Biogeochemical cycling of cadmium isotopes in the Southern Ocean along the Zero Meridian

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Abstract

We present depth profiles of Cd isotopes and concentrations from the Southern Ocean at four stations in the Atlantic sector along the Greenwich Meridian (47°S to 68°S) located across the main Antarctic frontal zones and productivity belt. The vertical profiles of Cd concentration typically show low values in surface waters, elevated values at intermediate depths, reflecting remineralization of sinking particulate organic matter, and constant values in deep waters. The surface-to-deep isotopic gradient shows "heavy" Cd isotope signatures in the mixed surface layer, becoming more pronounced northward, with values up to $\varepsilon^{112/110}$Cd of around +4.1 in the Subantarctic sector of the Southern Ocean. Deep Antarctic waters display a uniform and "light" $\varepsilon^{112/110}$Cd of +1.18 ± 0.38 and Cd concentrations of 0.761 ± 0.101 nmol/kg ($n = 23$, 2SD). Intermediate waters are characterized by $\varepsilon^{112/110}$Cd lying between those of surface and deep waters, with a constant value of about +0.8 in the High Nutrient Low Chlorophyll sector and a notably higher value of +2.3 in the Subantarctic sector.

The Cd isotope fractionation in the Southern Ocean closely follows a simple closed-system Rayleigh model, in which biological uptake of Cd imparts the $\varepsilon^{112/110}$Cd signature to the surface layer while that of deep waters is determined by the flux of regenerated isotopically-light Cd from sinking organic matter from the surface ocean and the degree of mixing of distinct water masses.

The vertical gradient documented for Cd isotopes and nutrient ratios, along with the meridional gradient in surface waters, highlights the important role played by upwelling in the Southern Ocean in closing the meridional overturning circulation via the export of Antarctic intermediate and mode waters which have a distinctive chemical (low Cd:P) and Cd isotope ("heavy") signature.

The combined Cd–Zn isotope systematics provide evidence for a strong link between the magnitude of biological Cd stable isotope fractionation and Zn availability in the contrasted nutrient and ecological regimes of the Southern Ocean. Substitution of Cd for Zn in the enzyme carbonic anhydrase appears to be the driving mechanism for Cd isotope fractionation in the Antarctic Circumpolar Current, while an "excess-uptake" mechanism seems to predominate in the Weddell Gyre.

Our study highlights some of the complexities of the biogeochemical cycling of Cd in the oceans. Nevertheless, systematic variations in Cd isotopic compositions with water mass distribution in the Southern Ocean suggest that Cd isotopes could, with some caveats, be useful tracers of changes in past nutrient utilization and deep water circulation.

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1. INTRODUCTION

Recent breakthroughs in analytical instrumentation and chemical separation of trace metals, along with ultra-clean seawater sampling, have led to improvements in both sensitivity and accuracy of concentration measurements of some key micronutrient elements in the oceans, such as zinc (Zn), cadmium (Cd) and iron (Fe). Of particular interest is the trace metal Cd, for which the first reliable vertical distribution profiles in the water column showed a surprisingly good correlation with the major nutrient phosphate – a result of the removal of both elements by phytoplankton from surface waters and re-mineralization of organic debris at depth (Boyle et al., 1976; Bruland 1980; Boyle, 1988).

While the role of P as an essential nutrient for microorganisms is well known, the role of Cd is still not very well understood. Although Cd is toxic at high levels, it appears to be assimilated by some phytoplankton species under certain conditions, for example under Zn limitation (Price and Morel, 1990) or in Fe-limited oceanic regions (Löscher et al., 1998; Cullen, 2006). More specifically, substitution of Cd for Zn in the enzyme carbonic anhydrase (CA) – which facilitates the conversion of bicarbonate to carbon dioxide, and plays a key role in photosynthetic CO_2 fixation (Badger and Price, 1994) – has been reported under Zn-limited conditions (Price and Morel, 1990; Morel et al., 1994; Lane and Morel, 2000). The discovery of a distinct cadmium-based version of carbonic anhydrase (CdCA) in certain diatoms indicates that Cd may have its own biochemical function as well (Lane et al., 2005; Xu et al., 2008).

In the Southern Ocean, this function might be particularly important, since large bloom-forming diatoms are the dominant phytoplankton species (de Baar et al., 1997). At the Antarctic Polar Front (APF), these intensive diatom blooms remove essentially all dissolved silicate from seawater (Queguiner et al., 1997), causing a major decrease in silica in surface waters from south of the APF into the Subantarctic Zone (Fig. 1). The concentration of the nutrient silicate thereby delimits the southern High Nutrient Low Chlorophyll (HNLC) Si-rich waters from the silicate-depleted waters north of the APF (see Fig. 1b). The same diatom blooms are also responsible for the preferential uptake of Cd over phosphate at the APF (Löscher et al., 1998). This, in combination with the potential substitution of Cd in carbonic anhydrase of some diatoms, suggests that some Cd uptake may be "biological" and may also be responsible for generating the Cd stable isotope fractionation observed in Southern Ocean surface waters (e.g., Abouchami et al., 2011). Recent experiments, on the other hand, indicate that Cd uptake in a genetically-modified bacterium, at least, is non-specific and unrelated to the expression of the gene for carbonic anhydrase (Horner et al., 2013).

Studies of stable Cd isotope fractionations in the oceans, have already added a new dimension to the understanding of the marine biogeochemical cycle and the mechanisms regulating Cd uptake by marine phytoplankton (e.g., Lacan et al., 2006; Ripperger et al., 2007; Schmitt et al., 2009a; Horner et al., 2010; Abouchami et al., 2011; Xue et al., 2012; Gault-Ringold et al., 2012; Yang et al., 2012).

Significant Cd isotope fractionation occurs in the oceans, as shown by the large isotopic contrast between "heavy" Cd in nutrient-depleted surface waters, due to preferential uptake of "light" Cd by phytoplankton, while "light" Cd in deeper waters is acquired from recycled organic matter.

The first surface water Cd isotope transect in the Southern Ocean, along the Greenwich Meridian, revealed a strong meridional isotope gradient separating two major biogeochemical provinces shaped by the interaction of biological Cd utilization and physical ocean circulation (Abouchami et al., 2011). Most notably, a doubling of the Cd stable isotope fractionation factor passing from the Weddell Gyre into the Antarctic Circumpolar Current (ACC) was linked to contrasting phytoplankton communities and mechanisms of cellular uptake of Cd in these distinct productivity zones of the Southern Ocean.

The opportunity to study the distribution of stable Cd isotopes in the oceans, fostered by the GEOTRACES program, provides means to unravel the marine cycle of Cd, akin to the classical breakthroughs and numerous applications of the ratio $^{13}C/^{12}C$ for understanding the ocean carbon cycle. Hopefully, this will establish a framework within which Cd isotopes ($\varepsilon^{112/110}Cd$ or $\varepsilon^{114/110}Cd$) can be used as a paleo-nutrient proxy in much the same way as other proxies, such as Cd/Ca, $\delta^{13}C$, $^{231}Pa/^{230}Th$ and $\delta^{15}N$. Given the control that oceanic nutrient inventories have on the efficiency and strength of the "biological pump" in sequestering atmospheric CO_2 and thus regulating the global carbon cycle (Sigman and Boyle, 2000), improving our understanding of the biogeochemical cycles of key nutrient elements is crucial. In this regard, the Southern Ocean is particularly important, considering its large nutrient inventory and potential role in glacial drawdown of atmospheric CO_2 (Broecker, 1982; Martin et al., 1990).

Here we examine the vertical distribution of Cd concentrations and stable Cd isotopic compositions in four depth profiles from the Southern Ocean along the Greenwich Meridian (Fig. 1). This new dataset complements the results from the surface water transect reported previously by Abouchami et al. (2011). The aim is to investigate spatial changes in nutrient distributions and Cd isotope fractionation in the water column in order to understand better how physical, chemical, and biological processes – which ultimately control the export of carbon to the deep ocean – affect Cd isotope fractionation.

2. THE SOUTHERN OCEAN: MAJOR NUTRIENT AND WATER MASS DISTRIBUTIONS

The Southern Ocean covers ~14% of the surface of the globe and comprises all waters south of the Subtropical Front (STF), which is situated at ~40°S (Fig. 1a). The more southward Antarctic Polar Front (APF) at ~50°S marks the northern boundary of the Antarctic Ocean proper.

The Antarctic Ocean is peculiar in that its surface waters contain ample major nutrients (i.e., phosphate, nitrate and silicate) – yet the abundance and growth of phytoplankton are both relatively low. This HNLC condition has been shown to be due to co-limitation by several factors,