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For the attention of: Emma Defew

MASTS small grant scheme 2012: Data report SG1: £500 to cover the cost of one day LA-ICPMS analysis at SAMS.

In-situ trace metal analysis of cultured coral *L. pertusa*

Cold-water scleractinian corals populate a large range of Scottish coastal environments; from the deep-sea to relatively shallow environments in high latitude fjords[1]. These species are highly sensitive to environmental perturbations from climate change (such as increase in seawater temperature) ocean acidification, pollution and trawling and deep ocean resource development. In addition, fossilised coral recovered from marine sediments provide a valuable archive of past climate change, provided that the physiology and chemical composition of modern species is understood[1]. Therefore, studying cold water coral in Scottish waters clearly engages with the key research theme of MASTS investigating the dynamics and properties of marine systems.

One current area of active investigation, utilising the expertise of SAMS ecologists and research aquarium facility, is the culturing of cold-water coral species *Lophelia pertusa*. *L. pertusa* is the most abundant cold-water scleractinian coral in the north east Atlantic, yet to date, only two studies have assessed its physiology in response to changes in environmental variables[2,3]. Scleractinian corals produce a calcareous exo-skeleton with trace metals being incorporated as a function of the physical and/or chemical parameters in the ambient seawater from which the skeleton was precipitated. **The funds from the MASTS small grant scheme allowed a one-day pilot investigation into trace metal variation within a specimen of *L. pertusa* collected from the west coast of Scotland**. Specifically, important biologically active and industrially polluting trace metal (lithium, magnesium, calcium, copper, cadmium, lead, uranium) concentration were measured via laser ablation inductively coupled mass spectrometry (LA-ICPMS). This instrument allows the *in-situ* analysis of biological or geological samples, which can resolve spatial variation in trace metal concentration. Understanding the natural chemical composition of this species is vital to 'ground-truth' our understanding of how environmental forcing may modify the chemical compositions observed in modern or fossil specimens.

Methods and results.

The modern sample of *L.pertusa* was imbedded in epoxy resin under vacuum and once hardened (overnight), sectioned and polished transversally to expose a cross section

of the coral (Diagram 1). This process exposed the microstructure of the skeletal wall (theca).

Analysis of the trace metal composition of the sample was undertaken using a quadrupole LA-ICPMS (VG Elemental PlasmaQuad 3) coupled to a New Wave UP 213nm wavelength (Nd:YAG) Laser Ablation Unit. High spatially resolved trace element composition was achieved by monitoring the abundances of 14 isotopes (^{7}Li, ^{24}Mg, ^{26}Mg, ^{43}Ca, ^{44}Ca ^{55}Mn, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{86}Sr, ^{88}Sr, ^{138}Ba, ^{208}Pb and ^{238}U). The major element Ca was measured for use as an internal standard. Normalising all isotope integrated counts per second to ^{43}Ca corrects for any variation in ablation yield between spots and samples. Initial sampling was carried out using ablation lines 55μm in diameter measured from the centre (youngest) of the coral to the outer wall (oldest). It was found that this technique was not sufficient to yield enough counts of some ultra-trace metals (Li, Mn, Cu, Zn and Pb). Therefore, multiple spots were also ablated close to transect analysis lines which allowed a greater number of counts of the low concentration trace metals. Two standards and gas blanks were measured before and after each transect to monitor instrument performance and background counts of the monitored metals. A precise gas blank correction was important to generate robust measurements of the lowest concentration metals.

The day trial was successful in generating a large data set of metal concentrations from 47 spots and 4 transects across the theca of *L.pertusa*. Considerable metal variation was found in profiles across the skeletal wall. Figure 1 shows an example of a profile of Sr and Mg across the theca of *L.pertusa*. Peaks and troughs are concurrent in both metal profiles, yet the Mg profile shows an overarching trend of increasing concentration from the centre of the coral to the outer wall.

Although Sr and Mg broadly follow similar peaks and troughs, we found other metals had an inverse relationship. For example the U/Ca and Mg/Ca of the spot analysis has a strong inverse correlation (Figure 2) with low U/Ca typically associated with high Mg/Ca and vice versa. We also investigated the use of standards to convert these raw counts recorded by the instrument into fully quantitative concentrations. This is a non-trivial task for in-situ analysis due to the varying ablation characteristics of different materials. Correcting the Cu/Ca measured during the trial using different standards (one fused glass, the other a pressed carbonate pellet) produces a slightly different response (Figure 3).

Conclusions

The mast small grant scheme provided the funds for a day trial to measure the trace metal variation within an important species of Scottish coral. In total 47 spots and 4 transect lines were measured and the concentrations of ^{7}Li, ^{24}Mg, ^{26}Mg, ^{43}Ca, ^{44}Ca ^{55}Mn, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{86}Sr, ^{88}Sr, ^{138}Ba, ^{208}Pb and ^{238}U monitored. Significant variation in the metal concentration was found as a result of the tight biological controls during biomineralisation that alter the chemical composition of the skeleton and in addition, changes in ambient seawater conditions which may modify this signal. These results add to the knowledge of this important species allowing an assessment of the biological and environmental controls on metal incorporation into the *L.pertusa*. The MASTS award has allowed the veracity of the technique to be proven and established here at SAMS and paves the way for further in-house geochemical investigations of this species.

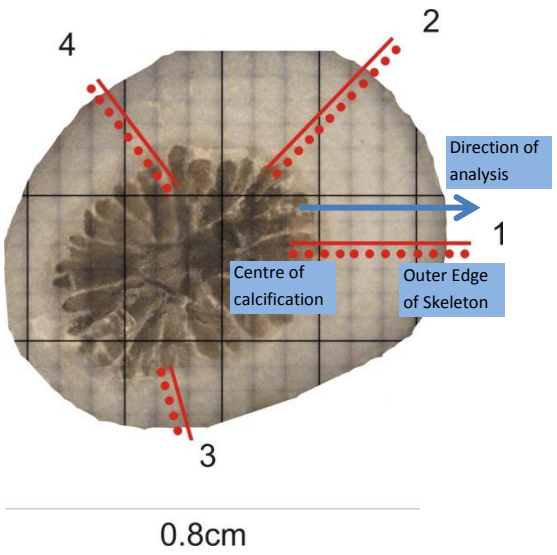

Diagram 1. Cross section of *L.pertusa* sampled during LA-ICPMS analysis. Red lines indicate location of time resolved analysis, circles show spot analysis.

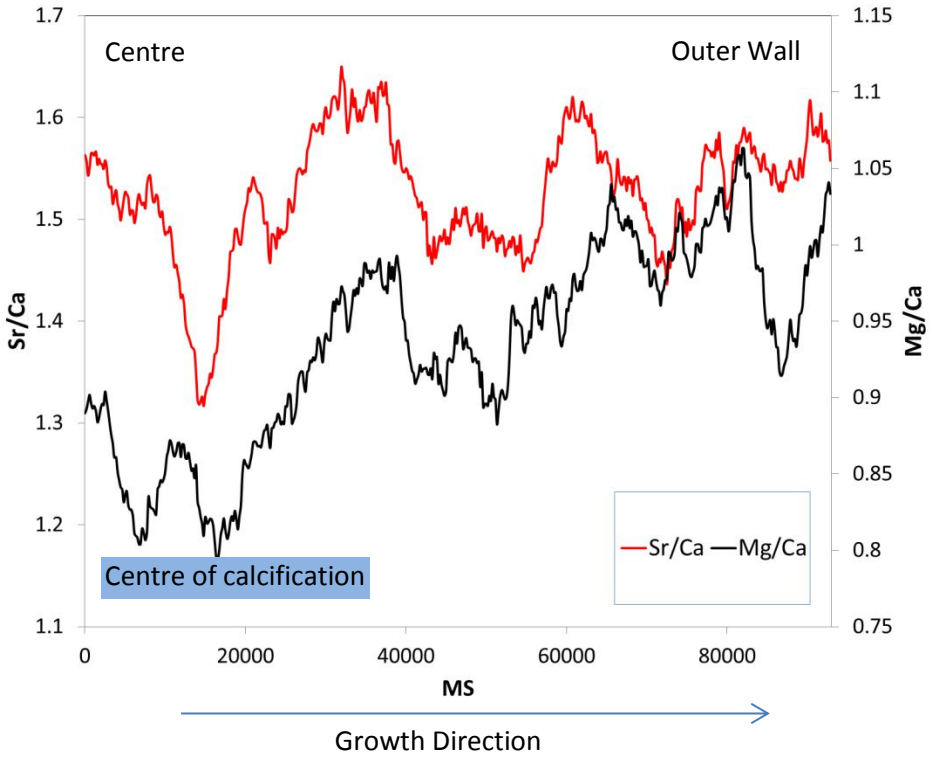

Figure 1. Example of trace metal variation (counts per second, 32 point running average) across the theca of *L.pertusa* (line '1' in Diagram 1). Both Sr/Ca and Mg/Ca are lowest in the young centre of the coral in the 'centre of calcification' demonstrating microstructural variation in trace metal concentration due to tight biogenic controls imposed during biomineralisation. Both Sr/Ca and Mg/Ca have coupled peaks and troughs across the theca with Mg/Ca having a trend of increasing concentration towards the outer (youngest) part of the theca..

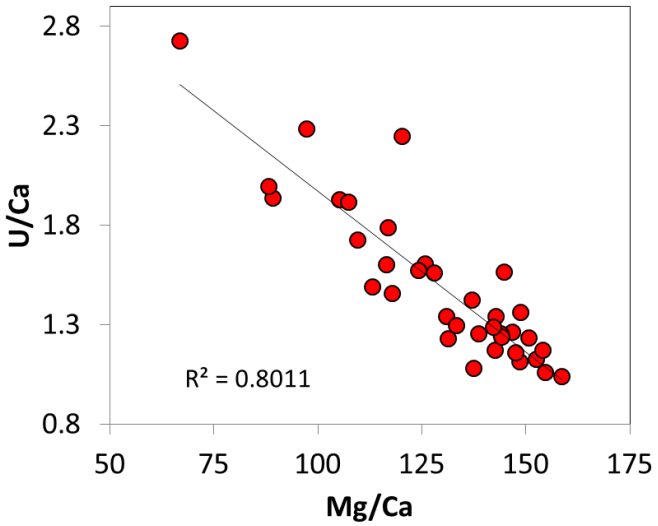

Figure 2. Results of spot analysis showing a strong (R^2 = 0.80) inverse relationship of U/Ca and Mg/Ca in *L.pertusa*.

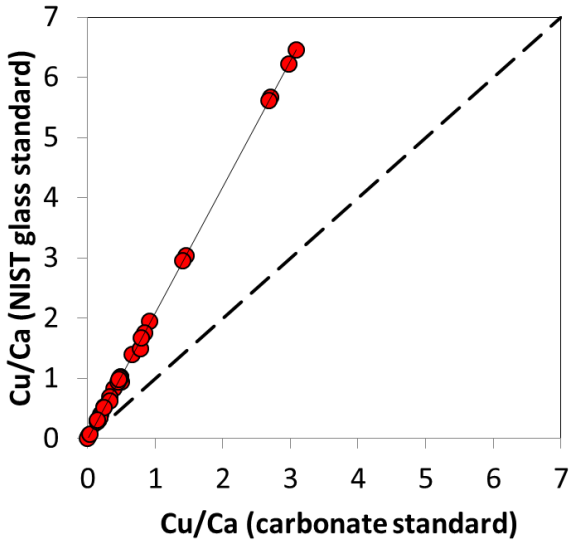

Figure 3. Results of two external calibrators used to correct the Cu and Ca raw counts recorded during the spot analysis. Using the NIST glass standard produces higher correct ratios than using the carbonate standard.

References.

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2. Dodds, L. A., Roberts, J. M., Taylor, A. C. & Marubini, F. 2007. Metabolic tolerance of the cold-water coral Lophelia pertusa (Scleractinia) to temperature and dissolved oxygen change. *Journal of Experimental Marine Biology and Ecology,* 349**,** 205-214
3. Maier, C., Hegeman, J., Weinbauer, M. G. & Gattuso, J. P. 2009. Calcification of the cold-water coral Lophelia pertusa under ambient and reduced pH. *Biogeosciences,* 6**,** 1671-1680