**MASTS VISITING FELLOWSHIP (VF41)**
**Project Summary**

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# COREE: The palaeoceanographic potential of rare earth element incorporation in coral aragonite

This MASTS Visiting Fellowship was to support Dr Ed Hathorne, a senior research scientist at the Helmholtz Centre for Ocean Research in Kiel, Germany, to carry out research at SAMS, Oban, in collaboration with Dr Kirsty Crocket for a period of 6 weeks (9 May to 19 June 2014). Dr Hathorne is a geochemist with expertise in the measurement and analysis of rare earth elements in marine/palaeoceanographic archive materials (in particular marine carbonates) and seawater.

The purpose of our work was to assess the suitability of scleractinian aragonite as an archive of seawater rare earth element (REE) concentrations, with a view to exploiting these as palaeoenvironmental proxies over shorter Holocene and longer Quaternary glacial/interglacial timescales. Reconstruction of seawater REE composition offers insights into weathering fluxes, ocean circulation, and ocean redox conditions. However, to accurately interpret skeletal REE data requires knowledge of (i) the sources of REE to corals (e.g. dissolved vs. colloidal material), (ii) the host site of REE within the skeletal structure (e.g. carbonate lattice vs. organics), and (iii) the influence on REE partitioning of environmental parameters (e.g. pH, water temperature, nutrient availability) in tandem with "vital effects" (i.e. the influence of biomineralisation on skeletal composition). As a first step to investigating the influence of these variables on coral REE concentrations, the objective of the Fellowship was to assess the variation of REE concentrations in aragonitic corals grown under controlled conditions of temperature and pH in coral from both tropical and cold water aquariums by means of sampling both the aquarium water and coral to determine partition coefficients.

## Networking with Scottish researchers

The nature of the research conducted during the 6 week Fellowship involved interaction with several researchers at Scottish universities:

- Dr Nicola Allison, University of St Andrews, is collaborating with Dr Hathorne and provided samples from her tropical coral aquarium for analysis. We had a meeting with Dr Allison in St Andrews to discuss the results of aquarium water sampling and future sampling of corals. We also had meetings with Dr William Austin, Dr Andrea Burke, Dr James Rae and others, at the University of St Andrews, to discuss ongoing research and potential future collaborations.
- Dr Seb Hennige and Prof Murray Roberts, Heriot Watt University, provided coral and aquarium water samples from their cold water culturing set up. We met with Dr

Hennige to discuss his methods and view his aquarium set-up, to collect further coral samples and to sample the aquarium water.

- Part of the research carried out during the Fellowship was based at the NERC ion microprobe facility, hosted at the University of Edinburgh, to measure REE concentrations in coral samples. During our visit, we had meetings with Prof Sandy Tudhope, Dr Alex Thomas and Dr Walter Geibert to discuss our work and future collaborations.
- Within SAMS, Dr Hathorne had the opportunity to meet and discuss his research with several members of staff. He also gave a seminar to staff and students at SAMS on his current research.

**Project objectives**

The overarching purpose of the visiting fellowship was to gather two key elements to ensure the best outcome for a collaborative research proposal to investigate REE incorporation in coralline aragonite for submission in summer 2014 to NERC, to be led by Kirsty Crocket as a new principal investigator. These elements are:

i. an exploratory dataset of REE concentrations from existing corals and ambient aquarium water, cultured under different seawater pH and temperature,
ii. an experimental design for future culturing experiments to be carried out at SAMS.

**Initial results**

Laser ablation/SeaFAST + ICP-MS:

After successfully setting up protocols to measure REE in seawater (SeaFAST + ICP-MS) and coral carbonate (laser ablation, SeaFAST + ICP-MS) at SAMS, our initial results from the analyses of cold water aquarium water and corals were partially successful. While new approaches and method development in laser ablation are broadening its application to low abundance samples, we found that the REE concentrations in pristine parts of the coral (*L. pertusa*) were below the level of detection of our laser ablation set-up. Use of the SeaFAST + ICP-MS, however, did yield measurable REE profiles of coral samples. The aquarium water samples (9 and 12 °C, 380 and 750 ppm $CO_2$) had exceptionally low REE concentrations, i.e. several times lower than the reference seawater standard we measured (BATS seawater, 2000 m water depth, NW Atlantic). This was unexpected and we believe this must be due to scavenging within the circulatory system, perhaps by organic films developing on some surfaces (e.g. pumps, pipes, filters). As a result, we were not able to establish seawater-carbonate partition coefficients for the cultured coral samples as had been hoped.

The laser ablation (and ion microprobe; see below) yielded unexpected results on dead pieces of coral placed in the cold water aquarium alongside living corals. Dissolution/precipitation rims on the dead coral that must have precipitated from aquarium water during the culturing experiment had significantly higher and detectable REE concentrations. These rims were identified in reflected light photos, in SEM (scanning electron microscope) images and by ion microprobe. They present an important finding for the interpretation of palaeoceanographic data obtained from corals, in that non-identification of dissolution rims within sample material will result in high trace metal concentrations and erroneous interpretation of data. Identification of the exact mineral phase of the dissolution rims was beyond the scope of this Fellowship but remains an important, albeit secondary, goal of future research in this field.

Ion microprobe:

We had access to the NERC ion microprobe hosted at the University of Edinburgh for one day, which permitted measurement of several elements (Na, Mg, Al, Si, P, Ca, Ti, Fe, Mn, Sr, Y, Ba, La, Ce, Nd, Th) in three coral samples (two cultured *L. pertusa*, and a natural *D. dianthus*). Analyses were carried out on the Cameca ims-4f. While clear and consistent

differences in Nd concentration were visible across different skeletal components, the concentrations were higher than expected (and would have been detectable by laser ablation). To provide the sensitivity necessary and to avoid the molecular interferences observed on the Cameca ims-4f, we envisage future measurements on the Cameca 1270 for a few select elements (rather than the 10 we attempted).

Experimental culturing design:

Our visits to the coral aquaria at both the University of St Andrews (Dr Allison) and Heriot Watt (Dr Hennige) proved very instructive in demonstrating different approaches to coral culturing.

The tropical coral aquarium (UoStA) employs a closed system with addition of salt and other chemical additives to water to maintain constant salinity and Ca concentration. The REE concentrations in the aquarium water had extremely unusual patterns due to the constant addition of chemical reagents.

The cold water coral aquarium (HW) is fed by a large volume of seawater collected from St Andrews Bay, which is circulated for a period of ~6 months through the tanks, with no additives. As mentioned above, the REE concentrations were barely detectable. Although nutrient levels in the aquarium are not excessively high, we believe the low REE concentrations in the aquarium water must be due to scavenging within the circulatory system, and perhaps also to the duration of circulation of the same batch of seawater over prolonged periods of time.

We benefited greatly from visiting and measuring aquarium water at both sites. Our conclusions were that neither of the above aquarium designs is practical for the purposes of measuring seawater REE partitioning into cold water corals (which was not the intended purpose of either aquarium). As a result of our findings, a different approach to culturing with additional monitoring steps of water REE concentrations has been described in the NERC proposal.

**Overall logistics during the MASTS Visiting Fellowship**

The work was conducted in the Department of Biogeochemistry and Earth Science at SAMS and at the NERC ion microprobe facility. Some prior analyses on aquarium water samples had been conducted by Dr Hathorne at his home institution before the start of the Fellowship. Expenses associated with the laboratory work and travel were covered by the MASTS grant.

**Significance and future prospects**

This research, and existing data collected by Dr Hathorne, constitutes the first of its kind. However, further work is necessary to complete the dataset for the purposes of publication, and is envisaged for the near future. The results from this study were an essential contribution to the NERC Standard Grant, submitted by Dr Crocket in July 2014 ("*Groundtruthing rare earth element behaviour in cold water corals*"). The proposal describes the development of REE in coral as a potential proxy for seawater carbonate ion concentration, and involves Dr Hathorne as a key project collaborator.

A sampling mission to Loch Etive was also conducted towards the end of the Fellowship with the purpose of investigating the influence of truly "dissolved" vs. colloidal transport of REE. Those analyses are ongoing in both GEOMAR and SAMS and will form a project on which staff from both institutions will collaborate.

**Concluding remarks**

Dr Hathorne would like to report that his stay at SAMS was very productive and enjoyable, from both scientific and social perspectives. He thanks the staff and students at SAMS for their warm welcome. The weather gods smiled kindly on him during his visit, and Dr

Hathorne profited by undertaking excursions by boat to sample Loch Etive waters, as well as visits to Rum, Staffa, and Mull.

The broader outcomes of this Fellowship have already been set in motion by collaboration on the NERC Standard Grant. More generally, the Fellowship will strengthen scientific relations between the two institutions and will foster increased collaboration between scientists at Scottish universities and GEOMAR. It is hoped that, on his return to GEOMAR, Dr Hathorne's report of his time at SAMS will encourage other researchers at GEOMAR to interact and develop new collaborations with researchers at SAMS.