



Fine-scale spatial and interannual cadmium isotope variability in the subarctic northeast Pacific

D.J. Janssen^{a,*}, W. Abouchami^b, S.J.G. Galer^c, J.T. Cullen^a

^a School of Earth and Ocean Sciences, University of Victoria, PO Box 1700 STN CSC, Victoria, BC V8W2Y2, Canada

^b Institut de Physique du Globe de Paris, 1 Rue Jussieu, 75005 Paris, France

^c Max Planck Institute for Chemistry, Climate Geochemistry Department, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

ARTICLE INFO

Article history:

Received 22 September 2016

Received in revised form 28 April 2017

Accepted 29 April 2017

Available online xxx

Editor: M. Frank

Keywords:

cadmium isotopes

northeast Pacific

GEOTRACES

biogeochemical cycles

low oxygen

ABSTRACT

We present dissolved cadmium (Cd) concentrations, [Cd], and stable isotope compositions, $\epsilon^{112/110}\text{Cd}$, in high-resolution depth profiles from five stations along the Line P transect in the subarctic northeast Pacific Ocean. In addition to profiles collected in 2012, subsurface isopycnal samples and surface samples were collected in 2013 and 2014 respectively, providing both temporal and spatial coverage. Surface waters are characterized by Cd depletion relative to phosphate (PO_4^{3-}) compared to deepwater $\text{Cd}:\text{PO}_4^{3-}$, and high inferred remineralization ratios in the nutricline ($0.45 \text{ nmol}\mu\text{mol}^{-1}$) are observed, consistent with Cd enrichment relative to phosphorus (P) in surface-derived biogenic particles. The correlation between Cd and PO_4^{3-} weakens at depths where oxygen is highly depleted as shown by local minima in dissolved [Cd] and the tracer Cd^* . The decoupling, which is driven by a deficit of Cd relative to PO_4^{3-} , appears consistent with the recent hypothesis of dissolved Cd removal in oxygen-depleted regions by insoluble metal sulfide formation.

Dissolved $\epsilon^{112/110}\text{Cd}$ indicates a biologically driven fractionation in surface waters with more positive (heavy) values in the upper water column and lower (light) values in deeper waters. The highest $\epsilon^{112/110}\text{Cd}$ observed in our sample set (5.19 ± 0.23) is comparable to observations from the Southern Ocean but is significantly lighter than maximum reported surface values from the subtropical North Pacific of $\epsilon^{112/110}\text{Cd} \geq 15$. A global compilation of low [Cd] surface water shows similar differences in maximum $\epsilon^{112/110}\text{Cd}$. A surface water intercalibration should be prioritized to help determine if these differences at low [Cd] reflect true physical or biological variability or are due to analytical artefacts. Surface samples from the 2012 sampling campaign fit a closed-system Rayleigh fractionation model; however, surface waters sampled in 2014 had much lower [Cd] with relatively constant $\epsilon^{112/110}\text{Cd}$ that cannot be explained by a closed-system Rayleigh model. These results correspond with a warm water surface anomaly found along Line P in 2014 and demonstrate that there is interannual variability in the biogeochemical cycling of Cd and its isotopes in the subarctic North Pacific. In contrast to other ocean basins where vertical variability in $\epsilon^{112/110}\text{Cd}$ is observed at depth, deep and intermediate waters in the North Pacific have a near-uniform $\epsilon^{112/110}\text{Cd}$ value (mean of 1.14 ± 0.37 , $n = 43$, 2SD) representative of nearly all samples at or below 1000 m depth. Imprinted upon this nearly homogeneous intermediate and deep North Pacific $\epsilon^{112/110}\text{Cd}$ signature are fine-scale spatial trends, with heavier values observed toward the coastal end of Line P than the oceanic end at intermediate depths, and with slightly heavier values in subtropical North Pacific deep water compared to the subarctic North Pacific. The nearly constant Cd isotopic composition of North Pacific deep waters is consistent with the inflow of Circumpolar Deep Water at depth in the Pacific basin, along with deep remineralization, and supports the potential of $\epsilon^{112/110}\text{Cd}$ as a tracer of global deepwater circulation.

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1. Introduction

Cadmium (Cd) behaves as a trace metal micronutrient in the global ocean with dissolved depth profiles reflecting biological

uptake in surface waters and remineralization of particulate matter at depth. The distribution of Cd (unless otherwise stated, Cd will refer to dissolved Cd rather than particulate) in the global ocean shows a strong correlation with phosphate (PO_4^{3-}) (Boyle et al., 1976; Bruland et al., 1978). There exist distinct $\text{Cd}:\text{PO}_4^{3-}$ relationships in the major ocean basins and water

* Corresponding author.

E-mail address: janssen.davej@gmail.com (D.J. Janssen).

masses (de Baar et al., 1994; Quay et al., 2015). These regional differences must ultimately be the result of processes that alter the relative concentrations of Cd ([Cd]) versus PO_4^{3-} ($[\text{PO}_4^{3-}]$) compared to the deepwater average Cd: PO_4^{3-} , such as (1) biological Cd uptake in the surface ocean (e.g. Sunda and Huntsman, 2000; Cullen et al., 2003; Cullen and Sherrell, 2005; Lane et al., 2009), (2) depth-dependent Cd remineralization or scavenging with sinking particles in the ocean interior (Janssen et al., 2014; Conway and John, 2015a; Waeles et al., 2016) and (3) scavenging and remobilization at ocean margins (e.g. van Geen et al., 1995). Cadmium: PO_4^{3-} anomalies generated regionally from the above mechanisms can be subducted or advected, resulting in transport of “pre-formed” Cd: PO_4^{3-} by water mass circulation and mixing in the global ocean (e.g. Abouchami et al., 2014; Baars et al., 2014; Quay et al., 2015; Xie et al., 2015).

Both species composition and the physico-chemical environment can contribute to variability in particulate Cd:P (phosphorus). Laboratory cultures of 15 eukaryotic phytoplankton representing major marine phyla maintained under identical growth conditions were found to have cellular Cd:P that varied by two orders of magnitude ($0.007\text{--}0.73 \text{ mmol mol}^{-1}$) (Ho et al., 2003). Within phyla, Cd uptake and cellular Cd:P are known to be modulated by the availability of other trace metals such as iron (Fe) and zinc (Zn) through antagonistic interactions at phytoplankton cell surface transport proteins which can be non-specific with respect to cation binding and permeability (e.g. Sunda and Huntsman, 2000; Cullen et al., 2003; Cullen and Sherrell, 2005; Lane et al., 2009; Baars et al., 2014). Uptake of Cd can be linked to carbonic anhydrase, an enzyme with a Zn cofactor involved in algal inorganic carbon acquisition, through the substitution of Cd for Zn (e.g. Price and Morel, 1990) or the incorporation of Cd into a Cd-specific form of the enzyme (e.g. Lane and Morel, 2000). Thus the species composition and physical-chemical conditions in ocean surface waters during phytoplankton growth can result in the formation and export of particles with a wide range of Cd:P. The relative importance of biological versus physical processes for shaping the global Cd: PO_4^{3-} correlation, and consequently the sensitivity of the relationship to changing environmental conditions in space and time, is at present unresolved.

The Cd: PO_4^{3-} correlation may also be modified by processes that are inherent to O_2 -depleted regions. Trace metals such as Cd, Zn and Cu show depletions in anoxic waters of fjords, inlets, and seas with restricted circulation, due to the formation of highly insoluble sulfides (Jacobs et al., 1985; Dyrssen and Kremling, 1990). While O_2 -depleted waters in open ocean regions, such as in the Eastern Tropical Pacific and the North Pacific, generally contain measurable dissolved $[\text{O}_2]$ and no detectable free sulfide, active communities of sulfur metabolizing bacteria – both sulfate-reducing and sulfide-oxidizing – are found in the water column (e.g. Canfield et al., 2010; Wright et al., 2012 and references therein). These bacteria provide evidence for the presence of free sulfide and an active sulfur cycle in non-anoxic low- O_2 waters, with possibly elevated concentrations in particle-associated microenvironments. Recent data suggest that formation of insoluble Cd sulfides in O_2 -depleted, but non-anoxic oceanic regions could be a significant sink of Cd in the oceanic budget of dissolved Cd (Janssen et al., 2014; Conway and John, 2015a, 2015b).

Studies of the distribution of stable Cd isotopes (reported as $\epsilon^{112/110}\text{Cd}$, the deviation of the $^{112}\text{Cd}/^{110}\text{Cd}$ ratio in parts per ten thousand relative to the reference material NIST SRM-3108) in the oceans have shed light on important processes controlling Cd cycling and, by extension, the variability of Cd: PO_4^{3-} in the global ocean. To a first order, dissolved [Cd] and $\epsilon^{112/110}\text{Cd}$ are inversely correlated with each other in the ocean. Surface waters with lower [Cd] have elevated $\epsilon^{112/110}\text{Cd}$ resulting from Cd iso-

topic fractionation during biological uptake (e.g. Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011). As particulate Cd is remineralized back into the dissolved pool, [Cd] is expected to increase while dissolved $\epsilon^{112/110}\text{Cd}$ decreases. Note that not all studies have seen a biological $\epsilon^{112/110}\text{Cd}$ fractionation signature in surface waters, potentially due to extremely low [Cd] resulting in diffusion-limited Cd supply to phytoplankton (Gault-Ringold et al., 2012) or local aeolian Cd inputs to the surface layer (Yang et al., 2012).

In addition to the Cd isotope fractionation measured in surface waters, deep waters show discernable inter-ocean Cd isotope variability, with low-Cd North Atlantic deep waters ($\epsilon^{112/110}\text{Cd} = 2.42 \pm 0.45$, 2SD) (Boyle et al., 2012; see also Conway and John, 2015a; Xue et al., 2012) being one epsilon unit heavier than Cd-rich Antarctic bottom waters of the Southern Ocean ($\epsilon^{112/110}\text{Cd} = 1.21 \pm 0.36$, 2SD, Xue et al., 2013; Abouchami et al., 2014; see also Conway and John, 2015a; Xie et al., 2017). This gradient and the preservation of deepwater $\epsilon^{112/110}\text{Cd}$ in authigenic deposits (e.g. Schmitt et al., 2009a; Horner et al., 2010) indicate a potential utility of Cd isotopes as tracer of past nutrient cycling and thermohaline circulation.

Subsurface Cd isotopic signatures may also be modified during the formation of Cd sulfides. Literature data on oceanic sulfides (Schmitt et al., 2009a; John et al., 2008) and hydrothermal vents (Abouchami et al., 2015) show a “light” Cd isotope enrichment relative to the remaining dissolved pool. Such a signature is also found in Cd-rich particulates from low- O_2 and Cd-deficient waters (Janssen et al., 2014; Conway and John, 2015a) and is consistent with theoretical calculations of Cd isotope fractionation in hydrothermal systems (Yang et al., 2015). However, it is important to note that: (1) the effect of Cd isotope fractionation by sulfide precipitation is not featured in the dissolved phase of all O_2 -depleted waters (Conway and John, 2015b), and (2) experimental Cd isotope fractionation studies constraining the influence of Cd sulfide formation on the dissolved oceanic Cd budget are still lacking.

In this study, we present the first Cd isotope transect in the subarctic North Pacific from the Line P time series, which extends from the margin to the open ocean and spans oxygen (O_2)-depleted waters, with five high-resolution dissolved $\epsilon^{112/110}\text{Cd}$ and [Cd] depth profiles distributed along the E-W transect. To date, depth profiles of dissolved $\epsilon^{112/110}\text{Cd}$ are available for transects in the North Atlantic (Conway and John, 2015a) and the Southern Ocean (Xue et al., 2013; Abouchami et al., 2014); however, data from the Pacific are limited to only a few isolated stations in the open North Pacific and marginal seas (Lacan et al., 2006; Ripperger et al., 2007; Yang et al., 2012, 2014; Conway and John, 2015b) and a seasonally sampled surface transect in the South Pacific (Gault-Ringold et al., 2012). Our new data show interannual $\epsilon^{112/110}\text{Cd}$ variability in surface waters and spatial variability in comparison with data from the subtropical the North Pacific, as well as fine-scale subsurface trends imprinted upon a nearly-homogeneous subsurface $\epsilon^{112/110}\text{Cd}$ signature.

2. Sampling site: the subarctic northeast Pacific

The Line P time series transect (Fig. 1) is a zonal onshore-offshore transect in the subarctic northeast Pacific which begins at 48.5° N , 125.5° W in coastally-influenced waters near Vancouver Island, BC and extends westward to Ocean Station PAPA/P26 (50° N , 145° W) in the Alaskan Gyre. Cadmium concentrations have been reported previously in the region along the north-south VERTEX T transect, which intersects Line P at station T7/P26, to a depth of around 1500 m (3910 m at T7/P26) (Martin et al., 1989). The Line P transect covers environments with elevated Fe near the continental shelf as well as the chronically Fe-limited High-Nutrient Low-Chlorophyll (HNLC) open subarctic

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