



On the origin of the marine zinc–silicon correlation

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ABSTRACT

The close linear correlation between the distributions of dissolved zinc (Zn) and silicon (Si) in seawater has puzzled chemical oceanographers since its discovery almost forty years ago, due to the apparent lack of a mechanism for coupling these two nutrient elements. Recent research has shown that such a correlation can be produced in an ocean model without any explicit coupling between Zn and Si, via the export of Zn-rich biogenic particles in the Southern Ocean, consistent with the observation of elevated Zn quotas in Southern Ocean diatoms. Here, we investigate the physical and biological mechanisms by which Southern Ocean uptake and export control the large-scale marine Zn distribution, using suites of sensitivity simulations in an ocean general circulation model (OGCM) and a box-model ensemble. These simulations focus on the sensitivity of the Zn distribution to the stoichiometry of Zn uptake relative to phosphate (PO_4), drawing directly on observations in culture. Our analysis reveals that OGCM model variants that produce a well-defined step between relatively constant, high Zn: PO_4 uptake ratios in the Southern Ocean and low Zn: PO_4 ratios at lower latitudes fare best in reproducing the marine Zn–Si correlation at both the global and the regional Southern Ocean scale, suggesting the presence of distinct Zn-biogeochemical regimes in the high- and low-latitude oceans that may relate to differences in physiology, ecology or (micro-)nutrient status. Furthermore, a study of the systematics of both the box model and the OGCM reveals that regional Southern Ocean Zn uptake exerts control over the global Zn distribution via its modulation of the biogeochemical characteristics of the surface Southern Ocean. Specifically, model variants with elevated Southern Ocean Zn: PO_4 uptake ratios produce near-complete Zn depletion in the Si-poor surface Subantarctic Zone, where upper-ocean water masses with key roles in the global oceanic circulation are formed. By setting the main preformed covariation trend within the ocean interior, the subduction of these Zn- and Si-poor water masses produces a close correlation between the Zn and Si distributions that is barely altered by their differential remineralisation during low-latitude cycling. We speculate that analogous processes in the high-latitude oceans may operate for other trace metal micronutrients as well, splitting the ocean into two fundamentally different biogeochemical, and thus biogeochemical, regimes.

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1. Introduction

As a phytoplankton micronutrient, zinc is a highly versatile element, playing a role as co-factor in metalloenzymes required for biological tasks as varied as carbon fixation (Price and Badger, 1989), gene expression (Twining and Baines, 2013) and the uptake of key macronutrients such as phosphorus and, poten-

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tially, silicon (Rueter and Morel, 1981; Sherbakova et al., 2005; Morel et al., 2014). Indeed, the physiological importance of zinc rivals that of iron (Fe), with more Zn-bearing metalloenzymes known than Fe-bearing ones (Morel et al., 2014). And yet the marine Zn cycle has received limited attention, most likely the result of a long-standing lack of observational data on the abundance of dissolved Zn in the sea. Within the last five years, the efforts of the GEOTRACES programme have produced an order-of-magnitude change in the volume of marine Zn abundance data (Mawji et al., 2015).

In a recent companion study, Vance et al. (2017) took advantage of this step-change in data availability to study the mechanisms

responsible for producing the observed oceanic Zn distribution. It has been known since the very first reliable analyses of oceanic Zn concentration (Bruland, 1980) that the Zn distribution mimics that of dissolved silicon, a macronutrient that is obligatorily required, and dominantly cycled, by the siliceous phytoplankton known as diatoms. The reasons for the very close, near-linear correlation (Fig. S3) between these two elements in the ocean has, however, remained unclear for over three decades. A direct mechanism, such as the incorporation of Zn into the siliceous frustules of diatoms (Broecker and Peng, 1982), is not permitted by the observation that the Zn content of diatom frustules is orders of magnitude too small to produce the observed correlation between Zn and Si (Ellwood and Hunter, 2000). Furthermore, recent cellular-level elemental mapping has revealed that Zn is mostly associated with the organic matter of diatoms (Twining et al., 2004), consistent with its important physiological role, and that cellular Zn is remineralised from sinking diatom detritus at shallow depths together with phosphorus, not at the greater depths at which siliceous hard parts dissolve (Twining et al., 2014). Thus, the simple correlation between the marine distributions of Zn and Si at the global scale appears at odds with their contrasting biochemical roles and marine biogeochemical behaviour.

Vance et al. (2017) resolved this apparent paradox by drawing on the observation that diatoms in the Southern Ocean have cellular Zn quotas 3–15× higher than those of low-latitude phytoplankton (Twining and Baines, 2013), a finding that is complemented by the observed stripping of Zn from Southern Ocean surface waters (Ellwood, 2008; Zhao et al., 2014). In analogy to the well-established control on the marine Si distribution by the export of Si-rich material from the surface Southern Ocean (Sarmiento et al., 2007), Vance et al. (2017) proposed that strong Zn drawdown by Southern Ocean diatoms with high Zn quotas is the main control on the global Zn distribution. Their ocean general circulation model (OGCM) results supported this hypothesis by reproducing the observed Zn–Si correlation when Southern Ocean Zn uptake was high, even in the absence of any explicit coupling between the cycles of these two elements.

The aim of this study is to identify the mechanisms by which this emergent large-scale Zn–Si coupling comes about. Our interest lies in understanding the series of interacting biological and physical processes that allows Zn uptake in the remote Southern Ocean to influence the global Zn distribution. We do this within the context of ocean biogeochemical models in which the cycling of Zn is explicitly tied to that of phosphorus (P), and go beyond the modelling work of Vance et al. (2017) by implementing a swathe of 24 OGCM sensitivity simulations as well as a 10,000-member box-model ensemble. Together, these simulations reveal that Southern Ocean Zn uptake exerts global control on the marine Zn distribution via its influence on the Zn status of the Subantarctic Zone (SAZ): sustained and elevated high-latitude Zn uptake leads to Zn-depletion in the Si-poor SAZ, producing a low-Zn, low-Si signal that is transported globally from this region by the subduction of the upper-ocean water masses Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW). The systematics of the models further suggest that this coupled biological–physical mechanism may apply more generally to other biologically-cycled elements in the sea.

2. Methods

2.1. Conceptual approach

We wish to assess the mechanisms by which a correlation between the marine distributions of Zn and Si may come about even in the absence of any explicit coupling between them. We do this in the context of ocean models, described in more detail below,

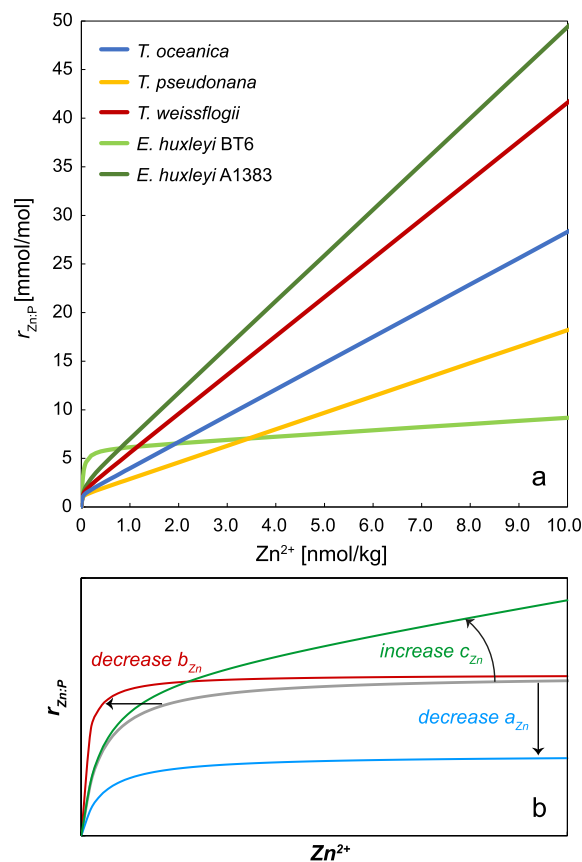


Fig. 1. Stoichiometry of simulated uptake. Panel a shows the dependence of the Zn:P uptake ratio $r_{Zn:P}$ on the ambient concentration of Zn^{2+} observed in culture experiments by Sunda and Huntsman (1992). Data in Sunda and Huntsman (given as Zn:C ratios) have been converted to Zn:P using the Redfield C:P ratio of 106 mol/mol. Panel b schematically illustrates the influence of the parameters α_{Zn} , b_{Zn} and c_{Zn} in Eqn. (1) on the shape of this dependency. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

that simulate the marine biogeochemical cycles of P, Zn and Si. In formulating the biogeochemical model, we were guided by the observations and constraints discussed in Section 1. Thus, our model explicitly couples the cycling of Zn to that of P, reflecting observations of Zn uptake in culture, our understanding of the physiological role of Zn as a micronutrient, and direct observation of the Zn distribution within phytoplankton cells (Sunda and Huntsman, 1992; Twining et al., 2004; Twining and Baines, 2013). The simulated surface–ocean uptake of Zn is directly tied to that of PO_4 by a stoichiometric parameter $r_{Zn:P}$, which is the key variable in our sensitivity analysis (see Section 2.2). Additionally, once exported from the surface ocean by sinking particles, Zn is remineralised over the same short length-scale as P, as indicated by observations of sinking diatoms (Twining et al., 2014). In contrast, simulated Si uptake is entirely independent of PO_4 uptake, and the length-scale of opal dissolution is greater than that of Zn or P remineralisation, rendering its cycling entirely biogeochemically independent.

2.2. Stoichiometry of simulated Zn uptake

The control parameter in our suite of sensitivity simulations is the stoichiometric parameter $r_{Zn:P}$, which links the uptake of Zn to the simulated PO_4 uptake. Our parameterisation of $r_{Zn:P}$ is based on results from laboratory cultures of three diatom species and two clones of the prymnesiophyte *E. huxleyi* by Sunda and Huntsman (1992). They observed that the Zn:C (and, by extension, Zn:P) ratio of phytoplankton uptake is a non-linear function of the Zn^{2+}

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