

Silicon and zinc biogeochemical cycles coupled through the Southern Ocean

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Zinc is vital for the physiology of oceanic phytoplankton. The striking similarity of the depth profiles of zinc to those of silicate suggests that the uptake of both elements into the opaline frustules of diatoms, and their regeneration from these frustules, should be coupled. However, the zinc content of diatom opal is negligible, and zinc is taken up into and regenerated from the organic parts of diatom cells. Thus, since opaline frustules dissolve deep in the water column whilst organic material is regenerated in the shallow subsurface ocean, there is little reason to expect the observed close similarity between zinc and silicate, and the dissimilarity between zinc and phosphate. Here we combine observations with simulations using a three-dimensional model of ocean circulation and biogeochemistry to show that the coupled distribution of zinc and silicate, as well as the decoupling of zinc and phosphate, can arise in the absence of mechanistic links between the uptake of zinc and silicate, and despite contrasting regeneration length-scales. Our simulations indicate that the oceanic zinc distribution is, in fact, a natural result of the interaction between ocean biogeochemistry and the physical circulation through the Southern Ocean hub. Our analysis demonstrates the importance of uptake stoichiometry in controlling ocean biogeochemistry, and the utility of global-scale elemental co-variation in the ocean in understanding these controls.

The spatial and vertical distributions of macro- (e.g. phosphate, nitrate, silicate) and metal micro-nutrients (e.g. iron, zinc) control sequestration of carbon by the ocean's biosphere. Zinc plays vital physiological roles in oceanic phytoplankton (e.g., ref 1) and Zn contents of phytoplankton cells are of the same order as the essential trace element, iron²⁻⁴. As a result, and like the major nutrients (P, N, Si), Zn shows extreme depletions in the surface ocean and enrichments at depth (Fig. 1, see Fig. 2 for locations and sources of all data used in the paper), a distribution that is often conceptualised in terms of one-dimensional vertical cycling involving uptake in the photic zone and regeneration beneath. Though the extent to which surface Zn concentrations limit primary productivity is still unclear (e.g., ref 12), the processes that control the removal of Zn from the photic zone, its

regeneration in the deep ocean, and its return to the surface via the ocean circulation, are a key part of the dynamics of oceanic nutrient chemistry.

A remarkable feature of global ocean nutrient profiles (Fig. 1) is the tight co-variation of Zn and Si in all three major ocean basins. Both elements increase to maxima for each profile in the abyssal ocean, in marked contrast to the intermediate-depth maximum for PO_4 . Though this coupling of Zn to Si has been repeatedly noted⁵⁻⁷, its origin has been a puzzle. Rationales for the deep maximum in Si relative to organic-associated nutrients, nitrate and phosphate, have emphasised two key processes: (1) vertical cycling with a greater regeneration length-scale of diatom opal relative to organic matter (e.g., 13, 14); (2) rapid depletion of Si relative to organic-associated nutrients in the surface Southern Ocean, creating distinct water mass signatures that are exported to the rest of the global ocean^{15,16}. For Zn it has been tentatively suggested that uptake of Zn and Si may be linked, and that increased Si uptake by diatoms due to Fe limitation may explain co-variation of Zn and Si observed in high-latitude nutriclines¹⁷. The first of these two views would suggest that the oceanic cycle of Zn is dominated by uptake into and regeneration from diatom opal. However, culturing studies¹⁸ have demonstrated that the Zn content of diatom opal is negligible (1-3% of the total cellular inventory), and that the Zn/Si ratio of diatom opal is nearly two orders of magnitude lower than observed in the deep ocean^{5,18}. This is confirmed by synchrotron micro-XRF data^{2,3} from both cultured and natural diatom cells, which clearly show that Zn is co-located with phosphorus in the organic matter of diatom cells and not in their opaline frustules, and that Zn is regenerated from this organic material in the upper ocean with phosphate, and not with Si from opal^{19,20}.

Diatom uptake in the Southern Ocean couples Zn and Si

We suggest that the solution to this paradox lies in the biogeochemistry and physical oceanography of the Southern Ocean. Water upwelled at the Antarctic divergence, and moved northward at the

73 surface by Ekman transport to the Sub-Antarctic zone, is stripped of Si and Zn much faster than
74 PO_4 (Fig. 3a, b). Thus, both Zn and Si concentrations drop by a factor of about 40 over the surface
75 transect shown in Fig. 3a, whereas PO_4 drops by only a factor of 3. This remarkable difference in
76 relative drawdown rates is consistent with the ecological dominance of diatoms in this region (e.g.
77 refs 22, 23), and their peculiarly high Zn/P uptake ratio, up to an order of magnitude greater than
78 the average for oceanic phytoplankton³. The Zn- and Si-depleted Sub-Antarctic surface layer is the
79 ultimate source of Sub-Antarctic Mode Water (SAMW), and it is the northward transport of this
80 water mass that, we suggest, sets the low dissolved Si and Zn concentrations, and low Si/ PO_4 and
81 Zn/ PO_4 ratios, of most of the global upper ocean (Fig. 1). The data in Fig. 3a also imply a rather
82 constant ratio for the removal of Zn and Si from the dissolved pool of the surface Southern Ocean,
83 despite the fact that Si is taken up into opal and Zn into organic material.

84
85 What is the ultimate fate of the large amounts of Zn and Si relative to PO_4 removed from the
86 surface Southern Ocean? The Sub-Antarctic winter mixed layer from which SAMW forms is of the
87 order of 200-400m thick (e.g., ref 24), beneath which the Southern Ocean water column is
88 vigorously mixed and rather homogeneous (e.g., ref 25), including for Si, Zn and PO_4 ¹¹. Thus, if
89 diatom cells are exported beneath about 200-400m, their high Zn/P and Si/P characteristics will be
90 imparted to the deep Southern Ocean regardless of the exact cellular location (opal or organic
91 matter) of Zn, Si and P, making the different regeneration length-scales of these particulate phases
92 much less relevant here than elsewhere in the ocean. This export, which may be aided by the rapid
93 blooming and equally rapid population collapse that is characteristic of diatom ecology (e.g., refs
94 22, 23), results in a Zn and Si deficit relative to PO_4 in the mixed layer, which is the source of upper
95 ocean water masses such as AAIW and SAMW.

In summary, the hypothesis we put forward here consists of three components: (1) extreme drawdown of Zn and Si relative to PO_4 in the surface Southern Ocean (Fig. 2a) consistent with the known stoichiometry of Southern Ocean diatoms³, thus setting the biogeochemical signature of the surface Southern Ocean and the upper ocean water masses derived from it; (2) export of diatom cells below the winter mixed layer depth, transferring both Zn and Si at high Zn/P and Si/P to the deep Southern Ocean, despite being located in two different components of the diatom cell with different regeneration length-scales, thus setting the biogeochemical signatures of deep and abyssal Southern Ocean-derived water masses (Fig. 1); and (3) lateral export of these water mass signatures to the low latitude oceans, as previously proposed to control Si- NO_3 nutrient systematics^{15,16}. The imprint of these processes can be seen in Fig. 3c. Zinc- PO_4 data for the Atlantic sector of the Antarctic zone of the Southern Ocean (including the surface transect in Fig. 3a and the entire water column at 67°S, black triangles¹¹) indicate co-variation along a line with a slope of about 8 mmol mol^{-1} , consistent with a control by diatom uptake and regeneration. Data for stations proximal to the Southern Ocean, at 40°S in the South Atlantic (entire water column, blue squares⁷) clearly show two different behaviours, with the deep ocean lying close to the Antarctic zone data, and the upper ocean data reflecting the much lower slope expected for water masses sourced in the mixed layer of the Southern Ocean, from which Zn has been stripped. The red dashed lines indicate, schematically, how water mass mixing in locations more distal from the Southern Ocean sources would confound these clear distinctions.

The Southern Ocean uptake hypothesis tested in an ocean model

To provide a quantitative test of these ideas, and taking advantage of the computational efficiency of the transport matrix method²⁶, we performed a series of 11 sensitivity simulations (see Methods and Supplementary Information) using an ocean general circulation model coupled offline to a biogeochemical model of P, Si and Zn cycling. In the biogeochemical model, PO_4 and Si cycling

are treated completely independently, whilst Zn cycling is explicitly tied to that of P. Zinc in the oceanic dissolved pool is present as both inorganic Zn ($\text{Zn}^{\text{'}}$) and complexed with an organic ligand (ZnL). Culturing studies²⁷ have shown that Zn uptake by phytoplankton, and their Zn/P ratios, can be parameterised using the quantitative dependence of Zn uptake on free Zn concentrations, the approach we adopt here. It is currently unclear exactly *why* Southern Ocean diatoms exhibit high Zn/P uptake ratios, but the high values seen in data³ emerge from the model simply from the fact that upwelled water in the Southern Ocean contains high concentrations of Zn so that not all of it is complexed by organic ligands, a finding that is also supported by data²⁸.

Although the lengthscale of Zn regeneration is identical to P in these simulations, and though its cycling is entirely decoupled from that of Si, our model reproduces the observed near-linear correlation between Zn and Si at the global scale (Fig. 4c). It also reproduces the slow increase with depth in Zn concentrations through the upper ocean at low latitudes (Fig. 1), despite the fact that Zn is regenerated in the shallow subsurface in the model. The mechanism behind this model behaviour is indicated by our model's sensitivity to the Zn/P uptake ratio in the Southern Ocean (see Supplementary Information for sensitivity tests): as the average Zn/P ratio of uptake in the Southern Ocean increases, the Zn distribution changes from being closely correlated with that of PO_4 (at Zn/P uptake ratios of $\sim 1 \text{ mmol mol}^{-1}$) to being very similar to the large-scale Si distribution (at values above $\sim 4.5 \text{ mmol mol}^{-1}$).

The key feature of the global Zn- PO_4 covariation (Fig. 4d) is the curvature in the model array. This arises because of the partitioning of the global oceans into the two broad regimes seen in Fig. 3c: an upper ocean that is severely depleted in Zn (and Si) relative to PO_4 as a result of the stripping of Zn (and Si) from the surface Southern Ocean, and the export of this water to the upper ocean globally; and a deep and abyssal ocean that is dominated by water masses originating in the deep Southern

147 Ocean, containing the regenerated counterpart of this surface uptake process. The model is less
148 good at representing the physical mixing of these end-members outside the Southern Ocean (see
149 schematic trajectories in Fig. 3c), so that it underestimates the scatter in the data in Fig. 4b,d.

150
151 We emphasise that our aim here is to provide an explanation for a first-order feature of global ocean
152 Zn-Si-P distributions and, as such, we have deliberately kept the model simple, attempting to
153 restrict the processes it represents to those that are well-established. Thus, Zn uptake is tied to that
154 of P as dictated by the results of culturing experiments, and there are no mechanistic links between
155 the uptake of Zn and Si. We have parameterised Zn speciation in the context of a single ligand
156 model (see Supplementary Information). The model does not consider the potential impacts of
157 variations in metal uptake stoichiometry across different taxonomic groups. It does not consider the
158 potential effects that Fe limitation may have on diatom physiology. Despite this simplicity, the
159 model is very successful in reproducing global dissolved nutrient distributions. Invoking further
160 complexity, such as a significant role for previously-proposed vertical processes such as scavenging
161 of Zn by particulate material or a second organic Zn pool associated with opal^{11,29,30} is not required
162 to reproduce first-order global Zn-Si-PO₄ relationships. We have also avoided tuning the model to
163 improve the fit to the data. For example, the slope of the model Zn-Si correlation on Fig. 4c is about
164 12% below that defined by the data, at 0.056 mmol mol⁻¹ versus 0.064 mmol mol⁻¹. The simulated
165 slope is entirely dependent on assumed model values for the average oceanic Zn and Si
166 concentrations, drawn from the literature (see Supplementary Information). The former, in
167 particular, given the comparative lack of data coverage, is certainly only an estimate at this stage.

168
169 Our analysis of Zn-Si-PO₄ systematics in the global ocean has important implications for both Zn
170 itself and for oceanic trace elements more broadly. The implication of our proposal is that Southern
171 Ocean diatoms dominate oceanic Zn cycling, transferring a large fraction of the oceanic pool to the

172 abyssal ocean and trapping it there, in a direct analogy with Si trapping^{15,16}. The finding that Zn
173 distributions in the global ocean are so profoundly influenced by the stoichiometry of uptake in the
174 Southern Ocean has relevance for studies of other trace metals, their oceanic distributions, and
175 relationships between different nutrients. For example, the “kink” in Zn-PO₄ is reminiscent of the
176 well established “kink” in the relationship between the trace metal cadmium (Cd) and PO₄, whose
177 precise origin is much debated³¹⁻³³. Phytoplankton uptake stoichiometry, speciation of metals in the
178 photic zone, and their systematics in regions of the ocean that are hubs for the physical circulation,
179 are likely as important for other metals as they are for Zn in determining global ocean distributions.
180 The implication is that oceanic metal micronutrient distributions are set by a combination of
181 Southern Ocean ecology and physical circulation, as for major nutrients^{15,16}. Therefore, changes in
182 the Southern Ocean forced by past and future climate change will have global impact.

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Author contributions

DV and SHL conceived the study. DV wrote the first draft of the paper. GdS constructed the biogeochemical model in collaboration of SPK, conceived and carried out the sensitivity simulations, and analysed the model output. MCL and RM were responsible for the Atlantic data in the GEOTRACES Intermediate Data Product and used in the figures. All authors read and commented on the paper.

Competing financial interests

The authors declare no competing financial interests.

Figure captions

Figure 1: Example depth profiles of Zn, Si and PO₄ in the three main ocean basins

The striking similarity in the depth distributions of Zn and Si stands in marked contrast to the dissimilarity with PO₄. The presence of Sub-Antarctic Mode Water (SAMW, potential density anomaly $\sigma_\theta = 26.80^{15}$) and Antarctic Intermediate Water (AAIW^{7,8}) in the South Atlantic and equatorial Indian Oceans is reflected in the low Si and Zn concentrations compared to P. In the North Pacific these depth levels are occupied by other water masses. Locations of stations depicted, as well as data sources, are given in Fig. 2.

Figure 2: Location map

The locations of the stations from which nutrient data are depicted in Figs. 1, 3 and 4. Pacific data from Bruland et al.⁵ (Station 17) and VERTEX profiles⁶. Atlantic (GA02 and GA10⁷) and Indian (GI04⁹) data from the GEOTRACES 2014 Intermediate Data Product¹⁰. Southern Ocean (IPY) data from Zhao et al.¹¹.

Figure 3: Contrasting variability in nutrient uptake in the Atlantic sector of the Southern Ocean

a,b: The strong depletion of Zn and Si versus moderate depletion of PO₄ as water is moved northward from the upwelling zone (data from dashed black line in Fig. 2^{7,11}). Physical features identified using WOCE hydrographic data along the zero meridian²¹: AD, Antarctic Divergence; PF, Polar Front; SAF, Sub-Antarctic Front; AZ, Antarctic Zone, PFZ, Polar Frontal Zone; SAZ, Sub-Antarctic Zone. **c:** Distribution of Zn and PO₄ in the Atlantic sector of the Southern Ocean. Antarctic Zone data¹¹ track removal of Zn and PO₄ at a very high ratio (Zn/P = 8 mmol mol⁻¹). South Atlantic 40°S data⁷ show contrasting Zn/P ratios, extremely low (0.3 mmol mol⁻¹) in the upper ocean, and high in the deep. Dashed red lines show possible trajectories for mixing between end-members on this diagram.

Figure 4: Coupled major and micro-nutrient distributions in the global ocean

a,b: Global Zn-Si-PO₄ systematics in all three ocean basins. Black arrows in **b** as in Fig 3c. Data plotted for all stations on each section shown in Fig. 2 (see caption for data sources), and for the entire water column. **c,d:** The same data as in **a,b** (grey), with the results of a three-dimensional model of ocean circulation and biogeochemistry superimposed (Simulation 11, see Supplementary

301 Information; colours represent the volume-weighted relative frequency of model cells with the
302 given Zn-Si or Zn-PO₄ characteristics).
303

Methods

Physical model: Ocean general circulation model simulations were carried out using the transport matrix method (TMM) of Khatiwala et al.²⁶ using transport matrices (TMs) derived from a coarse-resolution version of the MITgcm³⁴ with $2.8^\circ \times 2.8^\circ$ lateral resolution and 15 vertical levels forced with monthly mean climatological fluxes of momentum, heat and freshwater and with weak restoring of surface temperature and salinity to the Levitus climatology³⁵. Our sensitivity simulations were carried out using constant annual-mean circulation fields derived from the equilibrium state of the model after 5000 yr integration; thus, seasonal variability is not represented in our simulations. The physical model is coupled to a biogeochemical model that simulates the internal oceanic cycling of phosphorus (as phosphate, PO_4 , and dissolved organic phosphorus, DOP), zinc (Zn) and silicate (Si). Biogeochemical model simulations were initialized with constant nutrient tracer fields (ocean-mean concentrations of $2.17 \mu\text{M}$, 5.4 nM and $92 \mu\text{M}$ for PO_4 , Zn and Si respectively) and integrated forward for 5000 model years.

Biogeochemical model: The nutrient-cycling model that forms the basis of our simulations is based on the formulation developed for the OCMIP-2 project³⁶ and uses PO_4 as its nutrient currency. Phosphate uptake in the surface ocean is driven by restoring surface PO_4 concentrations^{37,38} towards the objectively-analysed annual-mean PO_4 field of World Ocean Atlas 2013³⁹ with a restoring timescale of 36.5 days. A fraction of PO_4 taken up is immediately shunted towards DOP, whilst the remaining fraction is exported as an implicit particulate flux to depth, which remineralises following a power-law dependency on depth^{40,41}. Any particulate flux reaching the bottom of the water column remineralises within the bottom ocean cell. Dissolved organic phosphorus is carried passively with the circulation and decays back to PO_4 with a first-order rate constant of $(0.5 \text{ year})^{-1}$.

The Zn-cycling model is explicitly coupled to the P-cycling model above. Zinc uptake in the surface ocean is tied to PO_4 uptake via a dimensionless stoichiometric parameter $r_{\text{Zn:P}}$ (see *Zn uptake parameterization* below). This surface-ocean uptake drives an implicit export flux of

particulate Zn, which remineralises identically to the implicit particulate P flux. The organic speciation of dissolved Zn is represented implicitly by assuming a constant ligand concentration of 1.2 nM with a conditional stability constant of 10^{10} M^{-1} , which reduces the calculation of the concentration of free Zn (i.e. organically and inorganically uncomplexed Zn^{2+}) to the solution of a quadratic equation (see Supplementary Information). Varying biogeochemical behaviours of the Zn-cycling model are achieved by the formulation of the stoichiometric parameter $r_{\text{Zn:P}}$, as detailed below.

Our silicon cycling model is conceptually very similar to our PO_4 -cycling model, and to the Si-cycling model of de Souza et al.⁴². Dissolved Si uptake in the surface ocean ($\leq 120\text{m}$ water depth) is driven by restoring surface Si concentrations towards the objectively-analysed annual-mean Si field of World Ocean Atlas 2013 with a restoring timescale of 36.5 days. This surface-ocean uptake drives an implicit particulate export flux, which dissolves following an exponential dependency on depth with a length-scale of 1000 m (ref. 41). Any particulate flux reaching the bottom of the water column remineralises within the bottom ocean cell. It is important to note that in our model formulation, Si cycling is entirely biogeochemically independent of PO_4 and Zn cycling.

Zn uptake parameterization

Details of the parameterization of Zn uptake, including the rationale behind choices made in defining this parameterization, can be found in the Supplementary Information. Broadly, our biogeochemical model represents the plasticity in the Zn:P stoichiometry of uptake by phytoplankton (diatoms and coccolithophorids) observed in culture experiments by Sunda and Hunstman²⁷. These authors observed that the Zn:P uptake ratio varies non-linearly with the concentration of free Zn (Zn^{2+}) in the culturing medium, a dependency with the following functional form (called the “two-site model”):

$$r_{\text{Zn:P}} = \frac{a_{\text{Zn}} \cdot \text{Zn}^{2+}}{b_{\text{Zn}} + \text{Zn}^{2+}} + c_{\text{Zn}} \cdot \text{Zn}^{2+} \quad (\text{Eqn. 1})$$

where $r_{Zn:P}$ is the molar Zn:P uptake ratio, and parameters a_{Zn} , b_{Zn} and c_{Zn} are constants analogous to maximum uptake rate, half-saturation constant and non-saturable uptake rate, respectively. The culture data of Sunda and Huntsman²⁶ were used to delineate the extent of variability of these parameters in our suite of sensitivity simulations, as detailed in the Supplementary Information. Parameters and key statistical metrics for the 11 sensitivity simulations carried out are listed in Table S1, together with a detailed discussion of the results.

Data availability. The data that support the findings of this study are available at <http://www.bodc.ac.uk/geotraces/data/idp2014>.

Code availability. The TMM code is available on GitHub (<https://github.com/samarkhathiwalatmm>), and the biogeochemical code can be provided on request.

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