



# A role for scavenging in the marine biogeochemical cycling of zinc and zinc isotopes



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## ABSTRACT

Zinc (Zn) and cadmium (Cd) are important biologically active trace-metals in the ocean. To date, the marine distributions of these elements have been understood primarily in terms of biological assimilation by growing phytoplankton and regeneration of sinking biological material. Initial studies of Zn and Cd concentrations and stable isotope ratios ( $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$ ) have therefore focused on their use as simple tracers of assimilation and regeneration in the oceans. However, these two processes are insufficient to explain new data on the marine distribution of Zn and  $\delta^{66}\text{Zn}$ . Here, using the first high-resolution paired marine depth profiles of Zn, Cd,  $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$ , we suggest that scavenging of Zn onto organic matter plays a major, yet largely unconsidered, role in the marine cycling of Zn. This hypothesis is supported by culture experiments, which show that Zn released from degrading phytoplankton is rapidly scavenged back onto organic matter, and that adsorbed Zn is isotopically heavier than the dissolved phase by 0.58‰. In contrast, very little Cd or phosphate was scavenged and Cd isotopes were not significantly fractionated during degradation. Our hypothesis is further supported by one-dimensional modeling, which reproduces observed marine  $\delta^{66}\text{Zn}$  profiles with <1% of Zn adsorbed to particles. Understanding how Zn cycling in the oceans is a balance between assimilation, scavenging, and regeneration is necessary in order to investigate  $\delta^{66}\text{Zn}$  as a tracer of marine productivity. We anticipate that paired analyses of  $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$  will prove to be valuable new tools in constraining patterns of global primary productivity, providing key information for the marine carbon cycle during periods of past and present global climate change.

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## 1. Introduction

Zn and Cd show nutrient-like distributions in the oceans, with surface depletion attributed to phytoplankton growth and gradual enrichment in deeper waters from dissolving organic material. Proxies for Zn and Cd and their stable isotope ratios have therefore been used to infer changes in biological productivity and circulation in the past ocean. For example, seawater Zn and Cd concentrations, as recorded in carbonate Zn/Ca or Cd/Ca, have been used to reconstruct paleonutrient distributions (Boyle, 1992; Marchitto et al., 2005, 2002).  $\delta^{66}\text{Zn}$  variations of 1‰ in a sedimentary carbonate record from the Equatorial Pacific were attributed to productivity changes over the past 175 kyr (Pichat et al., 2003). Similarly,  $\delta^{66}\text{Zn}$  variations in Ediacaran carbonates were attributed to changes in biological productivity following the Marinoan 'Snowball Earth' glaciation (Kunzmann et al., 2013). As new

analytical techniques for  $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$  are developed, we anticipate greater use of isotopes as tracers for past global change.

Although Zn and Cd are chemically similar elements, they have different marine distributions. Globally, the marine distribution of Zn is similar to the major nutrient silicate (Si), while the distribution of Cd is similar to the major nutrients nitrate (N) and phosphate (P). Zn and Si have deeper 'regeneration maxima' than N, P and Cd, and both Si and Zn are enriched 5- to 8-fold in the deep North Pacific compared to the deep North Atlantic, while N, P and Cd are enriched only about 3-fold at similar locations (Sunda, 2012). As with the marine distribution of Zn and Cd, the distribution of  $\delta^{66}\text{Zn}$ , and  $\delta^{114}\text{Cd}$  in the ocean have been attributed to active biological uptake (assimilation) of these metals by phytoplankton at the surface, and release (regeneration) of these metals from sinking biological particles. In culture, phytoplankton have been shown to fractionate Zn and Cd isotopes during assimilation due to the preferential uptake of lighter isotopes (John et al., 2007; Lacan et al., 2006). A biological preference for lighter Cd and Zn isotopes has similarly been invoked to explain increasing  $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$  towards the surface of the ocean (Bermin et al., 2006;

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Lacan et al., 2006; Ripperger et al., 2007). A correlation between surface productivity and manganese nodule  $\delta^{66}\text{Zn}$  has also been attributed to biological Zn fractionation (Maréchal et al., 2000), though the precise mechanism of this correlation is unclear. Finally, variations in diatom frustule  $\delta^{66}\text{Zn}$  in Southern Ocean core-top sediments are consistent with biological preferential assimilation of light Zn isotopes in surface waters (Andersen et al., 2011), though more recent measurements of seawater dissolved  $\delta^{66}\text{Zn}$  do not show a strong correlation between Zn uptake and increasing  $\delta^{66}\text{Zn}$  (Zhao et al., 2014).

Despite the use of  $\delta^{66}\text{Zn}$  as a tracer for biological productivity, the biological cycling of Zn is not fully understood. It has been hypothesized that the similarity between Zn and Si distributions is caused by the presence of Zn in a refractory phase that is similarly resistant to dissolution as diatom opal (e.g. Lohan et al., 2002). However, most Zn in diatoms, from both open-ocean and culture studies, is present in the soft tissue of phytoplankton, as determined by the spatial co-location of Zn with P, rather than Si (Twining et al., 2004, 2003). Only ~1–3% of diatomaceous Zn was found to be present in diatom opal (Ellwood and Hunter, 2000), though additional Zn is present associated with organic material in the frustules (e.g. Pokrovsky et al., 2005). The majority of intracellular Zn in carbon-limited diatom cells is thought to be present in carbonic anhydrase and alkaline phosphatase enzymes under conditions of carbon or phosphate limitation, respectively (Morel et al., 1994; Shaked et al., 2006). If Zn is largely located in the active site of enzymes, then Zn should remineralize at the same rate as N, P and Cd. An alternative explanation for the global similarity between Zn and Si concentrations is that both may be controlled by similar rates of biological assimilation in the surface of the Southern Ocean. Rapid uptake of Si by diatoms in the Southern Ocean has been invoked to explain the deficit of Si compared to N (negative Si\*) in the thermocline throughout the oceans (Sarmiento et al., 2004). By analogy, a relatively rapid uptake of Zn in the surface of the Southern Ocean may contribute to the Zn deficit, compared to N, P, and Cd, in the thermocline at lower latitudes; despite this, even models which stress the importance of assimilation in the surface Southern Ocean do not discount the potential importance of slow silicate redissolution on the global distribution of Si (Sarmiento et al., 2007). We are therefore motivated to seek possible reasons why Zn might dissolve more deeply in the water column than other nutrient elements such as N, P, and Cd.

Most prior studies have not considered scavenging, or have not found a significant role for scavenging influencing the distribution of Zn in the oceans. Experiments on degrading marine biogenic material confirm that Zn is released from particles more slowly than N, P or Cd (Collier and Edmond, 1984; Lee and Fisher, 1992). However, these experiments only measured the net rate at which elements were released into the dissolved phase, and did not attempt to quantify the importance of read-sorption or scavenging. Scavenging of Zn is thought to explain the high Zn:P ratios observed in South China Sea sediment traps (Ho et al., 2010, 2007), though most Zn in this region is delivered from anthropogenic aerosols, limiting applicability of this study to the open ocean. A 1-dimensional model with Zn input at the surface ocean and reversible-scavenging, similar to models originally developed for short residence elements such as Th and Pa (Bacon and Anderson, 1982), did not reproduce the global distribution of Zn (Little et al., 2013). However, given that this model did not include circulation, and the residence time of Zn in the ocean is much greater than the overturning of the ocean (~50,000 years compared to ~2000 years; Shiller and Boyle, 1985), the misfit between the model and data does not preclude a role for scavenging. Zn scavenging may play a role in Zn biogeochemical cycling in conjunction with other processes, such as biological uptake and remineralization, and ocean mixing and circulation.

Here, we explore the degree to which read-sorption onto sinking particles (scavenging) could influence the marine biogeochemical cycling of Zn, using Zn and Cd distribution and isotopic data from the North Atlantic, data from degrading phytoplankton cultures, and a simple 1-D model.

## 2. Methods

### 2.1. Sample collection and analysis

Seawater samples were collected on the US GEOTRACES A03 North Atlantic Zonal transect cruises in 2010 and 2011 at stations USGT10-9 (17.3° N, 18.3° W, Oct. 27th 2010), USGT10-10 (17.3° N, 20.8° W, Oct. 30th 2010), USGT11-10 (31.8° N, 64.2° W, Nov. 20, 2011), USGT11-12 (29.7° N, 56.8° W, Nov. 23th 2011) and USGT11-18 (24.1° N, 40.2° W Dec. 2nd 2011). Samples were collected using the US GEOTRACES trace-element clean carousel and filtered (0.4  $\mu\text{m}$ ) in a purpose-built clean van (Cutter and Bruland, 2012). Seawater dissolved Zn and Cd concentration,  $\delta^{66}\text{Zn}$  and  $\delta^{114}\text{Cd}$  were measured on a Thermo Neptune MC-ICPMS at the Centre for Elemental Mass Spectrometry at the University of South Carolina, with a double spike technique, after extraction onto Nobias PA-1 resin and purification by anion exchange chromatography following previously published methods (Conway et al., 2013).

Stable isotope ratios are presented as  $\delta^{66}\text{Zn}$  or  $\delta^{114}\text{Cd}$  where:

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

and

$$\delta^{114}\text{Cd} = \left( \frac{\left( \frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{sample}}}{\left( \frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{NIST-3108}}} - 1 \right) \times 1000. \quad (2)$$

For culturing experiments, the difference between two phases is given by:

$$\Delta\delta Y_{A-B} = \delta Y_A - \delta Y_B$$

for the two phases *A* and *B* (e.g. phytoplankton cells and the media in which they were grown).

### 2.2. Culture experiments

Cultures were grown and processed for isotope analysis in the MTEL laboratories at the University of South Carolina under ULPA-filtered air flow using acid-cleaned labware, ultrapure water (>18.2 M $\Omega$ ) and distilled high purity acids. The marine flagellate chlorophyte *Dunaliella tertiolecta* was grown for several months under non-axenic conditions, in *f/2* medium prepared with 0.2  $\mu\text{m}$  filtered seawater from the Baruch Marine Field Laboratory in Georgetown, SC. For our experiments, cells were transferred into a modified AQUIL media (Morel et al., 1979) containing  $10^{-4}$  M EDTA (Sunda et al., 2005) with a ~100-fold increase in Zn concentrations ( $10^{-5}$  M) compared to AQUIL and with the addition of Cd ( $10^{-6}$  M), in order to increase the quantity of these metals within the cells. Additionally, Fe concentrations were reduced 10-fold ( $10^{-7}$  M) compared to AQUIL in order to minimize cell-surface precipitation of metals, as Zn has been observed to co-precipitate with Fe oxyhydroxides on cell surfaces in media with high Fe concentrations ( $10^{-5}$  M) (John et al., 2007) but does not precipitate in similar media with lower Fe concentrations ( $10^{-6}$  M) (Sunda and Huntsman, 1992). The media free-inorganic ion concentrations of Zn and Cd (Zn' and Cd') were  $1.5 \cdot 10^{-9}$  M and  $5.9 \cdot 10^{-9}$  M, respectively, and the divalent ion concentrations (Zn<sup>2+</sup> and Cd<sup>2+</sup>) were  $1.0 \cdot 10^{-9}$  M and  $1.7 \cdot 10^{-10}$  M, respectively, as calculated using the equations of Sunda et al. (2005).

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