correlations between S and other elements (Sr/Ca, Mg/Ca and Ba/Ca ratios), which may imply that organic materials within the shell concentrate such elements and they play important roles for elemental distribution. On the other hand, coral skeleton shows a weak positive correlation between S and Mg/Ca ratio, which suggests that the effect of organic materials is not significant. Mg/Ca and Sr/Ca ratios show a positive correlation in all samples except for the deep-sea coral. Elemental distributions of deep-sea coral indicate calcification rate plays important roles for the elemental fractionation.

Reference

[1] Meibom et al. (2004) *GRL* **31**, GL021313.
[2] Sano et al. (2005) *Anal. Sci.* **21**, 1091-1097.