

# Undocumented water column sink for cadmium in open ocean oxygen-deficient zones

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**Cadmium (Cd) is a micronutrient and a tracer of biological productivity and circulation in the ocean. The correlation between dissolved Cd and the major algal nutrients in seawater has led to the use of Cd preserved in microfossils to constrain past ocean nutrient distributions. However, linking Cd to marine biological processes requires constraints on marine sources and sinks of Cd. Here, we show a decoupling between Cd and major nutrients within oxygen-deficient zones (ODZs) in both the Northeast Pacific and North Atlantic Oceans, which we attribute to Cd sulfide (CdS) precipitation in euxinic microenvironments around sinking biological particles. We find that dissolved Cd correlates well with dissolved phosphate in oxygenated waters, but is depleted compared with phosphate in ODZs. Additionally, suspended particles from the North Atlantic show high Cd content and light Cd stable isotope ratios within the ODZ, indicative of CdS precipitation. Globally, we calculate that CdS precipitation in ODZs is an important, and to our knowledge a previously undocumented marine sink of Cd. Our results suggest that water column oxygen depletion has a substantial impact on Cd biogeochemical cycling, impacting the global relationship between Cd and major nutrients and suggesting that Cd may be a previously unidentified tracer for water column oxygen deficiency on geological timescales. Similar depletions of copper and zinc in the Northeast Pacific indicate that sulfide precipitation in ODZs may also have an influence on the global distribution of other trace metals.**

biogeochemistry | paleoceanography | GEOTRACES | trace elements | marine chemistry

**C**admium has a nutrient-type depth profile in the open ocean, with low concentrations in surface water due to phytoplankton uptake and higher concentrations in deep water where sinking biological material remineralizes, releasing Cd (1–3). Cadmium can act either as a nutrient or a toxin, and therefore influences both phytoplankton growth and community composition (4–7). In addition to the direct impact of Cd on marine microbial communities, dissolved Cd is strongly correlated with the major algal nutrient phosphate ( $\text{PO}_4^{3-}$ ) (1, 2), in seawater. A paleoceanographic proxy for dissolved  $\text{PO}_4^{3-}$  therefore takes advantage of Cd incorporation into foraminiferal calcite tests, preserved in the sedimentary record (8, 9). Foraminiferal records of Cd have been used by a number of studies to reconstruct water mass distribution and nutrient utilization in past oceans (8–10).

Reliable tracers of paleoceanographic nutrient distributions in the ocean are vital to understanding past climate variability, and thus to predicting the potential impacts of anthropogenic climate change. Successful use of the foraminiferal Cd proxy to reconstruct past macronutrients requires a detailed understanding of Cd cycling and of factors which may influence the Cd: $\text{PO}_4^{3-}$  of the ocean. For example, it is well established that correlations between dissolved Cd and  $\text{PO}_4^{3-}$  may vary due to regional differences in the rates at which phytoplankton take up Cd and  $\text{PO}_4^{3-}$  (3, 11). Recent studies (12) of dissolved Cd isotope ratios in the ocean ( $\delta^{114}\text{Cd}$ ) indicate a nearly isotopically homogeneous deep ocean ( $\sim 0.3\%$ ), which is heavier than crustal  $\delta^{114}\text{Cd}$  ( $\sim 0.1\%$ ), indicative of an as-yet-unattributed sink for isotopically light Cd. The extent to which

this sink induces local changes in Cd: $\text{PO}_4^{3-}$  must be understood to correctly interpret paleoceanographic records.

## Results and Discussion

Cadmium and other trace metals such as copper (Cu) and zinc (Zn) are known to form solid sulfide precipitates in the ocean under conditions of anoxia where sulfide is present. For example, precipitation of Cd sulfide (CdS) (13) leading to dissolved Cd depletion is observed at oxic–anoxic interfaces in stratified basins with permanently or seasonally anoxic waters (14, 15). Here, for the first time to our knowledge, we provide evidence that CdS precipitation may occur in oxic open-ocean waters, operationally defined as containing measureable oxygen (typically  $< 3 \mu\text{mol kg}^{-1}$  using common methods) (16). At the surface of the ocean, oxygen saturation in seawater is usually  $200\text{--}300 \mu\text{mol kg}^{-1}$ . In regions where we observe evidence of CdS precipitation, oxygen concentrations are significantly depleted by heterotrophic respiration, but significantly above detection limits. The northeast subarctic Pacific hosts the world's most extensive oxygen-deficient zones (ODZ) (Fig. 1), with oxygen depletion ( $< 50 \mu\text{mol kg}^{-1}$ ) extending from 400 to 1,800 m depth and minimum oxygen concentrations of  $10\text{--}20 \mu\text{mol kg}^{-1}$  at  $\sim 1,000$  m (Fig. 2) (17). The ODZ in the eastern subtropical North Atlantic underlies the Mauritanian upwelling region and, like the Pacific ODZ, is most intense along the eastern margin (Fig. 1), where oxygen deficiency ( $< 75 \mu\text{mol kg}^{-1}$ ) extends from 100 to 750 m depth, with a minimum of  $45 \mu\text{mol kg}^{-1}$  near 400 m (Fig. 2).

In the Pacific and Atlantic ODZs we observe a decoupling between concentrations of dissolved Cd and  $\text{PO}_4^{3-}$ , compared with more oxygenated sites in the Southern Ocean and subantarctic South Atlantic, and the central North Atlantic (Figs. 1

## Significance

**Cadmium (Cd), a trace nutrient for marine algae, has a marine distribution that closely matches the macronutrients nitrate and phosphate. Sedimentary microfossil records of Cd provide reconstructions of past ocean nutrient distributions that facilitate understanding the role of the oceans in the carbon cycle and climate change. However, incomplete knowledge of processes that control the addition and removal of Cd in the ocean, and Cd's variability relative to major nutrients, limit use of the paleoceanographic proxy. We present coupled data of Cd concentration and isotopic composition in seawater and suspended marine particles, indicating direct removal of Cd via coprecipitation with sulfide in oxygen-deficient waters. Thus, the marine Cd cycle may be highly sensitive to the extent of global oceanic oxygen depletion.**

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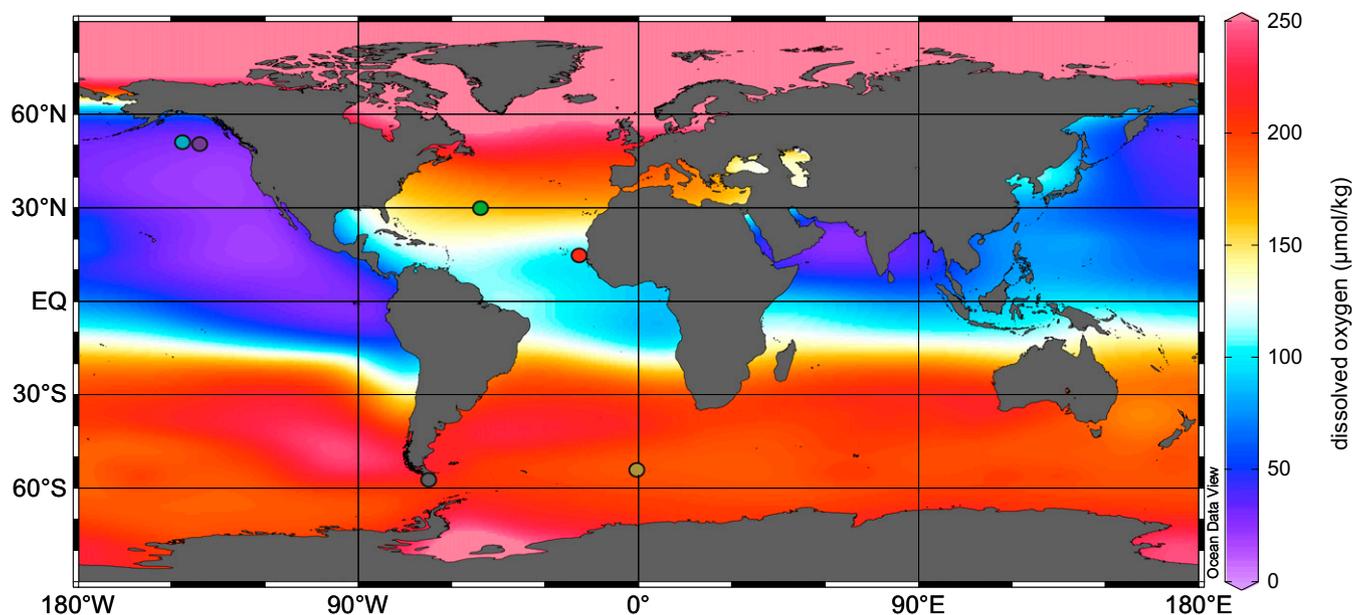


Fig. 1. Sampling locations for this study overlay on water column minimum dissolved oxygen concentrations (45). New data are presented here from the eastern North Pacific at station P20 (49.6°N, 139.7°W, purple) and North Atlantic at stations USGT11-14 (27.6°N, 49.6°W, green) and USGT10-9 (17.4°N, 18.25°W, red). Previously published data are presented from station T7/P26 in the eastern North Pacific (50.0°N, 145.0°W, light blue) (46), and Southern Ocean/subantarctic stations 249 (56.1°S, 63.8°W, gray) (47), and P571-113 (53.0°S, 0.3°W, tan) (21).

and 2), where Cd and  $\text{PO}_4^{3-}$  are well correlated throughout deep waters with average Cd: $\text{PO}_4^{3-}$  ratios of  $0.33 \pm 0.03 \text{ nmol } \mu\text{mol}^{-1}$  and  $0.23 \pm 0.04 \text{ nmol } \mu\text{mol}^{-1}$ , respectively ( $1\sigma$  SD) (3). However, within the northeast Pacific and Mauritanian ODZs, dissolved Cd decreases relative to  $\text{PO}_4^{3-}$  beginning near the point where dissolved  $\text{O}_2$  falls below about  $75 \mu\text{mol kg}^{-1}$ . In the northeast Pacific this is observed beginning at a depth of 400 m; whereas  $\text{PO}_4^{3-}$  continues to increase in a nutrient-like fashion to a maximum at 1,000 m, Cd concentrations do not (Fig. 2). In the eastern North Atlantic, the decoupling between  $\text{PO}_4^{3-}$  and Cd is observed as a much slower rate of increase in Cd concentrations below 80 m, compared with the rate at which  $\text{PO}_4^{3-}$  increases. The departure of Cd from expected concentrations within the ODZs, based on average deepwater Cd: $\text{PO}_4^{3-}$ , can be visualized by plotting the variable Cd\* (Methods), which is the excess or depletion of Cd compared with  $\text{PO}_4^{3-}$ . Depletions in Cd\* of up to  $100 \text{ pmol kg}^{-1}$  and  $250 \text{ pmol kg}^{-1}$  are observed within the ODZs at the northeast Pacific sites and eastern North Atlantic sites, respectively. At depths where the water column is more oxygenated, Cd\* depletions are generally  $<50 \text{ pmol kg}^{-1}$  (Fig. 2).

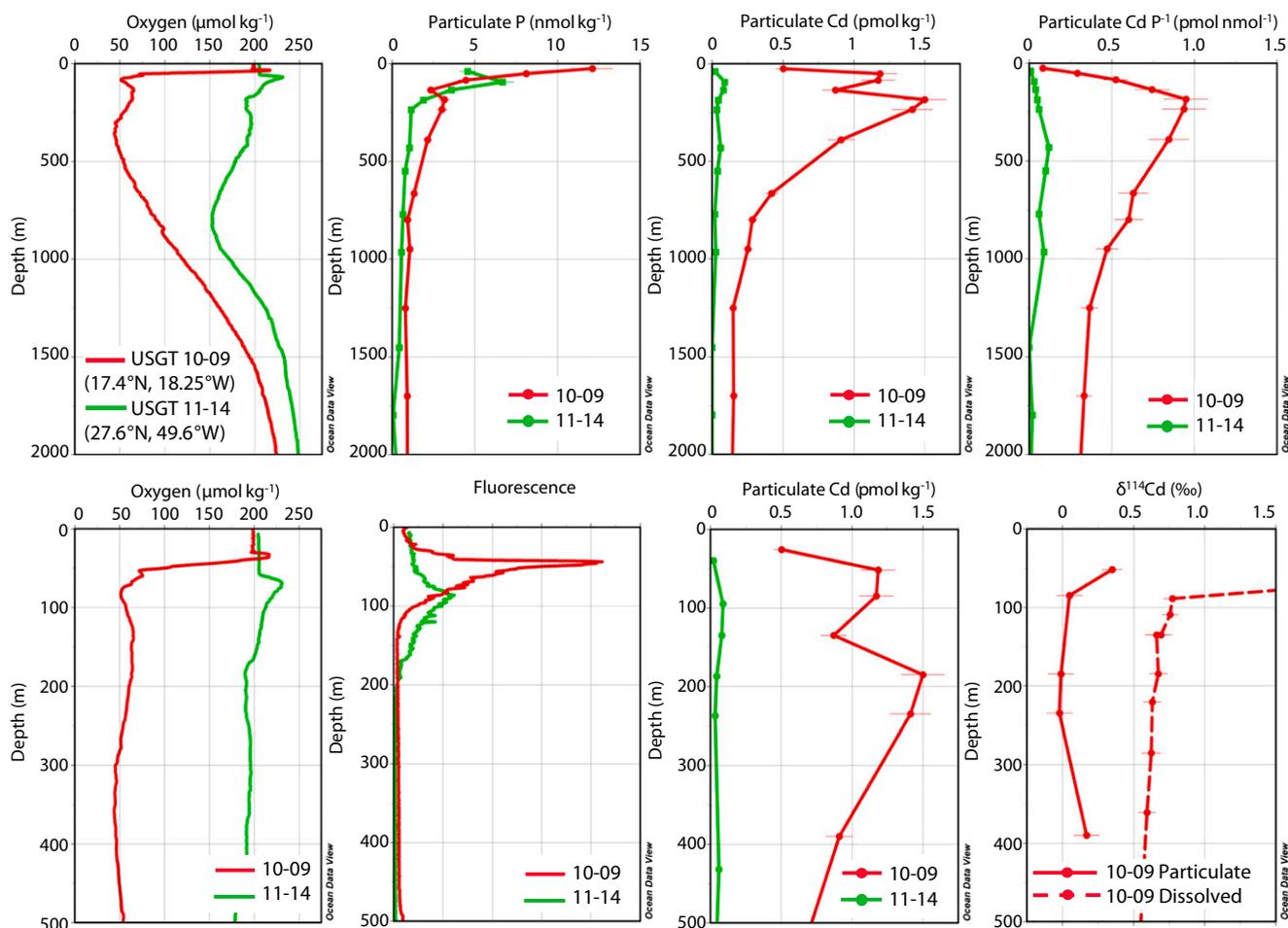
Suspended particles provide additional evidence of Cd precipitation within the North Atlantic ODZ (Fig. 3). The concentrations of both particulate Cd and P, like surface primary productivity, are higher in the eastern basin compared with the central basin. In the central North Atlantic where oxygen concentrations are higher, suspended particulate Cd and P are both high in surface waters where phytoplankton grow, and decrease monotonically with depth. Whereas suspended particulate P in the eastern basin also follows this trend, suspended particulate Cd concentrations and the Cd:P ratio reach a maximum within the ODZ. Elevated particulate Cd concentration and Cd:P ratios in the ODZ, compared with overlying waters including the chlorophyll maximum, suggests a source of particulate Cd within the ODZ in addition to sinking biogenic material.

Particulate  $\delta^{114}\text{Cd}$  within the ODZ is consistent with CdS precipitation (Fig. 3). Because Cd is nearly quantitatively removed by phytoplankton growing within the euphotic zone, we expect the biogenic particulate  $\delta^{114}\text{Cd}$  flux out of the surface

ocean to match the upward mixing flux of dissolved  $\delta^{114}\text{Cd}$  into the euphotic zone. Thus, assuming that the suspended biogenic particulate  $\delta^{114}\text{Cd}$  accurately reflects the biogenic flux, it should be  $+0.77\text{‰}$ , which is equivalent to dissolved  $\delta^{114}\text{Cd}$  at the base of the euphotic zone (89 m). Instead we observe particulate  $\delta^{114}\text{Cd}$  from  $-0.01$  to  $+0.35\text{‰}$ , significantly lighter than the expected biogenic signature. Isotopically lighter particulate  $\delta^{114}\text{Cd}$  compared with seawater is consistent with CdS precipitation, assuming nonquantitative precipitation of seawater Cd with a preferential precipitation of lighter Cd isotopes into sulfides, as observed in low-temperature hydrothermal systems (18). The highest  $\delta^{114}\text{Cd}$  ( $+0.35\text{‰}$ ) is observed just below the chlorophyll *a* maximum, perhaps reflecting a greater contribution of biogenic particulate Cd at this depth. The lowest  $\delta^{114}\text{Cd}$  values ( $-0.01\text{‰}$  at 185 m and  $-0.02\text{‰}$  at 235 m) are found within the ODZ at the same depths where we observe a maximum in particulate Cd:P. Together, the lighter  $\delta^{114}\text{Cd}$  of particles compared with seawater, and the increasing particulate [Cd] with depth within the ODZ, support a local dissolved source of Cd to particles rather than gradual remineralization of sinking biogenic Cd.

Several hypotheses have been advanced to explain the decoupling of Cd and P concentrations in the global ocean, although none seems appropriate to describe the decoupling observed in ODZs. Differences in the remineralization with depth of Cd and P are inconsistent with the relatively similar remineralization rates of Cd and P observed in a majority of existing vertical profiles (3). Biological uptake rates of Cd compared with  $\text{PO}_4^{3-}$  have been observed to vary with species composition, irradiance, trace metal concentration, and carbon dioxide availability (19). One consequence of this is that pre-formed dissolved Cd: $\text{PO}_4^{3-}$  is lower in waters which ventilate in the Southern Ocean (20). Recent measurements of dissolved Cd: $\text{PO}_4^{3-}$  and  $\delta^{114}\text{Cd}$  suggest that Cd and  $\text{PO}_4^{3-}$  mix conservatively along isopycnals in the well-oxygenated ocean interior (21), meaning that some portion of the lowered Cd: $\text{PO}_4^{3-}$  we observe in the northeastern subarctic Pacific may reflect mixing with low Cd: $\text{PO}_4^{3-}$  subantarctic and Antarctic waters. However, Cd: $\text{PO}_4^{3-}$  values at similar densities in the Southern Ocean are not low





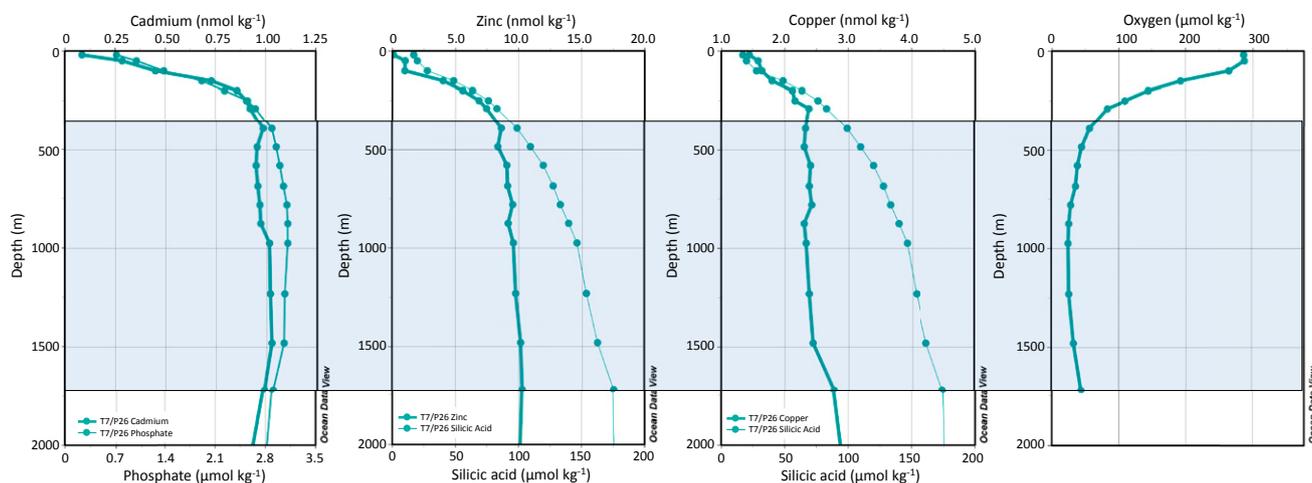
**Fig. 3.** Particulate cadmium and phosphorus concentrations and cadmium stable isotope ratios ( $\delta^{114}\text{Cd}$ ) from the US GEOTRACES North Atlantic Transect, shown with oxygen concentrations and fluorescence. Station USGT11-14 (27.6°N, 49.6°W) is shown in green and station USGT10-9 (17.4°N, 18.25°W) is shown in red. (Upper) Depth range of 0–2,000 m; (Lower) ODZ range from 0 to 500 m.

therefore be related to both the quantity and the composition of sinking organic particles. Microbial sulfide production in oxic waters of the Pacific ODZ is supported by genomic evidence for the presence of both heterotrophic sulfate reducing bacteria and sulfur oxidizing autotrophs (26, 28) and isotopically labeled incubation experiments showing sulfate reduction rates of up to  $0.5\text{--}1\text{ nmol L}^{-1}\cdot\text{S}\cdot\text{h}^{-1}$  in the core of the nearly anoxic eastern tropical South Pacific ODZ (28). CdS may also precipitate in waters with more extreme oxygen depletion such as the eastern tropical South Pacific ODZ, where sulfide concentrations of  $1\text{--}5\text{ }\mu\text{mol L}^{-1}$  have been found throughout an extensive region (19). CdS is supersaturated at these sulfide concentrations, allowing Cd to be rapidly scavenged from the water column (13).

The enrichment of Cd in oxygen-depleted sediments has previously led to the suggestion that CdS precipitation from sediment porewaters is the primary sink for Cd from the oceans (22, 23). Based on the areal extent of low oxygen sediments in the modern ocean and calculated Cd flux into the sediments, Rosenthal et al. (22) calculated a removal rate of  $0.6\text{--}2.3 \times 10^7\text{ mol y}^{-1}$ , which is similar to calculated Cd input from the atmosphere and world rivers ( $0.6\text{--}2.5 \times 10^7\text{ mol y}^{-1}$ ). Because the Pacific ODZ is the largest worldwide, we use the observed Cd depletion from the northeast Pacific ODZ ( $\sim 100\text{ pmol L}^{-1}$ ) and the volume of the global ocean with dissolved  $\text{O}_2 < 50\text{ }\mu\text{mol L}^{-1}$  ( $1.3\text{--}6.0 \times 10^{19}\text{ L}$ ) (29), to estimate a global depletion of  $0.1\text{--}0.5 \times 10^{10}\text{ mol}$  dissolved Cd from sulfide precipitation. Assuming that

this depletion occurs on a timescale as short as the residence time of water in an ODZ ( $\sim 100\text{ y}$ ) or as long as that of ocean mixing ( $\sim 10^3\text{ y}$ ) yields a Cd removal rate range from  $0.1 \times 10^7\text{ mol Cd y}^{-1}$  to  $0.5 \times 10^8\text{ mol Cd y}^{-1}$ . This calculation suggests that CdS precipitation in ODZs is an important vector for Cd delivery to suboxic sediments, possibly the primary sink for Cd from the oceans. As Cd associated with sinking particles is known to be the primary route to burial in suboxic sediments (30), the formation of particulate CdS species which are stable in oxic water (31) allows for distributed Cd burial in sediments and may represent a significant contribution to the sedimentary Cd enrichments seen in oxygen-depleted sediments.

A globally significant water column sink for Cd via Cd sulfide precipitation suggests that the distributions of other biologically used metals disposed to forming highly insoluble sulfides, such as Cu and Zn, may be similarly affected. Although particle and isotope data are not available for Cu and Zn, we note that Cu and Zn are depleted relative to Si for the same depths at which Cd is depleted relative to phosphate within the Northeast Pacific ODZ (Fig. 4), suggesting they may also be precipitated as sulfides. Cu and Zn are known to influence biological production and community composition (32–37) through taxon-specific requirements and toxic sensitivity. Indeed, removal of these metals relative to other bioessential trace metals like iron (Fe) and cobalt (Co) in the ocean interior could influence biogeochemical cycling through metal–metal antagonisms and colimitation when deep waters are brought to the surface in ocean upwelling zones. For example,



**Fig. 4.** Concurrent decoupling of cadmium, zinc, and copper from corresponding macronutrients in the northeast subarctic Pacific. The trace-metal–macronutrient pairs of Cd-PO<sub>4</sub><sup>3-</sup>, Zn-Si, and Cu-Si all show decoupling in the northeast subarctic Pacific ODZ (station P26, 50.0°N 145.0°W). Whereas macronutrients (shown in thin lines) continue to increase monotonically throughout the ODZ, the trace metals (shown in thick lines) reach stable values or decrease slightly. The onset of decoupling, which begins near the depth where oxygen concentrations drop below ~50 μmol kg<sup>-1</sup> (shaded region), shows strong agreement between the three trace metal–macronutrient pairs.

within oxygen-deficient upwelling regions observations have been made of Zn limitation in eukaryotic phytoplankton (38), and of an increased biogeochemical significance of prokaryotes (39), perhaps reflecting Zn deficiency in upwelling waters combined with the higher Zn requirements of eukaryotic plankton compared with prokaryotic plankton (40, 41).

## Conclusions

The implications for decoupling of Cd concentrations from macronutrient concentrations in ODZs span a wide range of timescales. On geological timescales, it suggests that in situ water column precipitation is at least a significant sink, if not the predominant sink of Cd from the oceans. Consequently, global variability in marine dissolved Cd concentrations and δ<sup>114</sup>Cd will be crucially dependent on the extent of ODZs in the world's oceans over geological timescales. For studies investigating macronutrient distributions on glacial–interglacial timescales, our results suggest that the commonly used foraminiferal Cd proxy must be interpreted with caution in oxygen-depleted regions. In the future, the predicted expansion of oxygen depletion in the global oceans (42) means that water column sulfide precipitation may be an increasingly important sink for Cd as well as Cu and Zn from the ocean, with significant consequences for marine biogeochemical cycles due to the dual roles of these metals as both toxins and essential micronutrients.

## Methods

Northeast Pacific Cd samples were collected along an onshore–offshore transect from the coast of Vancouver Island, BC, Canada to Ocean Station P (50°N, 145°W, depth 4,220 m) February 12–18, 2005, on board the CCGS *J.P. Tully* (43). Filtered (0.2 μm, Millipore Opticap) samples from 0 to 50 m were collected using a Teflon bellows pump. Samples from 50 to 600 m depth were collected using X-Niskin or GO-FLO (General Oceanics) bottles on a Kevlar line and were filtered immediately after collection through a 0.2-μm filter (Millipore Opticap). Samples below 600 m were collected on a standard metal frame rosette equipped with Niskin bottles and were not filtered. Duplicate samples were collected from the nontrace metal clean rosette and clean bottles on the Kevlar line to confirm that the standard rosette was of sufficient cleanliness for analysis (43). Samples were acidified with 12 mol L<sup>-1</sup> ultrapure HCl (SEASTAR Chemicals Inc.) within 48 h of collection. Cadmium was analyzed using the 1-pyrrolidine dithiocarbamate–diethylammoniumdiethyldithiocarbamate organic extraction method followed by isotope dilution inductively coupled plasma mass spectrometry, and nutrients were determined with standard colorimetric techniques (43).

North Atlantic samples were collected as part of the US GEOTRACES A03 North Atlantic transect at stations USGT10-9 (17.4°N, 18.3°W) and USGT11-14 (27.6°N, 49.6°W). Dissolved samples (0.2-μm filtered) were collected using the US GEOTRACES trace-metal clean sampling system, and particulate samples were collected onto 0.8-μm Supor filters using in situ large-volume pumps. Seawater samples were acidified onshore with 1 mL 12 mol L<sup>-1</sup> ultrapure HCl (VWR) and allowed to sit for several months before processing. Dissolved Cd was extracted from seawater onto Nobias PA-1 chelating resin, purified by an anion exchange chromatographic technique, and analyzed by Thermo Neptune multicollector inductively coupled plasma mass spectrometer at the Center for Elemental Mass Spectrometry at the University of South Carolina according to previously published methods (12). Particulate δ<sup>114</sup>Cd was determined following a pH 8 oxalate-EDTA (0.1–0.05 mol L<sup>-1</sup>) leach of particles; purification and analysis was performed according to the same procedures used for seawater. The stable isotope values for Cd are reported as δ<sup>114</sup>Cd relative to the National Institute of Standards and Technology Standard Reference Material 3108 standard by

$$\delta^{114}\text{Cd} = \left( \frac{\left( \frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{sample}}}{\left( \frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{standard}}} - 1 \right) \cdot 1,000.$$

Cd\* was calculated by

$$\text{Cd}^* = \text{Cd}_{\text{measured}} - \text{PO}_4^{3-}{}_{\text{measured}} \times \frac{\text{Cd}}{\text{PO}_4^{3-}{}_{\text{deep}}},$$

where Cd/PO<sub>4</sub><sup>3-</sup><sub>deep</sub> represents the average deepwater ratio in either the Pacific or Atlantic samples. A value of 0.25 is used for the deepwater ratio for Atlantic samples and 0.35 is used for Pacific and Southern Ocean–subantarctic samples. These values represent a best average composition for our North Atlantic and northeast Pacific samples and show agreement with published values. Because the absolute value of Cd\* will vary depending on the value chosen for deepwater Cd:PO<sub>4</sub><sup>3-</sup>, we focus mainly on trends in Cd\* within profiles and basins, which illustrate relative enrichments or depletions of Cd compared with PO<sub>4</sub><sup>3-</sup> independent of the Cd:PO<sub>4</sub><sup>3-</sup> used. Figures in the manuscript were produced using Ocean Data View (44).

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