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The cadmium–phosphate relationship in the western South Atlantic — The importance of mode and intermediate waters on the global systematics

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The correlation between dissolved cadmium (Cd) and phosphate (PO_4) in the modern ocean has been extensively studied. However, factors that cause the non-linearity in this global correlation are still largely debated and poorly constrained. In this study, we present vertical and meridional distributions of Cd concentrations along the GEOTRACES GA02 Leg 3 transect (53°S to 0°S) in the western South Atlantic. The vertical profiles of dissolved Cd show typical nutrient-like distributions, matching those of the macronutrient PO_4. In the surface ocean, low Cd concentrations of 0.34–45 pmol kg^{-1} are measured at all stations sampled. Below the fluorescence maxima, Cd concentrations increase with depth, reaching maxima at the depths of, or slightly below, the oxygen minimum. Similarly, surface waters have very low dissolved Cd/PO_4 ratios, followed by a sudden decrease at depths corresponding to the fluorescence maxima, below which the Cd/PO_4 ratios increase with depth.

These variations in Cd and Cd/PO_4 ratios are consistent with phytoplankton uptake in the surface ocean at higher Cd/PO_4 ratios compared to deep water Redfield Cd/PO_4 ratios, and remineralization of high Cd/PO_4 organic particles as they sink to depth. In addition, a comparison of Cd and PO_4 distributions in waters within the depth range of Subantarctic Mode Water (SAMW) in our study and those in the source regions suggests that SAMW plays an important role in the non-linearity of the Cd–PO_4 correlation in the global ocean. On the other hand, intermediate waters at the equatorial stations display significantly lower Cd compared to the southern stations in this study. We attribute this to the influence of low-Cd waters originating in the oxygen-depleted zone (ODZ) of the Angola Basin that are brought in via the Benguela and Equatorial Currents. In the deep ocean (>1000 m), the meridional distributions of dissolved Cd concentrations and Cd/PO_4 ratios reflect mixing between North Atlantic Deep Water (NADW) (low nutrients, low Cd/PO_4 ratios) and Antarctic Bottom Water (AABW) (high nutrients, high Cd/PO_4 ratios), showing that dissolved Cd and PO_4 can reliably trace deep ocean circulation in the modern ocean.

1. Introduction

The vertical distributions of the trace metal Cd in seawater resemble those of the major nutrients, with the lowest concentrations found in nutrient-depleted surface waters, due to uptake by phytoplankton, and maximum concentrations at the depths of PO_4 and nitrate maxima, as sinking biogenic particles remineralize (e.g., Boyle et al., 1976; Bruland, 1980; Bruland et al., 1978; de Baar et al., 1994). The fact that the vertical profiles are "nutrient-like" is undisputed, but whether or not the uptake of Cd in general involves biological utilization is a matter

of debate (Horner et al., 2013a,b; Morel, 2013). Nevertheless, a "biological" function for Cd in the marine environment is clear in some cases. This was first confirmed in cultured phytoplankton experiments under Zn-limiting conditions, where addition of Cd to the growth medium promoted significant phytoplankton growth by substitution of Cd for Zn in the Zn-specific carbonic anhydrase enzyme (Price and Morel, 1990). Similarly, the discovery of a Cd-specific carbonic anhydrase (Cd-CA) in *Thalassiosira weissflogii* (Lane and Morel, 2000) supports a metabolic role of cadmium in some species.

Throughout the global ocean, a remarkable linear correlation exists between dissolved Cd and PO_4, as first shown by Boyle et al. (1976), with a pronounced break — the so-called "kink" — occurring at PO_4 of ~1.3 μmol kg^{-1}, which is associated with a change in slope. Below the

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"kink", young North Atlantic waters and surface waters define a trend with a shallow Cd:PO$_4$ slope, while above this PO$_4$ threshold, waters from the Indian, Pacific, and Southern Oceans display a trend with a steeper slope (Boyle, 1988; Boyle et al., 1976; Bruland, 1980; Bruland et al., 1978, 1979; Cullen, 2006; de Baar et al., 1994; Frew, 1995; Frew and Hunter, 1992, 1995; Löscher et al., 1997; Yeats, 1998; and reference therein). Throughout the text, the term "Cd:PO$_4$ slope" is used to refer to the drawdown ratios of Cd to PO$_4$, while "Cd/PO$_4$ ratio" refers to the spot ratios, as measured in different water masses.

Although there exist local differences in surface water Cd/PO$_4$ ratios, waters deeper than 1000 m generally have constant Cd/PO$_4$ ratios within each ocean basin (e.g., de Baar et al., 1994). The increasing Cd/PO$_4$ ratios in aging deep waters, varying from ~0.18 nmol μmol^{-1} in the subarctic North Atlantic (Danielsson et al., 1985; Nolting et al., 1987) to ~0.33–0.35 nmol μmol^{-1} in the Indian Ocean and North Pacific (Bruland, 1980; Saager et al., 1992), are associated with increased dissolved Cd and PO$_4$ concentrations. Such an "aging" effect in seawater Cd and PO$_4$ concentrations reflects both the effects of deep remineralization and circulation control on nutrient distributions (de Baar et al., 1994; Yeats et al., 1995).

The overall linearity of the Cd–PO$_4$ relationship in deep waters allows Cd to be used as a proxy for the macronutrient PO$_4$ in the past ocean, enabling reconstruction of past variations in nutrient content and deep ocean circulation (Boyle, 1988). Analytically, this is done by determining the Cd/Ca ratios preserved in foraminifera tests and coral skeletons (e.g., Boyle, 1988; Boyle, 1992; Elderfield and Rickaby, 2000; Shen et al., 1987).

The use of Cd as a chemical tracer in paleoceanography is, however, strictly dependent on two assumptions — the first is that the modern Cd–PO$_4$ relationship remains the same as in the past oceans; secondly, that the distribution coefficient of Cd/Ca between foraminifera tests/ coral skeletons and ambient seawater has remained constant (Boyle, 1988). In this context, there is a need to document regional variations in Cd–PO$_4$ more fully in order to arrive at a more complete picture of the Cd–PO$_4$ distribution in the global ocean. Furthermore, the vertical biogeochemical cycling of Cd in the oceans will be better established once the mechanisms governing vertical variations in Cd–PO$_4$ and Cd stable isotopes in seawater (e.g., John and Conway, 2014; Gault-Ringold et al., 2012; Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011, 2014; Xue et al., 2013; Yang et al., 2012) are documented and understood.

Many mechanisms have been put forward to account for the Cd–PO$_4$ systematics observed in various oceanographic settings. It was originally suggested by Boyle (1988) that deeper regeneration of Cd with respect to PO$_4$ caused the "kink" observed in the global dataset. At the other extreme, Elderfield and Rickaby (2000) have drawn into question the need for a kink at all and instead argue that, since there is preferential uptake of Cd in surface waters compared to PO$_4$, the whole dataset is consistent with a Rayleigh model having a constant fractionation factor between organic particulates and ambient seawater.

More recently, increasing evidence has been brought forward for preferential removal of Cd with respect to PO$_4$ under micronutrient limiting conditions, and especially under iron limitation (Cullen et al., 1999; Lane et al., 2008, 2009; Löscher et al., 1998; Saager and de Baar, 1993; Sunda and Huntsman, 2000). Specifically, the Cd/PO$_4$ ratios in surface waters from Fe-limited, High Nutrient Low Chlorophyll (HNLC) regions are significantly lower than those from Fe-replete areas (Cullen, 2006). This has led, logically, to the suggestion that chronic Fe-limiting conditions in HNLC areas may have created the "kink" in the global Cd–PO$_4$ systematics (Cullen, 2006). On the other hand, during an open-ocean iron enrichment experiment, it was demonstrated that preferential utilization of Cd relative to PO$_4$ occurs regardless of iron availability (Frew et al., 2001).

A further complication, in addition to micronutrient co-limitation, is the differential regeneration of Cd and PO$_4$ observed in Oxygen Deficient Zones (ODZ, dissolved O$_2$ < 75 μmol kg^{-1}) (Yeats et al., 1995). Recent studies in the ODZ of the Angola Basin in the southeastern Atlantic

(Waeles et al., 2013) and in the northeastern Pacific and northeastern Atlantic (Conway and John, 2015; Janssen et al., 2014) have attributed the Cd–PO$_4$ decoupling, using the Cd* parameter, to cadmium sulfide (CdS) precipitation, which leaves ambient seawater depleted in Cd with respect to PO$_4$.

Another mechanism proposed for the Cd–PO$_4$ "kink" is injection of cadmium-depleted subantarctic surface waters — the precursor of Subantarctic Mode Water (SAMW) — into intermediate depths (Frew and Hunter, 1992, 1995). Such a model does not appear consistent with Cd–PO$_4$ profiles from the eastern Atlantic Ocean (Yeats et al., 1995) and is not supported by an isopycnal analysis of global dissolved Cd (Yeats, 1998). Yet, recent stable Cd isotope studies have suggested that SAMW plays an important role in the cycling of Cd in the Pacific (Gault-Ringold et al., 2012) and Atlantic sectors of the Southern Ocean (Abouchami et al., 2014; Baars et al., 2014).

In this study, we present vertical and meridional distributions of dissolved Cd concentrations along the western boundary in the South Atlantic along a transect running from 53°S to the Equator, where limited data have been available thus far. Our new dissolved Cd dataset, along with available PO$_4$ concentrations in the same transect, highlights the importance of SAMW and ODZ in the global oceanic distribution of Cd. Our study provides further evidence that Cd concentrations reliably trace deep water masses and vertical mixing in the modern ocean.

2. GEOTRACES GA02 cruise Leg 3 transect and hydrology

Seawater samples were collected during Leg 3 of the GEOTRACES GA02 cruise on board of the RRS James Cook (74JC057) from Punta Arenas (Chile) to Las Palmas (Canary Islands, Spain) in March 2011 (Fig. 1). The GEOTRACES GA02 line is a revisit of the West Atlantic GEOSECS (Geochemical Ocean Sections) 1972 cruise and is adjacent to the WOCE (World Ocean Circulation Experiment) A17 line (Schlitzer, 2000). This transect is situated along the western boundary in the South Atlantic and intersects the pathways of major intermediate and deep waters. The bathymetric configuration along the transect is shown in Figs. 1 and 2. From south to north, Leg 3 crosses the Argentine Basin, the Rio Grande Rise, and the Brazil Basin. In total, five stations (2, 6, 12, 17 and 18) distributed between 49°S, near the Antarctic Polar Front, and the Equator were sampled for depth profiles of dissolved Cd concentrations and Cd isotopic compositions. Here, only Cd concentrations are presented.

The western South Atlantic is an important pathway for major water masses within the Atlantic Meridional Overturning Circulation (AMOC), which includes SAMW, South Atlantic Central Water (SACW), Antarctic Intermediate Water (AAIW), North Atlantic Deep Water (NADW), Antarctic Bottom Water (AABW), and Upper and Lower Circumpolar Deep Water (UCDW and LCDW, respectively).

The physical and chemical properties of the water masses along the GA02 transect have been described recently (Deng et al., 2014; Dulaquais et al., 2014; Rijkenberg et al., 2014) and are briefly summarized here. Northward flowing AAIW is identified by a salinity minimum and an oxygen maximum at a depth of ~500 m at 49°S (Fig. 2a and b; Station 2). Along its flow path, the low-salinity core of AAIW is located between 600 and 1300 m at 35°S, and shoals northward to between 600 and 950 m at the Equator (Station 18; Fig. 2a). The high-oxygen tongue of AAIW lies slightly above the salinity minimum, but disappears north of 25°S, probably due to the basin-scale northwest flow of low-oxygen water originated in the Angola Basin (Suga and Talley, 1995; Tsuchiya et al., 1994). This basin-scale westward flow corresponds to the Subtropical–Subequatorial Front delimiting the subtropical and subequatorial gyres (Fig. 1; see Stramma and England, 1999), and separates the new, fresh AAIW of southeastern Pacific origin to the south of the front, from the older, recirculated AAIW of Indian Ocean origin north of the front (Suga and Talley, 1995).

Above AAIW, SAMW can be identified by its high oxygen content and extremely low Si concentrations. South Atlantic Central Water is