Advantages of Secondary Ion Mass Spectrometry for trace element studies of marine biomineralization

GRAHAM D. LAYNE AND ANNE L. COHEN

Woods Hole Oceanographic Institution, Woods Hole, MA, USA 02543 (glayne@whoi.edu, acohen@whoi.edu)

The analysis of Sr/Ca ratio in marine biomineralization (specifically, biogenic aragonite) is becoming widely used for environmental and paleoclimatic studies involving molluscs, fish otoliths, corals, and other organisms which provide temporal records of environmental change through sequential growth of skeletal layers. While the Sr concentrations involved (100-10,000 ppmw) are within reach of many analytical techniques, microbeam analysis of very small volumes is required to resolve time intervals of days or weeks.

Achieving intraday resolution of growth structures in organisms such as coral demands spatial resolutions of better than 10µm. Nominal (focused) probe diameters are often deceptive in comparing actual spatial resolutions of microanalytical techniques. A more useful measure is the practical crater dimension produced (SIMS, LA-ICP-MS) or sample volume activated (EPMA, PIXE) during an analysis. A typical LA-ICP-MS analysis of coral consumes $>6e^{-5}$ mm^3 of skeleton from a wide strip (50µm x 500µm) (Fallon *et al*, 1999). Typical SIMS analysis consumes more than 100 times *less* material, from a shallow 10µm diameter crater.

The application of Sr/Ca as an indicator of seawater paleotemperature demands an analytical reproducibility better than 1%. This can easily be achieved with SIMS, even using small format ion microprobes such as the Cameca IMS 3f. With these instruments, internal precision can readily be reduced to better than 0.1–0.2%, even for multi-element analyses. Internal precisions for LA-ICP-MS can approach 1% (Fallon *et al*, 1999), but with the concomitantly larger sample consumption requirement.

In comparison, solution ICP-MS is capable of extremely precise determination of Sr/Ca, but requires a minimum sample of ~10µg ($>3e^{-3}mm^3$) (Rosenthal *et al*, 1999). Conventional microdrilling studies often consume >1 mm^3 per sample, but some of this material may be used for companion $\delta^{18}O$ determination.

Both SIMS and LA-ICP-MS allow simultaneous determination of other trace elements in biogenic aragonite, including Na/Ca, Mg/Ca and Ba/Ca – and these same comparisons of sample consumption and relative precision are generally applicable. Both techniques also allow for the removal of surface contamination - by pre-sputtering, or pre-ablating - before the analysis is begun.

References

Fallon, S.J., McCulloch, M.T., van Woesik, R. and Sinclair, D.J., (1999), *Earth Planet. Sci. Lett.*, 172, 221-238.

Rosenthal, Y., Field, M.P. and Sherrell, R.M., (1999), *Anal. Chem.*, 71, 3248-3253.

The effect of diagenesis on the U system in live and Holocene corals from the Red Sea

B. LAZAR[1,2], M. STEIN[1], R. ENMAR[1], M. BAR-MATTHEWS[3] AND L. HALICZ[3]

[1] Institute of Earth Sciences, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel (boaz.lazar@huji.ac.il)

[2] The Moshe Shilo Minerva Center for Marine Biogeochemistry, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel

[3] Geological Survey of Israel, 30 Malkhei Israel, Jerusalem 95501, Israel

We investigated the effect of diagenetic precipitation of secondary (chemical) aragonite within live coral skeletons on the U/Ca ratio (as paleo-sea surface temperature [SST] proxy) and the U-series system (as coral chronometer). We drilled into large Porites coral-heads growing in the Nature Reserve Reef (NRR), northern Gulf of Aqaba, Red Sea, and Holocene corals from a subsurface fossil reef. We sampled the core material and porewater from the drill-hole and measured the U concentration and isotopic composition in the coral skeletal aragonite, aragonite cements, coral porewater and open NRR and Gulf of Aqaba waters.

U concentration in secondary aragonite filling the skeletal pores is significantly higher than in primary biogenic (skeletal) aragonite (17.3±0.6 compared to 11.9±0.3 $nmol \cdot g^{-1}$, respectively). The concentration difference reflects the close system incorporation of uranyl carbonate into biogenic aragonite with a U/Ca bulk distribution coefficient (D_U) of unity, versus the open system incorporation into secondary aragonite with D_U of 2.4.

U/Ca thermometry and the U-Th ages are only slightly affected by secondary aragonite pore filling. For example, reducing the porosity by 5% via continuous precipitation of secondary aragonite (during 1,000 y of reef submergence) would produce an apparent lowering of the calculated SST by 0.9 °C and apparent age rejuvenation effect (younger calculated age) of several percents, with virtually no effect on the calculated initial U isotopic composition. This would imply that finding elevated $\delta^{234}U$ initials in aragonitic coral skeletons is mainly due to variations in the U isotopic composition of the contemporaneous open reef water or coral porewater. While, all modern samples we analyzed (live coral and waters) show uniform $\delta^{234}U$ =143±2 similar to the modern ocean value, Holocene corals and beachrock cements from the buried reef yield significantly higher $\delta^{234}U$ values of ~180. This probably reflects contribution of groundwater uranium (flowing through the granitic country-rocks) with elevated $\delta^{234}U$. The uniformity of the $\delta^{234}U$ in all modern coral samples we analyzed suggests that flood and groundwater inflows (with high $\delta^{234}U$ values) were not effective during the past 100 y (the maximum age of the corals studied) along the shores of the Gulf of Aqaba.