Report for the Antarctic Science Bursary

Deep-sea sponges as sediment traps:
Archiving carbon export using zinc isotopes in spicules

Katharine R. Hendry MA MSci DPhil

Department of Marine Chemistry and Geochemistry

Woods Hole Oceanographic Institution

And

School of Earth and Ocean Sciences

Cardiff University

Guest scientist at Bristol University Dec 2010-Jan 2011

Introduction

Changes in atmospheric carbon dioxide over glacial cycles has been linked to fluctuations in the oceanic organic carbon sink ("export production") in the Southern Ocean surrounding Antarctica (see review by Sigman & Boyle, 2000). However, traditional archives of export production are subject to various caveats. For example, accumulation of organic carbon on the seafloor is influenced by preservation, and other geochemical archives (e.g. biogenic barium) are affected by oxidation/reduction reactions. Better constraints on carbon export may be achieved using chemical archives recorded in opal, which, unlike carbonates, is widespread in Southern Ocean sediments. The zinc content (denoted by Zn/Si) of deep-sea opaline sponges is controlled by the amount of Particular Organic Carbon (POC) reaching the seafloor during the lifespan of the sponge (Ellwood et al., 2004, 2005). Here, I investigated the Zn content and isotopic composition of sponges in the modern Southern Ocean, providing new insights into biological uptake of Zn. I also obtained some new organic chemistry data, continuing a previous Antarctic Science bursary project.

Methods

During a cruise to the Scotia Sea and Drake Passage on the R/V Nathaniel B Palmer in April-May 2008, over 100 sponge specimens were collected from a depth of 200-2500 m by benthic dredging and trawling (Fig. 1, 2; Hendry et al., 2010).

Zn analyses

Given their low Zn content, the double-spike method developed at Bristol University is ideal for accurate and precise measurement of small variations in Zn/Si and Zn isotopes in sponges. The samples were cleaned according to Hendry et al., 2010, and dissolved in dilute hydrofluoric acid. Zn concentrations, and a suite of other trace metals, were also measured using a Thermo Element2 ICP-MS (Bristol University). A ^{67}Zn-^{64}Zn double-spike was added to the samples, and Zn extracted using column separation (Archer & Vance, 2004; Bermin et al., 2006). Zn isotopes were measured on the Thermo Neptune Inductively-Coupled Plasma Mass Spectrometer at Bristol University (Bermin et al., 2006; Andersen et al., 2011). The Zn isotope composition is reported according to the following equation:

$$\delta^{66}Zn = \left\{ \frac{\left(\frac{^{66}Zn}{^{64}Zn} \right)_{sample}}{\left(\frac{^{66}Zn}{^{64}Zn} \right)_{std}} - 1 \right\} \times 1000$$

Organic carbon analyses

Sponge spicules were acid and peroxide-cleaned to remove external organic matter, then solvent washed. The stable isotope analyses were carried out by combustion of undigested spicules using a Fisons 1108 Elemental Analyzer. For the amino acid analysis, spicules were dissolved using concentrated hydrofluoric acid. Proteins within the residue were hydrolysed, and free amino acids derivatized (by esterification followed by acetylization, McMahon et al., 2010) prior to analysis by Gas Chromatography Mass Spectrometry (GC-MS) at the Marine Research Facility at Woods Hole Oceanographic Institution.

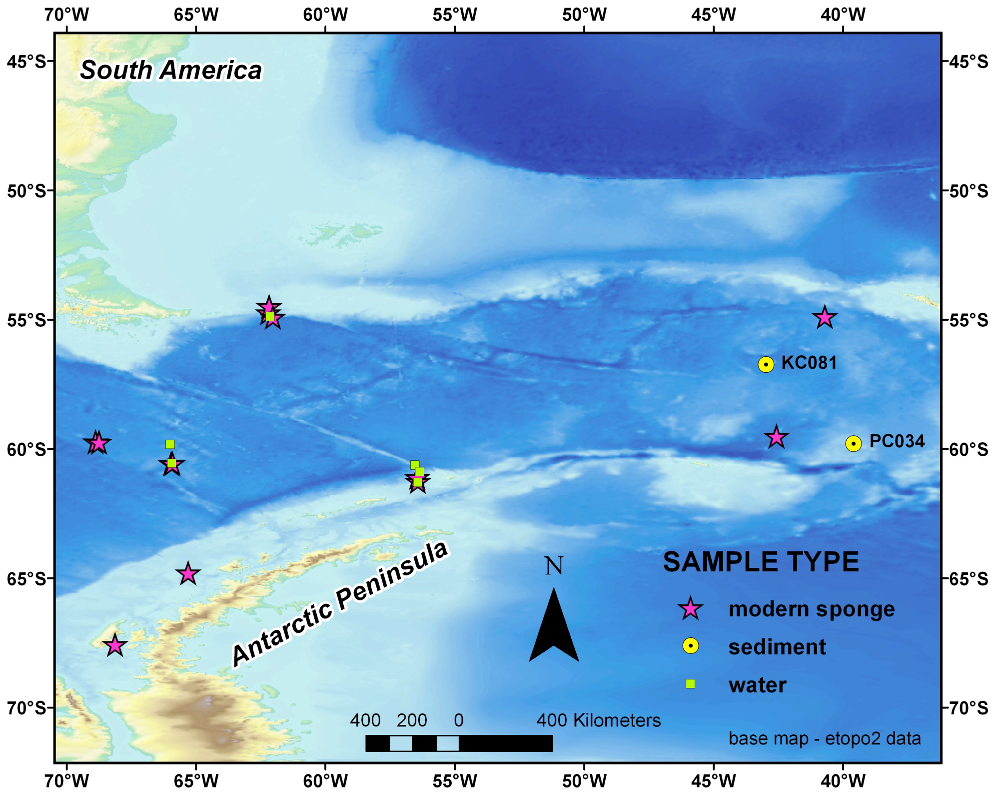

Figure 1: Map of sampling area on cruise NBP0805. Map by K. Scanlon, USGS.

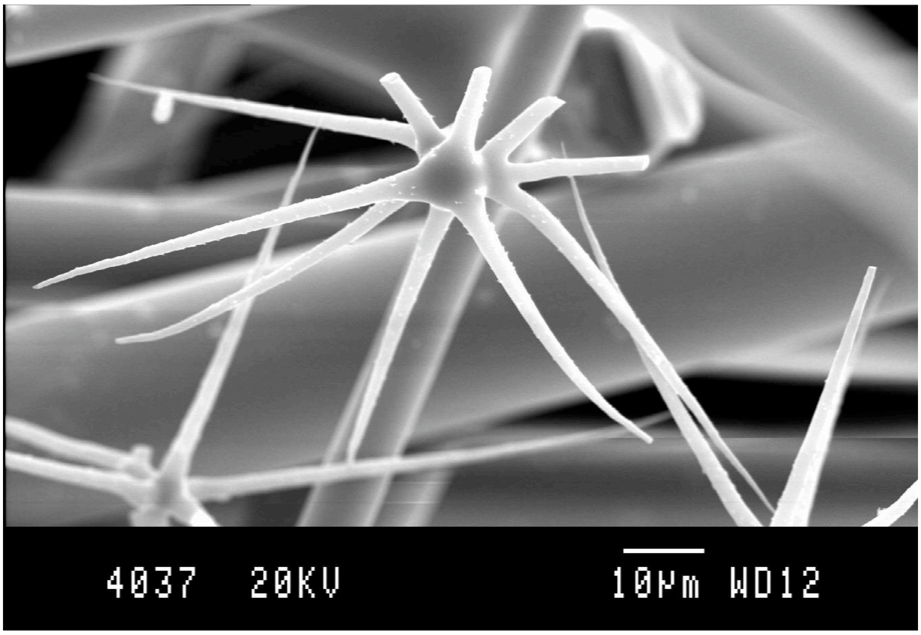

Figure 2: SEM image of Rosella spiules, collected from the Southern Ocean, taken by KRH in the Deparment of Earth Sciences, University of Oxford.

Results

1) *Zn concentration data*

The Zn concentration of the sponge spicules varied from 0.03 to 3.5 ppm. The concentration of Zn in two subsamples of the same specimen agreed within about 5%, and there was a consistent variation of Zn concentration with depth within species. The relationship supports the previous findings of Ellwood et al. (2004), who found that Zn/Si increases with Particulate Organic Carbon (POC), which generally decreases with depth as organic matter is remineralised. However, the new data suggest strong species specific vital effects.

2) *Zn isotope data*

The δ^{66}Zn of the sponge samples ranged from -0.35 to +0.81‰, with typical standard deviation of ± 0.05‰ (2SD), and subsamples from the same specimen agreed within ± 0.1‰.

There are four lines of evidence that the variations observed are not due to clay contamination. Firstly, the results encompass a range greater than the natural variation in marine sediments (δ^{66}Zn typically +0.2 to +0.3 ‰; Maréchal et al., 2000). Secondly, there is no systematic variation with other trace metals found in clays including aluminium (Al) and scandium (Sc). Thirdly, there is good agreement between two subsamples from the same specimen (sponge TB4-24). And, fourthly, the Al content of the sponge spicules is low (100 ppm maximum) compared to thoroughly cleaned sedimentary diatoms (ranging from 1000 to 10000 ppm, Hendry & Rickaby, 2008).

The new results show that the isotopic composition of sponges converges on that of seawater at depth (> 1500m), but is more variable in surface and subsurface waters. This could reflect uptake of Zn by sponges from both the dissolved (i.e. direct uptake from seawater) and particulate pool (i.e. dietary Zn). If both pools are utilised by sponges, then highly variable sponge δ^{66}Zn could result from variable seawater and particulate Zn isotopic compositions in relatively shallow regions resulting from biological fractionation of Zn by phytoplankton (Maréchal et al., 2000; Andersen et al., 2011). With depth, as particulate matter dissolves and remineralises, the Zn isotopic composition of organic matter becomes heavier, converging on seawater compositions (Maréchal et al., 2000), such that sponge δ^{66}Zn become less variable.

Our results highlight that sponge δ^{66}Zn is unlikely to be a useful proxy for determining the isotopic composition of particulate organic matter because the Zn appears to originate from both dietary particles and ambient seawater. However, sponges from deepwater settings may be useful indicators of the deep ocean Zn isotopic composition, and so be a recorder of whole-ocean δ^{66}Zn through time.

3) *Organic chemistry data*

I have continued analyses of the organic content of deep-sea sponge spicules, refining the method to improve the carbon yield. The method now yields a sufficient quantity of carbon for robust and repeatable analyses ($\geq 10\ \mu g$ C) of both bulk carbon isotopes and the isotopic composition of specific amino acids.

Future work

Four of the samples did not have sufficient Zn for a reliable δ^{66}Zn measurement to be made. More material from these samples will be cleaned and analysed.

More broadly, the study shows that deepwater sponges appear to record deep ocean Zn isotopes faithfully. This means that sponges could potentially be used to monitor the Zn isotopic composition of the ocean through time. In particular, sponges, which are the oldest multicellular organisms still alive today, could be used to measure the Zn isotopic composition of ancient oceans as far back as the Precambrian. Further work would be useful to test whether sponges record deep ocean Zn isotopic composition throughout the oceans, using samples from other ocean basins.

With the ability to measure the carbon isotope composition of sponge spicule-bound organic matter, it is now possible to assess whether sponges can record the isotopic composition of their diet, i.e. the POC pool sinking from surface waters.

Publications and conference proceedings

Hendry, K.R. & Andersen, M.B. (2011) Zn isotope fractionation by deep-sea sponges, Abstract submitted to the Goldschmidt Conference, August 2011, Prague.

Hendry, K.R., Andersen, M.B. & Vance, D. (in prep) Zn isotope fractionation by deep-sea sponges

Hendry, K.R., Houghton, L., McMahon, K.W., Johnson, C. & Eglinton, T.I. (in prep) Stable carbon isotope analysis of organic matter within Antarctic sponge spicules

Related publications

Hendry, K.R., Robinson, L.F., Meredith, M.P., S. Mulitza, C. Chiessi & H. Arz (under review at *Geology*). Abrupt changes in thermocline nutrients and biological productivity in the Atlantic over the last glacial cycle.

Hendry, K.R. & Robinson, L.F. (under review at *Geochim. Cosmochim. Act.*) The relationship between silicon isotope fractionation in sponges and silicic acid concentration: modern and core-top studies of biogenic opal.

Hendry, K.R., Leng, M.J., Robinson, L.F., Sloane, H.J., Blusztjan, J., Rickaby, R.E.M., Georg, R.B. & Halliday, A.N. (2011) Silicon isotopes in Antarctic sponges: an interlaboratory comparison. *Ant. Sci.* 23, 34-42.

Hendry, K.R., Georg, R.B., Rickaby, R.E.M., Robinson, L.F. & Halliday, A.N. (2010). Deep ocean nutrients during the Last Glacial Maximum deduced from sponge spicule silicon isotopes. *EPSL.* 292, 290-300.

Hendry, K.R., Meredith, M.P., Measures, C.I. & Rickaby, R.E.M. (2010) The role of sea ice formation in cycling of aluminium in northern Marguerite Bay, Antarctica. *Est., Coast. Shelf Sci.* 87, 103-112.

Hendry, K.R., Rickaby, R.E.M., J.C. de Hoog, Weston, K. & Rehkamper, M. (2009) The cadmium-phosphate relationship in brine: biological versus physical control over micronutrients in sea-ice environments. *Ant. Sci.* doi:10.1017/S0099938195410200.

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Hendry, K.R. & Rickaby, R.E.M. (2008) Opal (Zn/Si) ratios as a nearshore geochemical proxy in coastal Antarctica, *Paleoceanography*, 23, PA2218, doi:10.1029/2007PA001576.

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Bermin, J., Vance, D., Archer, C., and Statham, P. J., 2006. The determination of the isotopic composition of Cu and Zn in seawater. *Chemical Geology* **226**, 280-297.

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Ellwood, M. J., Kelly, M., Neil, H., and Nodder, S. D., 2005. Reconstruction of paleo-particulate organic carbon fluxes for the Campbel Plateau region of southern New Zealand using the zinc content of sponge spicules. *Paleoceanography* **20**, Art. no. PA001095.

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McMahon, K. W., Fogel, M. L., Elsdon, T. S., and Thorrold, S. R., 2010. Carbon isotope fractionation of amino acids in fish muscle reflects biosynthesis ad isotopic routing from dietary protein. *Journal of Animal Ecology* **79**, 1132-1141.

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Budget report

Cost	**£**
Flights	600
Ground transportation	180
Accommodation	300
Living costs	300
Lab costs	1500
Computing costs	100
Total	***2980***

Table 1: Budget breakdown of expenses to date. The remaining funds will be used to carry out the further research suggested.

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Katharine R. Hendry, 2011