



The zinc isotopic composition of siliceous marine sponges: Investigating nature's sediment traps

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ABSTRACT

The zinc (Zn) content and isotopic composition of marine biogenic opal have the potential to yield information about the nutrient availability, utilization and export of particulate organic matter from surface to deep waters. Here, we report the first measurements of the Zn isotopic composition of deep-sea marine sponge skeletal elements – spicules – collected in the Southern Ocean. Our results highlight different Zn uptake and isotopic fractionation behavior between the two major siliceous sponge clades (hexactinellids and demosponges), which is most likely linked to sponge feeding strategy. Hexactinellid spicule Zn isotopic compositions are not fractionated with respect to seawater, most likely due to Zn transport via the open internal structure of the sponges. In contrast, demosponge spicules exhibit a wide range of Zn isotopic compositions that are related to the opal Zn concentration, most likely reflecting variable Zn isotope compositions in the organic matter particles on which they feed, and internal fractionation processes.

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1. Introduction

Dissolved zinc (Zn) is an essential metallic co-factor in enzymes such as carbonic anhydrase (Lane and Morel, 2000), and may potentially play a role in phytoplankton growth under certain conditions (Morel et al., 1994; de la Rocha et al., 2000; Franck et al., 2003; Sunda and Huntsman, 2005). Zinc generally exhibits a seawater depth profile similar to that of major nutrients, with concentrations ranging over several orders of magnitude (from pmol to nmol kg⁻¹ levels), consistent with uptake by biological utilization, followed by remineralization at depth (Lohan et al., 2002; Croot et al., 2011). Furthermore in seawater, the dissolved Zn pool is dominated (>95%) by organic ligand bound Zn, particularly in the surface ocean, leaving the free bioavailable Zn²⁺ pool even smaller (Bruland, 1989; Bruland and Lohan, 2003).

Despite the evidence linking Zn with biological cycling and ocean productivity, there is a need for a greater understanding of the exact role that Zn plays as a micronutrient for phytoplankton (Sinoir et al., 2012). This limitation on the understanding of Zn ocean cycling has been hindered by analytical challenges, which are being addressed through general improvements in sampling and measurement

techniques, and through large-scale efforts such as the GEOTRACES program (e.g. Boyle et al., 2012). Furthermore, the advent of techniques for measuring Zn isotopes (Marechal et al., 1999) has added an extra tool for studying Zn oceanic cycling (e.g. Bermin et al., 2006).

The major Zn input flux to the oceans is likely to be rivers, with aerosols (and hydrothermal) potentially contributing some part as well. The Zn isotopic composition of crustal material appears to be homogeneous centered around a $\delta^{66}\text{Zn}$ (Eq. (1)) of +0.3‰ (Marechal et al., 2000; Archer and Vance, 2004; Cloquet et al., 2008):

$$\delta^{66}\text{Zn} = \left[\left\{ \frac{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{sample}}}{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{JMC-Lyons}}} \right\} - 1 \right] \times 1000. \quad (1)$$

The major Zn input flux to the oceans (rivers and aerosols) may be assumed to be in that range. Marine derived materials (e.g. diatom opal, manganese nodules, carbonate sediments, algae) show both lighter and heavier Zn isotope compositions (Marechal et al., 2000; Pichat et al., 2003; Andersen et al., 2011). Uptake of Zn into organic matter results in preferential incorporation of light Zn isotopes (Marechal et al., 2000; John et al., 2007; Cloquet et al., 2008; Peel et al., 2009), whereas adsorption processes may lead to heavier Zn isotopic compositions (e.g. Gelabert et al., 2006; John et al., 2007; Juillot et al., 2008). As already mentioned, due to the low abundance of Zn in seawater, measuring Zn is an analytical challenge and

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available seawater Zn isotope data are presently sparse (Bermin et al., 2006; Boyle et al., 2012). These limited data suggest that the Zn isotopic compositions of deep waters with high dissolved Zn concentrations (nM levels) from remineralization of organic matter at depth have a $\delta^{66}\text{Zn}$ close to the crustal material. For deep seawater samples (below 500 m depth) limited $\delta^{66}\text{Zn}$ data have been reported in Andersen et al. (2011) and Boyle et al. (2012). A mean $\delta^{66}\text{Zn}$ of $0.45 \pm 0.09\text{‰}$ was obtained for samples from the Indian and Pacific Oceans (Andersen et al., 2011), and a mean $\delta^{66}\text{Zn}$ of $0.42 \pm 0.12\text{‰}$, from GEOTRACES IC1 BATS station in the Atlantic Ocean (Boyle et al., 2012). Furthermore, recently a larger compilation of Zn isotope data of deeper seawater profiles (below 1000 m), with high dissolved Zn concentrations (nM levels) from the Atlantic, Pacific and Southern Oceans, exhibits relative uniform Zn isotope compositions with a mean $\delta^{66}\text{Zn}$ of $+0.53 \pm 0.14\text{‰}$ (Zhao et al., in review).

The nutrient like behavior of Zn suggests that the biological cycling of Zn and associated Zn isotope fractionation are the dominating processes controlling the marine Zn budget. Zn isotopes in carbonate sedimentary records over time have been interpreted in the context of changes in these biological processes: heavier isotopic compositions of carbonates are thought to reflect larger degrees of biological utilization, with the incorporation of lighter Zn leaving the residual seawater (and carbonate sediments) isotopically heavy (Pichat et al., 2003; Kunzmann et al., 2013). Furthermore, it has been shown, that the Zn/Si ratio of biogenic opal produced by photosynthetic diatoms relates to the availability of free Zn^{2+} ions in surface seawater, and is a potential proxy for environmental conditions (Ellwood and Hunter, 1999; Ellwood and Hunter, 2000; Hendry and Rickaby, 2008; Jaccard et al., 2009). A study of Zn incorporation and Zn isotope ratios in diatom opal across a transect in the Southern Ocean suggests that diatom opal chemistry may record the bioavailable Zn abundance and isotopic shifts in surface seawater (Andersen et al., 2011). The $\delta^{66}\text{Zn}$ in diatom opal appears to record $\delta^{66}\text{Zn}$ in surface seawater, which is driven isotopically heavier as a consequence of the biological utilization of Zn, taking up isotopically lighter Zn (Andersen et al., 2011). Conversely, the Zn/Si ratio of opaline skeletal elements (spicules) made by deep-sea sponges (Porifera) – belonging to the Class Hexactinellida – has been shown in one study to relate to the rain of Particulate Organic Carbon (POC; Ellwood et al., 2004). This raises the potential for the Zn/Si ratios of spicules produced by

sponges, which are simple, filter-feeding animals without tissue grade organization of cells, to be used as a measure of organic export flux (Ellwood et al., 2004; Ellwood et al., 2005). An archive of the flux of particulate organic matter to the seafloor would allow the quantification of past changes in the supply of nutrients to the benthos, an important parameter for the reconstruction of past carbon cycling and benthic ecology. To date, however, to the best of our knowledge there have been no further studies of sponge Zn/Si since Ellwood et al. (2005), or any studies investigating the Zn isotopic composition of spicules.

Here, we present new Zn concentration and isotope data from deep-sea sponges collected from the Southern Ocean. Our results highlight some specific differences in Zn uptake between the major classes of siliceous sponges, the hexactinellids and demosponges, and their potential uses as paleoenvironmental indicators.

2. Methods and materials

Sponges were collected by trawl and dredge from the Drake Passage and Scotia Sea (Fig. 1) from the R/V Nathaniel B. Palmer in April–May 2008. The specimens were dried for transport (see Hendry et al., 2010 for full details).

Subsamples were initially cleaned to remove external organic matter by heating three times in H_2O_2 (30%, reagent grade) at 80°C , rinsing three times in $18\Omega\cdot\text{cm}$ Milli-Q water, heating three times in concentrated in-house Teflon-distilled HNO_3 at 100°C and rinsing five times in Milli-Q water. Remaining lithic particles were removed physically from the samples. For some samples, generally those with smaller spicules, heavy liquid separation was used to remove remaining lithic particles (Hendry and Rickaby, 2008). The samples were then 1) reductively cleaned by heating twice in 1 M hydroxylamine chloride–acetic acid at 100°C for 1 h (Ellwood and Hunter, 1999), and were rinsed three times in Milli-Q water each time; 2) oxidatively cleaned by heating in strong acid solution (double Teflon-distilled $\sim 7\text{ N HNO}_3$, $\sim 1\text{ N HCl}$, University of Bristol) for at least 2 h on a hotplate at 120°C , and were rinsed five times in Milli-Q. The spicules were dissolved in $\sim 3\text{ N HF}$ (Romil ultra-pure), and dried down prior to repeat dissolution in $\sim 3\text{ N HF}$ to maximize the removal of Si, which can result in a polyatomic interference on Zn isotopes in plasma mass spectrometry (Andersen et al., 2011).

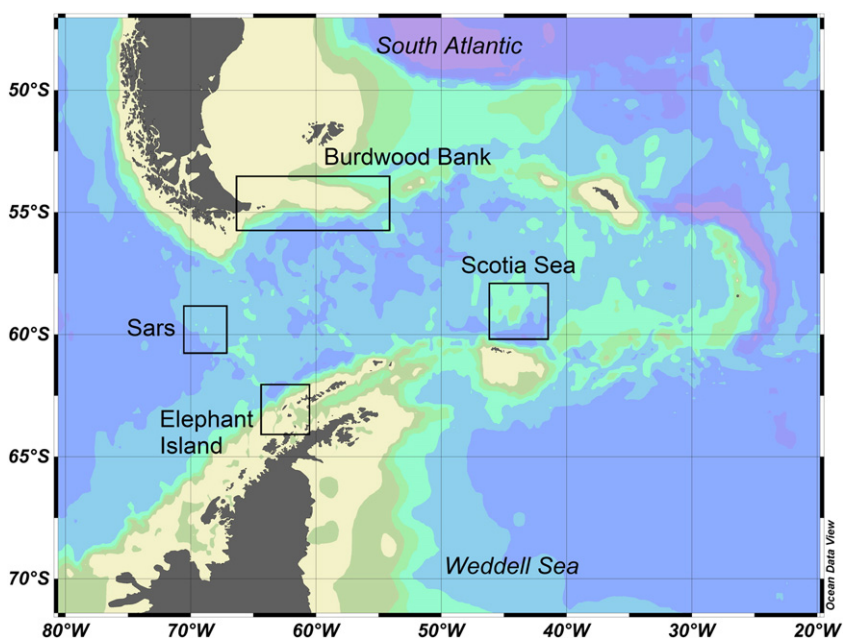


Fig. 1. Sample location map with key areas highlighted in boxes. Map drawn using Ocean Data View.

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