Earth and Planetary Science Letters 341-344 (2012) 94–103

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: Mechanistic constraints from cadmium isotopes

Melanie Gault-Ringold [a,b,*], Toyin Adu [a], Claudine H. Stirling [a,b], Russell D. Frew [a], Keith A. Hunter [a]

[a] Department of Chemistry, University of Otago, Union Place West, Dunedin 9016, New Zealand
[b] Centre for Trace Element Analysis, Department of Chemistry, University of Otago, Union Place West, Dunedin 9016, New Zealand

ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form
13 February 2012
Accepted 4 June 2012
Editor: G. Henderson
Available online 7 July 2012

Keywords:
Cadmium
stable isotopes
MC-ICPMS
double spike
Marine biogeochemistry

ABSTRACT

Cadmium, a highly toxic metal, exhibits a nutrient-type profile in the oceans that is closely correlated to that of the major nutrients phosphate and nitrate. Despite its complexity, the relationship between cadmium and phosphate has been used to infer historic phosphate utilization and biological controls on oceanic CO_2 concentrations. Cadmium isotopes offer the potential to constrain the mechanisms controlling cadmium cycling in the oceans, reducing uncertainty associated with the cadmium paleonutrient proxy. Using techniques in double spiking and MC-ICPMS, we report seasonal Cd isotopic and concentration data along with major nutrients and other essential trace metal (Fe, Zn, and Co) concentrations from subantarctic surface waters. We show, for the first time, a 50-fold seasonal decrease in dissolved cadmium concentrations in subantarctic waters that is due to biological uptake. However, this drawdown in Cd is decoupled from phosphate and shows no coincident shift in cadmium isotopic composition. These data, along with the preferential removal of Cd from surface waters relative to Zn, imply that cadmium is supply-limited to phytoplankton and may have a more significant biological role in these low Zn subantarctic surface waters than in regions with higher Zn concentrations.

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1. Introduction

The ability of the oceans to sequester atmospheric carbon dioxide (CO_2) is intimately related to nutrient utilization and oceanic primary production (Knox and McElroy, 1984). Major nutrients, such as nitrate (NO_3^-) and phosphate (PO_4^{3-}), and trace nutrients, such as iron (Fe), zinc (Zn), and cobalt (Co), are fundamental to phytoplankton growth (Morel, 2008; Morel and Price, 2003). More recently, cadmium (Cd) has been shown to be beneficial to phytoplankton growth in Zn-limited conditions (Cullen et al., 1999; Lane and Morel, 2000; Price and Morel, 1990).

Cadmium and phosphate initially appeared to have a very clear relationship (Bruland, 1980) that has been used to infer deep water nutrient circulation (Boyle, 1992), historic phosphate utilization, and biological controls on CO_2 concentrations in the oceans on glacial–interglacial timescales (Elderfield and Rickaby, 2000), with the assumption that Cd/PO_4^{3-} remains constant both spatially and temporally. This is patently not the case for the surface waters of the Southern Ocean, leading to empirical corrections to be applied (Elderfield and Rickaby, 2000) and thus raising questions about the role of Cd as a nutrient. Specifically, there is significant variability in global surface water Cd/PO_4^{3-} values (Cullen, 2006; de Baar et al., 1994), as well as deviations in these ratios from the more consistent global deep water compositions (de Baar et al., 1994), especially in surface waters of the subantarctic (Frew and Hunter, 1992, 1995). Direct productivity-related variations in Cd/PO_4^{3-} have also been observed (Frew et al., 2001).

Recent studies have shown that biological uptake of Cd is associated with isotopic fractionation (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007). The limited observations to date show that this uptake is governed by kinetic processes, whereby the lighter isotopes are preferentially removed from a finite pool, and follows a closed-system Rayleigh distillation fractionation model (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007). Stable isotopes of Cd may, therefore, provide critical insight into the mechanism(s) controlling Cd uptake in the oceans and how they differ from those controlling PO_4^{3-} utilization, and may themselves provide an effective paleoproxy for historic primary production.

The total seawater Cd isotopic data set is small, comprising of only four published seawater datasets (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007; Xue et al., 2012), and mostly composed of depth profiles. Some of the shortcomings of these data include there being only one high resolution surface

* Corresponding author at: Department of Chemistry, University of Otago, Union Place West, Dunedin 9016, New Zealand. Tel.: +64 3 479 7905; fax: +64 3 479 7906.
E-mail address: melaniegr@chemistry.otago.ac.nz (M. Gault-Ringold).

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http://dx.doi.org/10.1016/j.epsl.2012.06.005

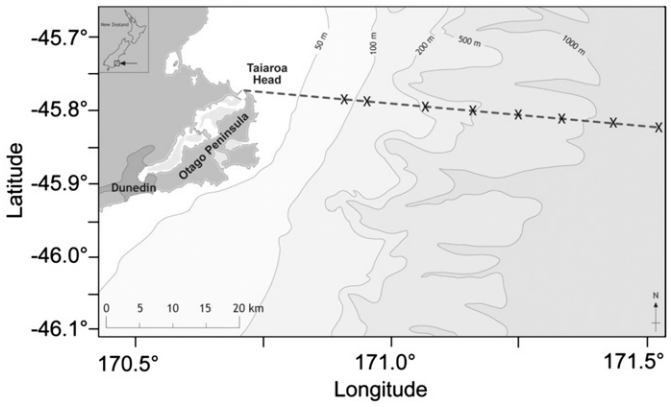

Fig. 1. (a) Map of the 65 km Otago transect off the southeast coast of New Zealand. Based on nutrient composition and Fe distribution, the stations west of the Subtropical Front are considered to be in the Southland Current and the stations east of the Subtropical Front are considered to be in subantarctic water.

ocean transect (Abouchami et al., 2011) and only one data point for the climatically important subantarctic region of the Southern Ocean (Abouchami et al., 2011; Sigman et al., 2010), which nonetheless, has some of the most anomalous Cd/PO_4^{3-} (Frew and Hunter, 1995). More importantly, there are very few seasonal observations of dissolved Cd and no seasonal Cd isotopic data are available to fully evaluate the relationship between Cd uptake and primary productivity under changing oceanographic conditions.

To address these issues we present measurements of Cd stable isotopes and dissolved and particulate Cd concentrations, together with dissolved trace nutrient (Fe, Zn and Co) and major nutrient (PO_4^{3-}, NO_3^- and $Si(OH)_4$) concentrations for samples collected over a two year period from subantarctic waters along the Otago Munida transect off the southeast coast of New Zealand (Fig. 1). The level of temporal detail achieved for the combined dataset is unprecedented and provides critical insight into the mechanisms controlling the uptake of Cd in subantarctic waters, having important implications for the global Cd/PO_4^{3-} relationship and the validity of the Cd/PO_4^{3-} paleoproxy.

2. Study site

The subtropical front (STF), known locally as the Southland Front, is a major circum-global front at ~40°S and is the northern boundary of the Southern Ocean. It divides warm nutrient-depleted, high-iron sub-tropical water (STW) characteristic of mid-latitudes (Croot and Hunter, 1998), from colder nutrient-rich, low-iron subantarctic water (SAW) to the south (Boyd et al., 2001).

New Zealand and its continental shelf intercept the STF, forcing the front south down the western coast and then north along the east coast (Fig. 1). As the front is compressed along the southeast coast of New Zealand, modified STW and SAW mix to form the Southland Current (SC). Approximately 90% of water supplied to the SC is of subantarctic origin (Sutton, 2003).

The Otago Munida transect extends from the tip of the Otago Peninsula, off the southeast coast of New Zealand, offshore for 65 km. The transect crosses the neritic and SC waters that overlay the continental shelf (~40 km from shore to shelf break), and the STF into SAW. Temperature and salinity data for extended transects, continuing for up to 220 km to the east of the Otago transect endpoint, well into SAW, verify that the water sampled along this transect is representative of the subantarctic water mass (Currie et al., 2011).

The physical aspects (e.g. temperature, salinity, position, and flow rates) of the SC and this region of the STF have been described in detail in many studies (Hopkins et al., 2010; Jillett, 1969; Sutton, 2003). The main contribution of fresh water and continental run-off to this region is the Clutha River located ~100 km south of the transect, with a mean annual flow of 533 $m^3\ s^{-1}$ (Murray, 1975).

This region is known for very low Cd concentrations in surface waters and anomalous Cd/PO_4^{3-} ratios (Frew and Hunter, 1992, 1995). Unusually high Cd concentrations have also been found in filter feeding organisms that grow in this region (Frew et al., 1989). These unusual Cd results suggest that this is a critically important region for investigating the biogeochemical cycling of Cd in the surface ocean.

Surface waters were sampled on a bi-monthly basis (depending on weather conditions) over a period of two years from May 2008 to March 2010 (Table S1). Eight stations were sampled at roughly even intervals along the transect (Fig. 1, Table S2). As discussed in Hopkins et al. (2010), the location and width of the STF varies seasonally, and its location during each sampling trip was determined based on temperature and salinity gradients (Jillett, 1969) (Table S1). The outer four sampling stations (5–8) were typically well within SAW. The STF was located less than 40 km from shore during five of the seven sampling trips in this study, the two exceptions being July and September 2009. In July 2009, when the STF appeared to have two steps at 35 km and 45 km from shore, the outer four stations had temperatures below 9 °C, and therefore were considered SAW (Jillett, 1969). In September 2009, the location of the STF was difficult to define as the salinity and temperature measurements showed a larger gradient, created by more mixing and resulting in less definition between water masses. Therefore, stations with temperatures below 10 °C, which included the outer four stations, were considered representative of SAW. During all cruises, stations one to four were considered modified subtropical water or neritic water. All stations were analyzed for general oceanographic parameters (e.g. temperature, salinity) in parallel.

3. Sampling

Samples were collected from on-board the University of Otago R/V *Polaris II*. Trace metal clean HDPE (high density polyethylene) tubing was fed through an epoxy coated steel 'fish' and lowered to approximately 3 m below the surface. This tubing was connected to a Teflon pump (Almatec SL20) situated on a plastic lined bench on deck. From the pump, a Y-connection allowed for the simultaneous collection of both filtered and unfiltered samples. Once all tubing connections were made and before sampling commenced, the sampling system was rinsed with 0.1% v/v HCl for at least 20 min. The tubing was rinsed with seawater for at least 3 min (~20 tubing volumes) before samples were collected at each station.

Filtered samples were collected for measurements of Cd isotopes, and Cd, Zn, Fe, and Co concentrations using a 0.45 μm capsule filter (AquaPrep™ 600 capsule). Unfiltered samples were collected for total trace metal (Cd, Zn, Fe, and Co) analysis. Sample bottles were rinsed three times with seawater before filling. Samples were transported back to the laboratory where they were acidified to pH 1 with high purity 8 M HCl (for Cd isotopic analysis) or HNO_3 (for trace metal analysis) and stored at room temperature (~15 °C) until processed.

Nutrient samples were collected through the same filter system used for trace metal collection. Nutrient samples were refrigerated until returned to the laboratory where they were frozen until needed for analysis.

Chlorophyll-*a* samples were collected through a boat deck hose into 500 ml polyethylene bottles and filtered upon return to

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