Report for the Antarctic Science Bursary:

Do deep-sea sponges record ocean chemistry?

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Introduction

The marine silicon (Si) cycle is linked to global climate through coupling with the carbon cycle (1). Hence, one key to past changes in the important atmospheric greenhouse gas carbon dioxide (CO_2) is the distribution of Si in the oceans. In the modern ocean the removal of silicic acid, $Si(OH)_4$, from seawater is dominated by biological precipitation of amorphous silica (opal) by diatoms. Diatoms are a group of phytoplankton that is responsible for approximately half of the primary production in the oceans, and are efficient conveyors of organic carbon to the seafloor. Such efficient utilization has led to a progressive depletion of $Si(OH)_4$ in surface waters, such that modern diatom blooms are reliant on upwelling Si-rich deep-waters. Quantitative constraints on the past $Si(OH)_4$ of deep-waters would allow patterns of ocean ventilation to be reconstructed and would yield insight into both the efficiency of biological export and whole-ocean changes in Si cycle, which are ultimately linked to CO_2 and global climate. However, understanding past deep-water nutrients requires the use of geochemical proxies, which until now have focused on carbon and phosphate (e.g. 2), which are decoupled from $Si(OH)_4$. The aim of this bursary was to further understanding in the marine Si cycle and its relationship to atmospheric CO_2 by investigating the use of sponge silicon isotopes (3,4) as a proxy for past $Si(OH)_4$, and the development of other sponge opal-based proxies. The bursary allowed me to extend my postdoctoral research and collaborate with workers at Woods Hole Oceanographic Institution (WHOI), USA and the National Isotope Geochemistry Laboratory (NIGL), Keyworth.

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 (Figure 1, 2). Water samples were collected by niskin bottles attached to CTD rosettes and to a towed camera system operated by WHOI. Further water samples were also collected from the British Antarctic Survey vessel, the James Clark Ross, and other sponge samples were donated by Rhian Waller, University of Hawaii. Fossil sponge spicules were picked from deep-sea sediment cores from the Scotia Sea (KC081 and PC034, British Antarctic Survey).

The modern and downcore spicules were chemically cleaned and dissolved by wet alkaline extraction (6). Seawater samples were processed using a co-precipitation method I have successfully adapted and tested at the University of Oxford (7). Dissolved sponges and seawater precipitates were analysed for silicon isotopes ($\delta^{30}Si$) using the NuPlasma Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the University of Oxford (6).

Other analyses included Zn/Si ratios, measured by Quadrupole ICP-MS (University of Oxford), $\delta^{18}O$ & $\delta^{30}Si$ (Melanie Leng, NIGL) and $\delta^{13}C$ & $\delta^{15}N$ on spicule-bound organic matter (WHOI). The Antarctic Science Bursary funded my Guest Investigator position at WHOI from April 28 to June 16th 2009, during which I carried out the organic matter analyses. For the organic matter analyses, sponge spicules were acid and peroxide-cleaned to remove external organic matter, then solvent washed. Spicules were either analysed raw, or initially demineralized in hydrofluoric acid. The stable isotope analyses were carried out using a Fisons 1108 Elemental Analyzer.

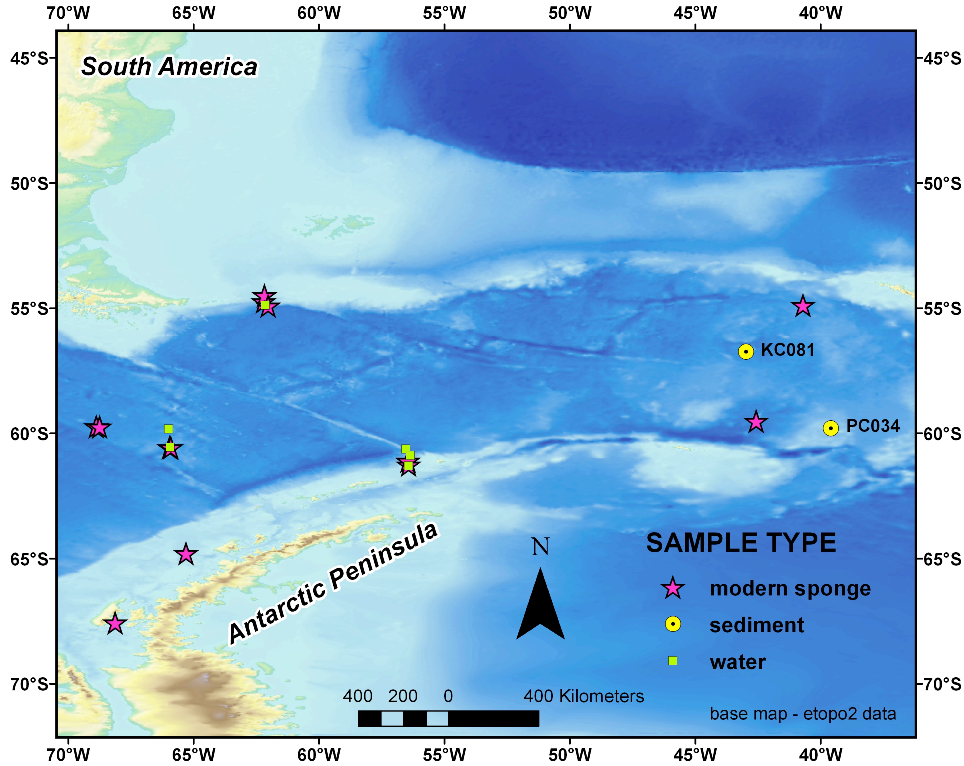

Figure 1: Map of sampling area on cruise NBP0805. Map by K. Scanlon, USGS.

Figure 2: Recovery of a trawl on the R/V Nathaniel B. Palmer, May 2008 and an hexactinellid sponge, Rosella. Photos by Dann Blackwood, USGS.

Results and outcomes from bursary

1) A new calibration of modern specimens from the Southern Ocean shows spicule $\delta^{30}Si$ records the concentration of $Si(OH)_4$ in deep-waters (Henry et al,. in review). This result provides the first means to reconstruct $Si(OH)_4$ in deep waters, using measurements of $\delta^{30}Si$ of spicules from deep sea sediment cores.
2) Measured $\delta^{30}Si$ in Southern Ocean deep-waters confirm modelling predictions (8), and show a clear relationship with $Si(OH)_4$ concentration.
3) Previous work has suggested the Zn content of sponge opal may correlate with organic carbon export (10). However, here the Zn/Si ratios in modern sponge opal did not correlate with obvious environmental parameters, limiting it's potential as a paleoproxy. Furthermore, the Zn/Si ratios are significantly lower than for diatom opal, and are more susceptible to contamination.
4) Both $\delta^{30}Si$ and $\delta^{18}O$ analyses were carried out at NIGL on subsamples of the sponges. The $\delta^{30}Si$ data agreed very well (within error) with the data collected at the University of Oxford, verifying the accuracy of the analyses and providing an excellent inter-laboratory comparison. The $\delta^{18}O$ values were very variable, and not highly reproducible. This is probably a result of exchange of oxygen atoms within the silica structure with external media. Further testing will be carried out to explore this possibility using exchange experiments, in collaboration with Dr Melanie Leng (NIGL) and Dr Jon Tyler (University of Oxford).
5) Stable isotope measurements of bulk organic matter from within sponge spicules show the raw spicules comprise ~0.1% organic carbon and less than 0.1% organic nitrogen. The $\delta^{13}C$ values range from -17 to -28‰; insufficient material was collected for reliable $\delta^{15}N$ values. High Precision Liquid Chromatography (HPLC) spectra suggest this organic matter comprises amino acids and long chain polyamines, similarly to diatom-bound organic matter (11). Our initial work shows promise that organic matter can be successfully extracted from spicules, and further work will continue at WHOI including radiocarbon measurements of sponge-bound organic matter.

Further work

Although the $\delta^{30}Si$ of modern sponges from the Southern Ocean shows an empirical relationship with $Si(OH)_4$ in seawater, the specific biological processes that cause this fractionation are not understood. Further insight into what controls these processes can be gained by investigating $\delta^{30}Si$ of modern sponges grown in other ocean basins under different conditions (temperature, pH, salinity, $Si(OH)_4$, other nutrients).

The $\delta^{30}Si$ proxy can be applied to a wide range of paleoceanographic questions, including whether the amount of Si exported in intermediate water masses from the Southern Ocean changes on glacial-interglacial timescales (the "Silicic Acid Leakage Hypothesis", 5).

The initial organic geochemical work shows that it is possible to extract organic matter from within sponge spicules in quantities sufficient to carry out stable isotope analysis. Further, there is excellent potential to extract organic matter from within spicules for radiocarbon dating.

During the period of the bursary, I was awarded a postdoctoral fellowship at WHOI, and will be continuing the work on sponge spicule chemistry and geochemistry in the next two years.

Budget report

Cost	**Notes**	**£**
Flights	London to Boston	400
Ground transportation	Car hire, buses, petrol	1150
Accommodation		500
Living costs	Based on £10 per diem	500
Lab costs		500
Total		***3050***

Table 1: Budget breakdown of expenses to date.

Publications and conference proceedings

Hendry, K.R., Georg, R.B., Rickaby, R.E.M., Robinson, L.F. & Halliday, A.N. (in review, *Science*) Silicon isotopes in sponges and climatic effects on deep ocean nutrients.

Hendry, K.R., Robinson, L.F., Georg, R.B., Rickaby, R.E.M. & Halliday, A.N. (in prep) The isotopic composition of silicic acid from the Southern Ocean: Implications for marine biological fractionation of silica.

Hendry, K.R., Robinson, L.F., Rickaby, R.E.M., Georg R.B., and Halliday, A.N. (2009) Silicon uptake by biological organisms in the Southern Ocean: the silicon isotope perspective. To be presented at Biochemistry of marine waters and sediments, past and present; Geological Society, London, Sept 2009

Hendry, K.R., Georg, R.B., Rickaby, R.E.M., Robinson, L.F. & Halliday, A.N. (2009) Sponge Spicules as Recorders of Deep-Water Silicic Acid. *Geochim. Cosmochim. Acta*, 73, A522. Talk presented at Goldschmidt, Davos, June 2009.

Hendry, K.R., Georg, R.B., Rickaby, R.E.M., Robinson, L.F. & Halliday, A.N. (2008) Modern deep-sea sponges as recorders of bottom water silicon isotopes, *EOS Trans. AGU,* 89(53), Fall Meet. Suppl., Abstract PP33C-1596. Poster presented at AGU Fall Meeting, San Francisco, December 2008.

Related publications

Hendry, K.R., Rickaby, R.E.M., J.C. de Hoog, Weston, K. & Rehkamper, M. (accepted, *Antarctic Science*) The cadmium-phosphate relationship in brine: biological versus physical control over micronutrients in sea-ice environments.

Hendry, K.R., Rickaby, R.E.M., Meredith, M.P. & Elderfield, H. (2009) Controls on stable isotope and trace metal uptake in *Neogloboquadrina pachyderma* (sinistral) from an Antarctic sea-ice environment, *Earth and Planetary Science Letters*, 278, p67-77, doi:10.1016/j.epsl.2008.11.026.

Hendry, K.R., Rickaby, R.E.M., J.C. de Hoog, K. Weston & Rëhkamper, M. (2008) Cadmium and phosphate in coastal Antarctic seawater: implication for Southern Ocean nutrient cycling, *Marine Chemistry*, 112, p149-157, doi:10.1016/j.marchem.2008.09.004.

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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(1) West, A.J., Galy, A., and Bickle, M., 2005, Tectonic and climatic controls on silicate weathering: *Earth Planet. Sci. Lett*. **235**, 211-228; (2) Boyle, E., 1988, Cadmium: chemical tracer of deep water paleoceanography: *Paleoceanography*. **3**, 471-489; (3) de la Rocha, C.L., 2003, Silicon isotope fractionation by marine sponges and the reconstruction of the silicon isotope composition of ancient deep water: *Geology*. **31**, 423-426; (4) de la Rocha, C., and Bickle, M., 2005, Sensitivity of silicon isotopes to whole-ocean changes in the silica cycle: *Mar. Geol*. **217**, 267-282; (5) Beucher, C.P., Brzezinksi, M.A., and Crosta, X., 2007, Silicic acid dynamics in the glacial sub-Antarctic: Implications for the silicic acid leakage hypothesis: *Global Biogeochem. Cycle*s. **21**, doi:10.1029/2006GB002746; (6) Georg, R.B., Reynolds, B.C., Frank, M., and Halliday, A.N., 2006, New sample preparation techniques for the determination of Si isotopic composition using MC-ICPMS: *Chem. Geol*. **235**, 95-104; (7) Reynolds, B.C., Frank, M., and Halliday, A.N., 2006, Silicon fractionation during nutrient utilization in the North Pacific: *Earth Planet. Sci. Lett.* **244**, 431-443. (8) Wischmeyer, A.G., de la Rocha, C., Maier-Raimer, E., and Wolf-Gladrow, D.A., 2003, Control mechanisms for the oceanic distribution of silicon isotopes: *Global Biogeochem. Cycles*, **17**, doi:10.1029/2002GB002022. (9) Toggweiler, R., 1999, Variation of atmospheric CO2 by ventilation of the ocean's deepest water: *Paleoceanography*, **14**, 571-588. (10) 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**, PA001095. (11) Ingalls, A. E., et al., 2004, Radiocarbon dating of diatom-bound organic compounds, *Marine Chemistry,* **92**, 91-105.

Katharine R. Hendry, August 2009