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Coastal Sources, Sinks and Strong Organic Complexation of Dissolved Cobalt within the US North Atlantic GEOTRACES Transect GA03

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Abstract

Cobalt is the scarcest of metallic micronutrients and displays a complex biogeochemical cycle. This study examines the distribution, chemical speciation, and biogeochemistry of dissolved cobalt during the U.S. North Atlantic GEOTRACES Transect expeditions (GA03/3_e), which took place in the fall of 2010 and 2011. Two major subsurface sources of cobalt to the North Atlantic were identified by increased abundances of dissolved cobalt relative to surrounding waters. The more prominent of the two was a large plume of cobalt emanating from the African coast off the Eastern Tropical North Atlantic coincident with the oxygen minimum zone (OMZ) likely due to a confluence of processes including reductive dissolution, biouptake and remineralization, and aeolian dust deposition. This occurrence of this plume in an OMZ with oxygen above suboxic levels implies a high threshold for persistence of dissolved cobalt plumes. The other major subsurface source came from Upper Labrador Seawater, which may carry higher cobalt concentrations due to the interaction of this water mass with resuspended sediment at the western margin or from transport even further upstream. Minor sources of cobalt came from dust, coastal surface waters and hydrothermal systems along the mid-Atlantic ridge. The full depth section of cobalt chemical speciation revealed near complete complexation in surface waters, even with the regional high dust deposition. However, labile cobalt was found below the euphotic zone, demonstrating that strong cobalt binding ligands were not present in excess of the total cobalt concentration there and implying mesopelagic labile cobalt was sourced from the remineralization of sinking organic matter. Significant correlations were observed in the upper water column between total cobalt and phosphate, and between labile cobalt and phosphate, demonstrating a strong biological influence on cobalt cycling across much of the North Atlantic transect. Along the western margin off the North American coast, this linear relationship with phosphate was no longer observed and instead a relationship between cobalt and salinity was observed, reflecting the importance of coastal input processes on cobalt distributions. In deep waters, both total and labile cobalt were lower in concentration than at intermediate depths, providing evidence that scavenging may remove labile cobalt from the water column. Total and labile cobalt distributions were also compared to a previously published South Atlantic GEOTRACES-compliant zonal transect (CoFeMUG, GAc01) to discern regional biogeochemical differences. Together, these Atlantic sectional studies highlight the dynamic ecological stoichiometry of total and labile cobalt. As increasing anthropogenic use and

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subsequent release of cobalt poses the potential to overpower natural cobalt signals in the oceans, it is more important than ever to establish a baseline understanding of cobalt distributions in the ocean.

1 Introduction

Cobalt is the scarcest of biologically utilized metals and has a complex marine biogeochemical cycle. The small inventory of oceanic cobalt is maintained by a combination of supply mechanisms, including sedimentary, aeolian, riverine/coastal, and hydrothermal inputs. In particular, the high abundances of cobalt that have been observed as major plumes within the low oxygen waters of major oxygen minimum zones of the South Atlantic and South Pacific (Hawco et al., 2016; Noble et al., 2012), and from more limited datasets from the North Pacific (Ahlgren et al., 2014; Saito et al., 2004; Saito et al., 2005), are likely due to reductive dissolution and advection of sedimentary sources in regions with low-oxygen bottom water sediment-water interfaces (Heggie and Lewis, 1984). Coastal and island sources in oxygenated environments have also been observed, for example, off the North American continental shelf (Saito and Moffett, 2002) and near the Kerguelen Islands (Bown et al., 2012a). While there is limited information regarding the riverine and coastal fluxes of particulate and dissolved cobalt to the oceans, earlier datasets show a significant "desorbable" load of particulate cobalt as well as estuarine sources of organic cobalt complexes (Kharkar et al., 1968; Zhang et al., 1990). The contribution of cobalt from dust has been more difficult to directly observe because of the small amounts of cobalt present in dust relative to iron, with a Co:Fe ratio in crustal material of 1:2600 (equivalent to 30ppm per 3-8% Fe by mass; Taylor and McLennan, 1985), and its likely rapid utilization in the photic zone. Nevertheless, laboratory and field studies have shown evidence for potentially significant dust contributions to upper water column cobalt from anthropogenic and natural dust sources (Shelley et al., 2012b; Thuróczy et al., 2010). While cobalt has been found to be enriched in end-member hydrothermal fluids up to 2570 nM at TAG in the North Atlantic Mid-Atlantic Ridge (Metz and Trefrey, 2000), input is thought to be relatively localized to near-vent environments due to rapid removal by precipitating manganese and iron oxyhydroxides.

In addition to these natural sources, there has recently been tremendous growth in the economic market for cobalt through the use of lithium batteries and their cobalt lithium oxide cathode (Scrosati and Garche, 2010). This makes up a relatively new and large mobile

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reservoir of cobalt throughout the world within electronics, homes, powerplants, cars, and other devices. The environmental impacts of cobalt pollution via mining, smelting, and inappropriate disposal of batteries will likely significantly increase in the future (Banza et al., 2009). A baseline assessment of riverine and oceanic cobalt distributions is critical to inform the development of sustainable economies with regard to trace metal biogeochemical cycles and the future study of the industrial ecology of cobalt.

The chemical speciation of cobalt is dynamic in the oceans. Cobalt tends to be strongly bound to organic complexes in the upper water column, but some fraction of dissolved cobalt remains unbound or weakly bound as labile cobalt below the euphotic zone in intermediate and deep waters. In the photic zone and upper water column, saturating concentrations of cobalt binding ligands are often observed, particularly in oligotrophic regimes where cyanobacteria are well represented (Saito and Moffett, 2001; Saito et al., 2005). These ligands are extraordinarily strong, with conditional stability constants on the order of $>10^{16.8}$ (Bown et al., 2012b; Saito et al., 2005), which is significantly higher than those for other transition metals such as iron (FeL_1), for which measured stability constants are on the order of $10^{13.1}$ (Rue and Bruland, 1997, Buck et al., 2015). To achieve stability constants in this range, the cobalt-ligand complexes almost certainly have a redox state of Co(III) (Baars and Croot, 2015; Saito and Moffett, 2001; Saito et al., 2005), which is consistent with Co(III) being a textbook example of an inert metal redox state (Lippard and Berg, 1994). The structure of cobalt ligands in seawater is currently unknown, but may be related to precursors or degradation products of vitamin B_{12}, a cobalt-containing biomolecule. This complexation by strong organic ligands likely protects and/or slows cobalt from scavenging (Saito and Moffett, 2001), as is similarly thought to occur for iron (Johnson et al., 1997). These ligands also have a strong influence on the bioavailability of cobalt to microorganisms (Saito et al., 2002), and the resultant microbial and phytoplankton ecology (Saito and Goepfert, 2008; Saito et al., 2010; Sunda and Huntsman, 1995). While the strongly complexed cobalt is likely somewhat protected from scavenging, the presence of labile cobalt in much of the oceanic water column, should make that fraction particularly vulnerable to scavenging processes. Because complexed and labile cobalt have different physicochemically driven cycles but are inherently linked by biological transformations, cobalt speciation must be considered in efforts to fully understand the biogeochemical cycling of cobalt in the oceans.

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In recent years, there has been an emergence of ocean studies with high-throughput analyses of dissolved cobalt (Bown et al., 2011; Bown et al., 2012b; Dulaquais et al., 2014a; Dulaquais et al., 2014b; Noble et al., 2012) and labile cobalt (Noble et al., 2012), as a part of the prelude to, or as part of, the international GEOTRACES program (Boyle et al., 2015). These studies have considerably increased the available datasets on dissolved cobalt in the oceans and have contributed to an understanding of cobalt cycling across several diverse biogeochemical regimes. The Benguela Upwelling system appears to be a major source of dissolved Co to the South Atlantic Ocean with a plume extending more than halfway across the basin. Cobalt was also observed to be scavenged more slowly than other hybrid-type metals like Fe and Mn, likely due to its slower oxidation kinetics and lower oxygen abundances in the oxygen minimum zone (Noble et al., 2012). Additional datasets have explored the distribution and speciation of cobalt in the Atlantic and Pacific sectors of the Southern Ocean (Bown et al., 2011; Ellwood, 2008), the Ross Sea and McMurdo Sound of Antarctica (including seasonal variability and under ice early spring conditions)(Noble et al., 2013; Saito et al., 2010), the Eastern Tropical North Pacific and Costa Rica Dome (Ahlgren et al., 2014), the eastern tropical North Atlantic (Baars and Croot, 2015), near the Bermuda, Hawaiian, and Kerguelen Islands (Bown et al., 2012a; Noble et al., 2008; Shelley et al., 2012b), and throughout a meridional transect of the western Atlantic Ocean (Dulaquais et al., 2014a; Dulaquais et al., 2014b). The establishment of these high-throughput sampling and analytical methods for cobalt, largely in response to the GEOTRACES program, has greatly improved our ability to assess and monitor the biogeochemistry of this key micronutrient throughout the global oceans. In fact, before 1990, there were fewer than 200 dissolved cobalt measurements throughout the entirety of the oceans.

In this study, we examined the distributions of total dissolved cobalt and labile cobalt in the North Atlantic during the U.S. GEOTRACES North Atlantic Transect (GA03/3_e). The resulting ocean section from this study is compared to the GEOTRACES-compliant zonal section in the South Atlantic Ocean (the CoFeMUG expedition, GAc01; (Noble et al., 2012)). The North Atlantic is an ideal region for the study of biogeochemical processes given the major contributions from aeolian dust deposition from the Sahara desert and Northern hemisphere anthropogenic sources, proximity to coastal and continental sources, strong hydrothermal sources associated with the mid-Atlantic ridge, and recently-formed North Atlantic Deepwater. Moreover, based on previous studies in the South Atlantic, the Mauritanian Upwelling region and the associated oxygen minimum zone were expected to

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also exert strong influences on the distribution of cobalt in the ocean interior. Two companion manuscripts describe this large dataset: the first describes the methodology, intercalibration and preservation, oceanic distributions, chemical speciation, and major sources of cobalt to the North Atlantic Ocean (Noble et al., this study). The second manuscript examines the ecological stoichiometry of cobalt in zonal transects of the North and South Atlantic Ocean (Saito et al., submitted).

2 Methods

Samples were collected along the U.S. GEOTRACES North Atlantic Transect, GA03/3_e chief scientists: William Jenkins, Ed Boyle, and Greg Cutter). This transect was sampled in two legs aboard the R/V Knorr: USGT10 (October 14, 2010 – November 3, 2010; GA03_e) and USGT11 (November 4, 2011 – December 14, 2011; GA03). The first leg (USGT10) departed from Lisbon, Portugal and followed a transect southward, sampling Mediterranean Outflow Water (MOW) and concluding with a short westward transect along 17.4°N, crossing the northern reach of the oxygen minimum zone associated with the Mauritanian Upwelling system. This leg concluded at Station TENATSO at 24.5°W (USGT10-12). The second leg (USGT11) departed from Woods Hole, MA and sampled stations along Line-W to the Bermuda Atlantic Time Series (BATS) Station (USGT11-10, Fig. 1). At an approximately 3° longitudinal spacing, the subsequent stations were sampled across the North Atlantic Subtropical Gyre, including sampling the TAG hydrothermal plume and concluding with a reoccupation of Station TENATSO (USGT11-24).

2.1 Sample Collection

Samples were collected using the Old Dominion University GEOTRACES Carousel on both the 2010 expedition (USGT10) and the 2011 expedition (USGT11). Following the retrieval of the carousel, the pre-conditioned, Teflon-coated Go-Flo bottles were moved to the GEOTRACES Program class-100 trace metal clean van, pressurized with HEPA filtered air, filtered through 0.2 µm Acropak filters in accordance with published methods (Cutter and Bruland, 2012), and immediately refrigerated. Further information regarding deployment of the GEOTRACES carousel can be found on the GEOTRACES website and in the GEOTRACES cookbook (www.GEOTRACES.org). Samples were also collected using the surface towed fish. These samples were collected by suspending the towed fish off the

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starboard side with a boom, and sampled water at approximately 2m depth using a Teflon diaphragm pump following the GEOTRACES Program Cookbook sampling recommendations.

Sample storage bottles were prepared by soaking overnight in the acidic detergent, Citranox, rinsed thoroughly with Milli-Q water (Millipore), filled with 10% HCl to soak for 10 days (Baker Instra-analyzed HCl), rinsed thoroughly with Milli-Q water adjusted to pH 2, and double-bagged, empty. Samples were kept in clean and rinsed 60mL LDPE bottles, and either stored for a short time (<7 days) at 4˚C and double-bagged prior to analysis, or for a longer time (6-40 days) at 4˚C, double-bagged with gas absorbing satchels and with the outer bag heat-sealed to allow for longer-term sample preservation by removal of oxygen. The gas absorbing satchels were iron-free, obtained from Mitsubishi Gas Chemical (model RP-3K), and each satchel was rated to absorb 60mL of O_2 per 300mL of air. Each heat sealed bag (Ampac™ Flexibles SealPAK Heavy-Duty Pouches, clear polyester 4.5mil) held 6-7 60mL LDPE sample bottles and 3-4 gas absorbing satchels. The satchels come in impermeable, vacuum sealed bags of 25. It would take a few days to use a full bag of 25 satchels, so the bags were expended of air and re-heat-sealed after the required number of satchels were removed in order to limit the exposure of the unused satchels to air. A heat sealer (Kapak by Ampac) was used to seal each bag. After allowing the heat sealer to heat up for 3 minutes, the bags were sealed by lining up the open ends of the bag in the heat sealer and sealing for 1-2 seconds. When samples were ready to be analyzed, the bags were cut open and all samples in the bag were analyzed within a week. Both labile and total dissolved cobalt were analyzed from this sample bottle, and the sample identifier is the allocated GEOTRACES number.

2.2 Total dissolved and labile cobalt analyses

Concentrations of total dissolved and labile cobalt during USGT10 were determined shipboard using a previously described cathodic stripping voltammetry (CSV) method (Saito and Moffett, 2001; Saito et al., 2004). Measurements were made using the Eco-Chemie μAutolabIII systems connected to Metrohm 663 VA Stands equipped with hanging mercury drop electrodes and Teflon sampling cups within 7 days of sampling on double-bagged samples that were kept in the dark at 4°C until analysis. Standard additions of cobalt were carried out with Metrohm 765 Dosimats using a programmed dosing procedure (Noble et al., 2008). Concentrations of total dissolved and labile cobalt from USGT11 were measured on land between 1 and 6 weeks after the sampling date, using the same protocol as that employed

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for USGT10. Analyses were performed on samples preserved in the dark and in gas impermeable bags with gas absorbing satchels to ensure that no degradation of the sample occurred during that time.

For total dissolved cobalt analyses, samples were UV-irradiated for 1 h prior to analysis using a Metrohm 705 UV digester to degrade the organic ligands that bind cobalt and allow binding by the added electroactive cobalt ligand, dimethylglyoxime. Samples were analyzed in 8.5 mL aliquots with the addition of 30 µL recrystalized dimethylglyoxime (DMG, Sigma-Aldrich 0.1 mol L^{-1} in methanol), 1.5 mL purified sodium nitrite (Fluka Analytical A.C.S. reagent grade ≥ 99.0%, 1.5 mol L^{-1} in Milli-Q water), and 50 µL purified N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS) buffer (Sigma-Aldrich 0.5 mol L-1 in Milli-Q water). Reagent purification protocols were modified from those previously published (Saito and Moffett, 2001) in order to accommodate large batches. The DMG was recrystallized after dissolving in an aqueous solution of EDTA to remove any traces of metals. Nitrite solutions were prepared by equilibration overnight on a shaker with Chelex-100 to remove any trace metals. The nitrite solution was then filtered and removed from the chelex, the chelex was rinsed with copious amounts of milli-Q water, and added back to the nitrite solution to equilibrate for a second night on the shaker, followed by filtration into acid-washed HDPE or LDPE bottles. Nitrite was prepared in 500 mL batches and the batches were blank-checked before shipping to sea. Cobalt concentrations were determined by the standard additions technique, with initial concentrations measured in triplicate followed by four 25 pmol L^{-1} cobalt additions. A 0.01 mM Co stock solution was prepared by the addition of 14.7 µL of a 1000 ppm cobalt standard to a 25 mL Teflon volumetric flask of Milli-Q water adjusted to pH 2. 100 µL batches of 5 nM Co dosing solutions were prepared by the addition of 50 µL of the stock solution to a 100mL HDPE trace metal cleaned volumetric flask of Milli-Q water that was adjusted to pH 3 using Whatman pH indicator paper. This dosing solution was added to the Dosimats and used for the standard additions. Final concentration calculations were adjusted for dilution by the nitrite addition.

The analytical blank was determined by analyzing low-trace metal concentration seawater that had been UV-irradiated for 1 h, equilibrated overnight with prepared Chelex 100 resin beads (Bio-Rad), and UV-irradiated a second time to degrade any leached synthetic ligands. This metal free seawater was kept at room temperature in trace metal cleaned Teflon bottles of 250ml and 500ml capacity. Blanks for each reagent batch (nitrite, DMG, EPPS) were

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subtracted from the initial sample concentration. Blank analyses for each reagent batch were made at the beginning and end of use to confirm that the blank remained constant during analyses. The averaged blank for all reagent batches for the entire dataset was 4pM ± 1.2 with a range of 1.7 - 6.3pM (n = 38 for individual blank analyses). For a given reagent batch, the standard deviation was smaller, and we report a detection limit (3 times the standard deviation of the blank) of 1.8pM, representing the average of the detection limits estimates for reagent batches with at least 3 blank analyses (n = 6).

For labile cobalt analyses, 8.5 mL of sample was pipetted into acid washed Teflon vials that were preconditioned with a small aliquot of sample water. 30 µL aliquots of DMG were added to each vial and allowed to equilibrate overnight in the dark prior to analysis (Saito et al., 2004). Analyses were then performed as described for total concentrations using the standard addition technique with the addition of the remaining two reagents immediately before analysis. Previously, we determined that natural cobalt is strongly bound to ligands in seawater with a conditional stability constant of $>10^{16.8}$ (Saito et al., 2005). We define labile cobalt (LCo) as the fraction of total dissolved cobalt (dCo) that is exchangeable with the DMG complexing agent, indicating it is either bound to weak organic/inorganic ligands in seawater or present as free Co(II) (Saito et al., 2004; Saito et al., 2005). Where labile cobalt is detectable, the strong cobalt ligand concentration is defined as the difference between the total dissolved cobalt and the labile cobalt.

Two full electrochemical systems were utilized for analyses, with one dedicated to total cobalt analyses and the other to labile cobalt analyses. GEOTRACES standard seawater and internal standard lab seawater were analyzed periodically to ensure that the two electrodes were intercalibrated and functioning properly (Table 1). GEOTRACES standard seawater was UV irradiated and neutralized using 1N Optima ammonium hydroxide to increase the pH to 7.5. An oligotrophic seawater standard internal to our lab (described as CSW for consolidated seawater standard in Table 1), was prepared by UV irradiation in 500mL batches and stored in trace metal clean Teflon bottles at room temperature. The standard was not acidified at any point, thus avoiding the introduction of error and reagent blank associated with adding acid and base (Saito and Moffett, 2002), and allowing regular re-analysis without any further treatment. These standards were used to troubleshoot when the electrodes malfunctioned and to ensure consistency when operational. These batches were measured to be 53 ± 3 pM (n = 4), 74 ± 3 (n = 9), 71 ± 3 pM (n = 16) and 54 ± 6 pM (n = 35) over the course of the USGT-11

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cruise analyses, and 53 ± 5pM (n = 24) for the USGT-10 cruise analyses, measured across all reagent batches and both electrode systems. These results demonstrate that the methodologies employed to produce this dataset detect concentrations within the standard deviation of current consensus values for UV-irradiated samples, which can be found on the International GEOTRACES Program website (www.geotraces.org, see below). On occasion analyses were repeated due to obvious electrode malfunction or to confirm oceanographic consistency of measured values. If the repeated measurement was similar to the initial measured value, the initial value is reported. If the repeated analysis was more oceanographically consistent with adjacent values in the water column, that analysis was used instead.

2.3 Intercalibration efforts and data repository

Our laboratory has participated in the GEOTRACES intercalibration effort using this electrochemical analytical technique. We report our laboratory values for the GEOTRACES and SAFe standard analyses using the above-described electrochemical technique, including those conducted during analysis of the US North Atlantic GEOTRACES Section samples to be: SAFe S1 = 5.4 ± 2.6 (n = 9), SAFe D2 = 48.3 ± 5.5 (n=7), GEOTRACES GS = 31.4 ± 4.1 (n = 24), GEOTRACES GD = 66.9 ± 6.2 (n = 30). These results are in good agreement with those from the GEOTRACES intercalibration effort for Co using different methods all using UV-oxidation to degrade strong cobalt ligands.

Comparisons of our CSV data with ICP-MS and flow injection methods at the Bermuda Atlantic Time Series station, a crossover GEOTRACES station, from this expedition and the Dutch GEOTRACES section GA02, generated values that were similar in the photic zone but higher than others' studies in the mesopelagic (Dulaquais Refs). These observations were reported to the GEOTRACES Intercalibration committee and have delayed incorporation of Atlantic dissolved cobalt data into the Intermediate Data Products. The higher mesopelagic values we observed on fresh and "gas-satchel" preserved samples appear to be real based on comparisons with our own unpreserved samples (see Section 3.3 below)

All data generated by this lab and discussed in this paper have been submitted to BCO-DMO and are available at <http://www.bco-dmo.org/dataset/3868>. If using this data for future publication or analyses, please cite: Saito, M. (2013) Total dissolved Cobalt and labile Cobalt concentrations from R/V Knorr cruises KN199-04 and KN204-01 in the Subtropical northern Atlantic Ocean from 2010-2011 (U.S. GEOTRACES NAT project). Biological and Chemical

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Oceanography Data Management Office (BCO-DMO). Dataset version: 2013-04-26. URL: http://www.bco-dmo.org/dataset/3868.

3 Results and Discussion

3.1 Oceanographic Setting

The US GEOTRACES North Atlantic expedition track (Fig. 1) was chosen to investigate multiple processes and provinces within the constraints of an approximately zonal section and was completed in two legs. USGT10 sampled from Portugal to the Cape Verde Islands and consisted of stations USGT10-01 to USGT10-12 (October 2010), and USGT11 sampled from Woods Hole, MA, USA to the Cape Verde Islands, and consisted of stations USGT11-01 to USGT11-24 (November-December 2011). From west to east, the track transited from seasonally productive New England coastal waters, to shelf and slope waters, crossing the deep western boundary current (DWBC) and the Gulf Stream along the repeat hydrography section, Line W. After occupying the Bermuda Atlantic Time Series station (BATS), the track crossed through the oligotrophic Sargasso Sea, the North Atlantic Subtropical Gyre, and the Mid-Atlantic Ridge hydrothermal Trans-Atlantic Geotraverse (TAG) site. From there, the transect continued east, traversing over the northern reach of the tropical North Atlantic Oxygen Minimum Zone near the Cape Verde Islands and Mauritanian Upwelling region off the coast of Northwest Africa. The most eastward samples collected were along a meridional section from Portugal to the Mauritanian Upwelling, and sampled Mediterranean Outflow Water (MOW).

3.2 Vertical Profiles and Sections of Total Dissolved Cobalt and Labile Cobalt in the North Atlantic Ocean

The dissolved cobalt data product from USGT10 and USGT11 consisted of 11 and 21 profiles, respectively, totalling 717 total dissolved cobalt and 717 labile cobalt data points that were compiled into ocean sections that were rendered with Ocean Data View (Figs 2, 3A-B, Schlitzer, 2011). Visual examination of the vertical profiles (Fig 2) and sections (Fig 3) showed oceanographically consistent results. The two expeditions included a repeat occupation of a station at TENATSO (Tropical Eastern North Atlantic Time-Series Observatory, USGT10-12 and USGT11-24) where the mean difference between the two profiles was 8 pM overall, and 2.2 pM below 2000m. These profiles are expected to be

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similar given the slow timescale of deeper watermass movement relative to the 1 year sampling interval, and this resampling provides a unique opportunity to examine temporal variability on this time scale throughout the water column. Larger differences were observed in the surface and mesopelagic waters, with little to no difference below 2000m depth. In surface waters, this difference is explained by the fast movement of surface waters and timescales of the processes affecting cobalt cycling in this highly biologically active part of the water column. In mesopelagic waters (particularly between 1500 – 2000m), differences were observed within a water mass characterized as >55% Upper Circumpolar Deepwater (UCPDW) *via* OMPA analysis (Jenkins et al., 2015), indicating some temporal variability at these depths even within the relatively short time scale between samplings.

3.3 Preservation and accuracy of total dissolved cobalt using gas absorption satchels

The measurement of total dissolved cobalt has always been a challenge due it having the lowest concentrations of any biologically used metal. During the CoFeMUG expedition slight differences between at-sea analyses and samples returned to the laboratory were observed within the cobalt maximum inside the oxygen minimum zone that raised suspicions of a preservation issue for dissolved cobalt (Noble and Saito, unpubl. data). Moreover, during GEOTRACES intercalibration efforts, two issues have arisen that also contribute to this difficulty in accurate and reproducible total dissolved cobalt measurements. First, during the initial GEOTRACES intercalibration effort, it was confirmed that UV-irradiation was required in all methods to release cobalt from organic ligands that do not degrade or dissociate bound cobalt at low pH. This lack of sensitivity of cobalt ligands to dissociation at low pH is not surprising: it is well known that the cobalt-containing biomolecule vitamin B_{12} survives similarly low pH in the human stomach without dissociation, and that Co(III) complexes are classic examples of kinetic inertness and stability (Lippard and Berg, 1994). As a result, all samples reported as total dissolved cobalt here and in all of our previous studies have been UV-irradiated. More recently, we have become concerned that some intermediate depth samples are prone to loss of dissolved cobalt during storage via redox or other unknown reactions. To document this phenomenon, we present three full profile repeat analyses of USGT10-9 off the coast of Mauritania, analyzed by three preservation protocols: A) at-sea analyses performed within 2 days of sample collection, B) in-lab analyses performed after four months of storage at 4° C in the dark, and C) in-lab analyses of sample

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duplicates after four months of storage at 4° C in the dark, where the bottles were additionally preserved in air-tight, heat-sealed bags with gas absorbing satchels (Fig. 4). Seawater for the unpreserved, stored analyses (B above) was taken from the same bottles as the at-sea analyses, thus the sample bottles had a large headspace (60 mL bottles with ~50% headspace). These analyses and the at-sea analyses showed similar dissolved cobalt concentrations at the top and base of the water column but showed a large deviation at all other depths (Fig. 4). Use of the gas absorbing satchels to store samples for the same length of time (C above) allowed for excellent recovery of dissolved cobalt with a slope close to the 1:1 coherence of 0.96 and an r^2 of 0.99. Interestingly, almost all of the labile cobalt measured at sea had disappeared in unpreserved samples, indicating the movement of cobalt between chemical forms on the timescale of these experiments (data not shown; Noble and Saito in prep). This has major implications for cobalt speciation on preserved samples in certain biogeochemical regimes, especially the North Atlantic. Interestingly, samples from the Ross Sea did not experience this loss, showing excellent reproducibility on stored, unpreserved samples for both total dissolved and labile cobalt after 17 months (Noble and Saito in prep). However, given the successful recovery of total cobalt demonstrated by this new technique in a region prone to low oxygen and heavy dust inputs, we encourage research groups measuring dissolved cobalt to adopt the preservation method used in this study.

A GEOTRACES crossover station was also included at the Bermuda Atlantic Time-Series Station (BATS, USGT11-10). Data were compared between our lab and two labs that relied on an ICP-MS method (Middag *et al*. 2015) at this station as well as at a second station in the North Atlantic Subtropical Gyre (USGT11-20). Our laboratory results were found to be consistently higher than those of the other groups (intercomparison data not shown). The largest discrepancies (~20pM) were observed at intermediate depths associated with the highest labile cobalt concentrations (up to 36pM). Discrepancies were generally smaller in deeper waters (where labile concentrations were often ≤10pM), and concentrations were often within a few pM of each other in the upper few hundred meters where labile concentrations were below 10pM and often below our detection limit. Based on our comparison and preservation experiments in this and other locations, the preservation and storage issue appears to be exacerbated in the North Atlantic, and has only a minor influence at some depths in the South Atlantic, Ross Sea, and South Pacific. Hence, we hypothesize that the preservation effects may be related to the extensive dust- and subsequent colloidal-loading of the North Atlantic region. Ultimately, because comparison of our method with GEOTRACES

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standards and our internal laboratory standard showed excellent accuracy and reproducibility (see Table 1), we interpret our higher concentrations at intermediate depths to be due to loss of cobalt associated with different preservation techniques used in other methods.. Again, this preservation effect appears to be strongest in the North Atlantic, demonstrating only a minor influence in other regions.

3.4 Major sources of cobalt to the North Atlantic Ocean

The dissolved cobalt data highlight continental margin sources of cobalt to the intermediate waters of the North Atlantic from both eastern and western margins: a large plume emanated from the African coast along the eastern margin (Section 3.4.1), and another large plume was observed along the western margin within Upper Labrador Seawater (ULSW) (Section 3.4.2). In addition, regional contributions from coastal inputs (Section 3.4.3) were observed and a small, localized plume of cobalt was detected above the Mid-Atlantic Ridge hydrothermal vent site at TAG (Section 3.4.5). Atmospheric deposition over the tropical and subtropical North Atlantic is a significant source of a number of metals (e.g. Fe and Mn), but trace cobalt appears to be only a small contribution to the water column inventory. Notably, all elevated source signals of total dissolved cobalt were coincident with elevated labile cobalt as well. While the magnitude of the signals differed between the two species, this elevated signal coincidence may indicate sources carried within a water parcel that experiences slower scavenging relative to surrounding waters (*e.g.* due to low oxygen concentrations) or that the inputs were relatively recent and the maxima were captured in this sampling effort before they were fully scavenged (*e.g.* close to hydrothermal inputs). The following sections discuss these cobalt sources to the North Atlantic Ocean and compare the relative magnitudes of those sources to those observed in a prior study of the South Atlantic Ocean (Noble et al., 2012).

3.4.1 A large plume of cobalt off the Mauritanian Coast

The largest feature of this dataset was the dissolved cobalt plume observed along the eastern margin off of North Africa (Fig. 3). This subsurface plume of dissolved and labile cobalt extended from the Mauritanian coast more than 2000 km into the basin, based on a conservative definition of the plume of exceeding 100 pM total dissolved cobalt (Fig. 3). Centered around the oxygen minimum zone, the highest concentrations of dissolved cobalt (160 pM) were detected at ~400 m depth and were primarily associated with Atlantic Equatorial Waters (AEW). Wind- and circulation-driven upwelling occurs along the

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Mauritanian coast, leading to higher overall productivity that supports important local fisheries. The subsequent substantial remineralization of organic matter contributes to low oxygen waters at intermediate depths. This Northwest African/Mauritanian Upwelling region contains the smallest of five major marine oxygen minimum zones in the oceans, with the others located in the Eastern Tropical North and South Pacific, the Eastern South Atlantic, and the Arabian Sea (Keeling et al., 2010). Previous cobalt studies have shown that the South Atlantic OMZ and the two Pacific OMZs all harbor high concentrations of cobalt (Ahlgren et al., 2014; Hawco et al., submitted; Noble et al., 2012; Saito et al., 2004; Saito et al., 2005). The current study confirms high cobalt concentrations in the North Atlantic oxygen minimum zone as well, despite this OMZ having higher O_2 concentrations and lacking the substantial suboxic and anoxic waters found in other OMZs.

The elevated cobalt observed in the Mauritanian Upwelling is due to a combination of processes: 1) low bottom water oxygen allowing reductively dissolved cobalt to escape from sediments and be transported long distances with minimal removal,, and 2) the poorly ventilated shadow zone waters of the OMZ allowing accumulation of cobalt from vertical export of remineralized biogenic and aeolian cobalt. Similar coupling of processes and elevated cobalt were observed in the South Atlantic OMZ on a GEOTRACES-complaint zonal section (GAc01 also known as CoFeMUG, (Noble et al., 2012). These two parallel transects afford a unique opportunity to compare contributions from multiple sources that result in similar large-scale dissolved cobalt features. The biogeochemistries of the two regions are somewhat distinct: the North Atlantic is heavily influenced by aeolian input from the Sahara Desert and North America, and upwelling off the coast of Mauritania is ~1.8 Sv according to ^{3}He measurements (Jenkins et al., 2015). In contrast, the South Atlantic experiences very low overall dust deposition, and upwelling in the Angola dome and Benguela Upwelling has been estimated to be 2.2 Sv (Frame et al., 2014; Skogen, 1999). In the South Atlantic, the cobalt plume was also centered around the oxygen minimum and was coincident with elevated dissolved manganese and iron (Noble *et al*. 2012). Similarly, elevated manganese and iron were observed coincident with the North Atlantic OMZ, suggestive of similar processes influencing these trends (Hatta et al., 2015). In the South Atlantic, we suggested that the high OMZ concentrations of these hybrid metals, and cobalt in particular, were due to a combination of reductive dissolution, upwelling, advection, and remineralization (Noble et al., 2012). Reductive dissolution can be a source of cobalt *via* release of cobalt associated with manganese oxides in sediments along the coast, as we

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previously suggested for the South Atlantic OMZ system (process #1 above). This process likely contributes to the plume in the North Atlantic; however, the fraction of the cobalt plume supported by aeolian contributions to the vertical export (process #2 above) would be expected to be higher. Moreover, oxygen concentrations in the North Atlantic are not as low as those observed in the South Atlantic, but particulate FeS_2 has been observed in both the sediments and suspended particulate matter near the Mauritanian Upwelling sampling sites (Lam et al., 2012), suggesting that there may be sufficiently low oxygen concentrations along the shelf to allow the escape of reduced cobalt from the sediments without reprecipitation as oxides. Despite higher mesopelagic oxygen concentrations in the North Atlantic, the dissolved cobalt concentrations were also higher here, likely due to a larger contribution from dust sources in the North Atlantic study area (see Section 3.4.4) and/or through less time exposed to scavenging processes within the ocean interior. With the addition of the GA03/3_e section in the North Atlantic, four of the five world's major coastal OMZ regions have now been found to harbour high concentrations of cobalt (Hawco et al., submitted; Noble et al., 2012; Saito et al., 2005). This adds to the growing evidence that oxygen minimum zones and their accompanying coastal regions are important sources of dissolved cobalt to the oceans. Importantly however, for a basin-scale plume to be observed in the North African OMZ region implies that cobalt plume formation and persistence by slowed scavenging has a higher (low) oxygen threshold than other OMZ processes (e.g. denitrification) that require suboxic or anoxic conditions.

3.4.2 **Advected sedimentary source from Upper Labrador Seawater**

Strong total dissolved cobalt and labile cobalt plumes were also observed in the western Atlantic along Line W (USGT11-01 to the Bermuda Atlantic Time Series station (BATS, USGT11-10) between 1000-1500m depth, with no accompanying low oxygen signal. Water mass analyses using Optimum Multi-Parameter Analysis (OMPA, Jenkins et al., 2015) constrains the dissolved cobalt feature to be contained within Upper Labrador Sea Water (ULSW). Low silicate concentrations are a differentiating feature of ULSW and can be used to illustrate this by overlaying silicate contours on a Western Margin section of dissolved cobalt (Fig. 5). Two processes, which are not mutually exclusive, may explain the observed feature: 1) advection of a water mass that contains a higher inventory of cobalt than the surrounding waters and/or 2) coastal input of cobalt released from shelf sediments as ULSW comes in contact with the coastal shelf and slope during the transit south. Hatta *et al.* (2015)

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observed high Fe and Mn on this same GEOTRACES transect within this water mass and invoked release of these metals from sediments into the water column. Previous studies have also invoked continental margin interaction to explain Fe enrichment in Labrador Sea Water at a station further northeast into the Atlantic basin (Laes et al. 2003), and recent data suggests that Arctic waters may contain very elevated concentrations of cobalt (Saito and Noble unpublished data, Bundie and Saito, unpublished data) which could provide a source of high cobalt to the locations of ULSW ventilation.

The ULSW cobalt plume appears to be different in composition from that of the eastern margin Mauritanian Upwelling feature. First, the percentage of labile cobalt is higher (35-40%) in the western margin ULSW feature than within the eastern margin Mauritanian Upwelling (20-25%). Higher particulate cobalt is also observed along the western margin (Fig. 3), and could be related to the higher abundance of both dissolved phases, reflecting increased interaction with this phase via shelf inputs and/or scavenging. The transport of labile cobalt to depths below the photic zone may prevent entrainment of labile cobalt into microbial cycling and its transformation to complexed cobalt. This could explain the speciation differences relative to the eastern basin where the plume is shallower and labile cobalt is a smaller fraction of total cobalt. Oxygen concentrations are also much higher in ULSW than within the Mauritanian Upwelling plume, and further demonstrating that low oxygen is not necessarily critical to sustaining subsurface cobalt plumes. Another possible contribution to the western margin plume could come from remineralized cobalt transported within ULSW from its origin to the north. Cyanobacteria are thought to be major contributors to the oceanic cobalt ligand inventory and their virtual absence in polar regions has been invoked to explain the often higher fraction of labile cobalt found in the euphotic zone of those regions (Noble et al., 2013; Saito et al., 2010). It appears that the cold polar-sourced Labrador Sea waters may also carry that imprint of higher labile cobalt. These potential contributions are not mutually exclusive: it is likely that both continental shelf inputs and advected remineralization signals from cooler regions contribute to this high cobalt feature of the North American continental shelf and slope environment.

3.4.3 Coastal sources along the North American Margin

In the upper 40-60m along the western margin, surface coastal sources dominate cobalt distributions, and an inverse linear relationship with salinity is observed, indicative of a freshwater endmember source (Fig. 6). While biological processes often drive relationships

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of cobalt with phosphate instead of salinity, including at most of the stations sampled during GA03/3_e (see section 3.7), these Co:PO_4^{3-} correlations (Co:P hereon) were absent in the Line-W region (Fig. 6). Previous work characterized a similar relationship between salinity and cobalt in the North American margin region (Saito and Moffett, 2002), as well as between salinity and other elements such as copper and nickel (Bruland, 1980). In the current study, the relationship with salinity was similar for labile cobalt, supporting a labile source from the coast. This input of cobalt in conjunction with lower salinities implies potential sources from freshwater input such as rivers or groundwater from the coastal Atlantic region.

3.4.4 Evaluating Aeolian sources to the North Atlantic

The North Atlantic Ocean is strongly influenced by atmospheric dust deposition, which provides an important source of iron and other metals and has been shown to have impacts on regional nitrogen fixation (Moore et al., 2009). The influence of aeolian input from the Sahara Desert increases moving eastward toward the North African margin (Mahowald et al., 2005; Shelley et al., 2012a, Ohnemus and Lam, 2015). The Sahara is an important source of iron and other metals to the North East Atlantic (Measures 1995; Measures et al. 2008, Shelley et al. 2015). The two legs of the GA03/3_e section both occurred during autumn/winter months in successive years (October-December 2010, 2011), coinciding with the period of lower atmospheric deposition to the western Atlantic as measured at Bermuda, where spring is the major period of deposition (Engelstaedter et al., 2006; Jickells et al., 1990). Dust samples collected on-board this North Atlantic section (GA03/3_e) showed aerosol cobalt loadings associated with lithogenic elements such as Ti, Al, and Fe, with minor contributions from other aerosol types (Shelley et al., 2015), suggesting that desert dust sources were more significant than anthropogenic sources during the GA03/3_e expeditions. Lithogenic dust sources are likely a less significant source of cobalt to the North Atlantic Ocean than they are for other metals such as iron and aluminum because cobalt is much less abundant in crustal material (average Co:Fe ratio of ~1:2600, Taylor and McLennan, 1985), resulting in aeolian influences competing with the large coastal cobalt sources described above. In this section, we examine the contribution of dust to dissolved cobalt inventories using cobalt distributions across the basin, correlations with dissolved aluminum in the eastern basin, and estimates of dust flux contributions and relative to upwelling fluxes.

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Unlike iron or aluminum profiles, which show persistent surface maxima on GA03/3_e, dissolved cobalt profiles within the upper water column of the oligotrophic gyre were consistently nutrient-like (Fig. 2), with surface concentrations of total cobalt as low as 9 pM due to biological uptake (Fig. 7A-B). This was consistent with the low-dust sampling timing and prior observations. Intriguingly, previously published profiles of total dissolved cobalt at BATS station have displayed either nutrient-like or atmospheric deposition surface maximum-type depending on the time of year sampled, the seasonality of dust deposition (atmospheric deposition is highest during late spring/ early summer), and mixed layer depth (Saito and Moffett, 2002; Shelley et al., 2012b). The absence of a surface maxima at BATS during GA03 was consistent with low dust fluxes during fall and winter months, and with the deepening of the mixed layer, which acts to dilute dust-borne cobalt dissolved into shallow mixed layers during summer.

Dust deposition to the oligotrophic gyre appeared to have a small impact on the surface cobalt inventory during the low fall/winter dust flux and deep seasonal mixed layer sampled by the GA03 expedition. Aerosol cobalt deposition near Bermuda can be estimated as the product of aerosol cobalt concentrations determined from shipboard bulk aerosol sampling (0.15 pmol m^{-3} for BATS and 0.44 pmol +/- 0.28 m^{-3} including 12 surrounding deployments to BATS," BATS region" hereon (Shelley et al., 2015)) and a typical dry deposition rate of those aerosols (1000 m / d for the Bermuda Atlantic Time-Series crossover station, Duce et al. 1991). This results in a cobalt deposition flux of 0.15 nmol / m^2 / d (BATS) and 0.44 nmol / m^2 / d (BATS region). The solubility of cobalt in Saharan-derived aerosols collected in the Sargasso Sea has been estimated to be 10% during periods of high dust deposition (Shelley et al., 2012a), similar to longer term dissolution experiments on lithogenic-rich aerosols collected in the Red Sea (17 +/- 7%, Mackey et al., 2014). Combining these three facets (flux, solubility and mixed layer depth) with an observed mixed layer depth of 80m observed during GA03, dust dissolution is estimated to add ~0.06 (BATS) to 0.17 (BATS region) pM Co per month. This was a relatively low flux compared to the measured mixed layer inventory of 30 pM at BATS during GA03 for this period of low dust deposition and deep mixed layers.

We can also consider the conditions of high dust deposition coincident with the seasonally stratified mixed layer to capture the maximum potential dust contributions to the shallow cobalt inventory. Dust deposition and mixed layer depth at BATS tend to experience strong seasonality with similar phasing (low dust coincident with deep mixed layers and high dust

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deposition with shallow mixed layers). During the summer when dust fluxes are highest, mixed layers can be < 10 m deep (Steinberg *et al*. 2001). Shallow mixed layers intensify the assimilation of metals from atmospheric deposition because the fluxes are diluted over a smaller volume (Jickells 1999). Annual aerosol cobalt fluxes at BATS were calculated to be 944 nmol Co m^{-2} $year^{-1}$ using ^{7}Be isotopes and data from July 2011 to June 2012 (Kadko et al., 2015). Considering the extreme case where 100% of this annual dust deposition is deposited under highly stratified summer conditions (10m mixed layer depth), with an assumed 10% Co solubility results in an estimated 9.4 pM increase per year to the mixed layer cobalt inventory. This is a potentially significant contribution compared to the dissolved cobalt observed during GA03 (9-36 pM). Moreover, solubility increases with seawater exposure time (Mackey et al., 2014), episodic dust loadings of high intensity, and/or an increased anthropogenic component with higher solubility (Thuróczy et al., 2010) could also enhance the fractional magnitude of aeolian sourced dust to the mixed layer. As a result, higher dust deposition and shallower mixed layer depths that occur in the spring and summer at BATS could explain the non-nutrient-like profiles previously observed (Hansell and Carlson, 2001; Saito and Moffett, 2002; Shelley et al., 2012b).

Taken together, these results imply that the strong seasonal cycle at the BATS station creates a dichotomy of aeolian influences on the cobalt inventory in mixed layer. As winter time convective overturning homogenizes the upper water column, the spring and summer dust deposition becomes diluted. When applied to a 100m mixed layer, the same annual dust deposition flux decreases to 0.9 pM per year, increasing the dissolved inventory by a few percent overall (2.5-10% of the range described above). As dissolved cobalt concentrations increase with depth, winter mixing also provides a considerable flux of cobalt to the surface from deeper waters (Saito and Moffett, 2002). As a result, atmospheric cobalt deposition is most apparent in the mixed layer cobalt inventories on seasonal timescales in the North Atlantic.

Despite the expectation that dust sources of cobalt from the Sahara Desert may have an even stronger influence on eastern margin cobalt inventories, sedimentary sources appear to be dominant. Closer to the Saharan dust sources to the east, increasing surface cobalt concentrations were observed on GA03/3_e (Fig. 7A-B). Previously, surface cobalt concentrations of up to 110 pM (higher than those observed on GA03/3_e) were measured in this region and attributed to dissolution of Saharan aerosols (Bowie *et al*. 2002). Yet, because

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both dust deposition and coastal upwelling occur in this region, elevated surface concentrations near the eastern margin cannot be solely attributed to dust deposition. Similarly elevated dissolved cobalt was also observed near the coastal margin across the South Atlantic zonal transect, which experiences much lower dust inputs than the North Atlantic (Fig. 7C). Moreover, eastern margin profiles of dissolved cobalt from both expeditions were similar in structure and concentration despite major differences in dust supply and a closer proximity of North Atlantic margin profiles to the coast than those in the South Atlantic, implying that sedimentary sources were dominant in both OMZ regions (Figs. 7E-F, see caption).

Upwelling can be demonstrated to be the major source of cobalt to the euphotic zone in the North East Atlantic. Similar to the estimates at BATS, the contribution of aerosol dust to dissolved cobalt can be estimated from the aerosol cobalt concentrations measured on GA03/3_e (Shelley et al., 2015), standard deposition velocities (Duce et al., 1991), and relative solubility (Shelley et al., 2012). Dust inventories in North African dominated aerosols along USGT10 averaged 17 pmol Co m^{-3} (Shelley et al., 2015), over 100-fold higher than that measured at BATS (0.15 pmol Co m^{3-}, discussed above). These measurements imply a soluble cobalt flux on the order of 1.7 nmol m^{-2} d^{-1} to the mixed layer between USGT10-08 and USGT10-12. Due to the elevated cobalt in the OMZ plume described above, upwelling fluxes of dissolved cobalt to the mixed layer are significant here. Jenkins et al. 2015 estimated upwelling rates during GA03/3_e to be 5 m d^{-1} (Jenkins et al., 2015). A dissolved cobalt concentration at the base of the mixed layer of ~50 pM implies an upward flux 250 nmol m^{-2} d^{-1}. As a result, the soluble cobalt flux from dust during GA03/3_e (1.7 nmol m^{-2} d^{-1}) is only ~1% of the upwelling flux (250 nmol m^{-2} d^{-1}). However, Ohnemus and Lam also observed that the particulate material found in the mesopelagic of this region had a strong lithogenic signal that they attributed to dust fluxes, presumably through sinking dust material (Ohnemus and Lam, 2015), raising the possibility for a gradual dissolution of cobalt from sinking lithogenic particles, as observed experimentally by Mackey et al. (2014). Overall, these flux calculations show that the sub-surface cobalt inventory observed on the eastern portion of this transect buffered the cobalt inventory from dynamic dust deposition, although there may also be a component of dust supply within this subsurface inventory with particle sinking and dissolution.

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Tracers of dust input can help distinguish external sources of cobalt from dust, and comparisons between dCo:dAl in the North and South Atlantic surface waters show significant differences. Despite the dominance of upwelling fluxes of cobalt in the Eastern North Atlantic, dissolved cobalt was observed to correlate with dissolved aluminum, a tracer of lithogenic dust deposition in surface waters between USGT10-08 and USGT10-12 (r^2 = 0.96, Fig. 7, dissolved aluminum data from Measures et al. (Measures et al., 2015)). The slope of this relationship (1-2 mmol dCo: mol dAl) was much steeper than that expected from their relative abundance in aerosols on GA03/3_e (0.16 mmol Co : mol dAl), despite their similar solubilities in North African aerosols (5-15% Buck *et al*. 2010; Mackey *et al*. 2015; Shelley *et al*. 2012b). Perhaps this deviation was related to artifacts in solubility measurements or differential biological processing: productivity is quite high in the Mauritanian Upwelling region and this dCo:dAl relationship in surface waters may reflect rapid uptake of both elements (biological uptake for cobalt and scavenging for aluminum) and subsequent release by remineralization. This influence was evident in depletion of both elements in the upper water column (Figs. 2, 3), and in dAl's lower abundance in the eastern (near Africa) portion of the GA03/3_e transect relative to the west (near BATS, (Measures et al., 2015)). Intriguingly, this dCo:dAl relationship was not observed in surface waters of the Benguela Upwelling where dust input was much lower, but upwelling was also strong (Noble et al., 2012). This coupling of dCo and dAl in the North Atlantic implies both an influence of dust and a complex interaction with the high productivity of the upwelling region.

As demonstrated above, high cobalt concentrations in the underlying OMZ cause upwelling fluxes of cobalt to be much larger than dust dissolution. Since cobalt in the surface ocean is acquired by phytoplankton, exported to depth and then remineralized, it is possible that atmospheric deposition of cobalt contributes to the OMZ cobalt plume indirectly, thereby returning to the surface ocean when these waters are upwelled. Tritium/helium ages of these water masses have ventilation ages on the order of several decades (Jenkins et al. 2015), allowing cobalt originally delivered to the surface ocean to accumulate in the OMZ after it is remineralized. Continued dissolution of cobalt from dusts that have already sunk below the euphotic zone may provide an additional cobalt source to these depths (Mackey et al. 2014). Therefore, despite instantaneous dust fluxes that are dwarfed by ocean mixing, storage of dust-derived cobalt in the mesopelagic ocean may cause dust-borne cobalt to be significant in sustaining the cobalt inventory in the North Atlantic Ocean on longer timescales.

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3.4.5 Hydrothermal source of cobalt to the deep North Atlantic

The influence of hydrothermalism on dissolved and particulate cobalt was clearly detectable in near-field mid-Atlantic ridge samples, but unlike iron and manganese, these effects did not persist appreciably beyond the ridge station. In the North Atlantic deep water concentrations of cobalt were low (39-55 pM), likely due to scavenging and the intrusion of deep water masses with a smaller cobalt inventory. Samples taken at the TAG hydrothermal field (USGT11-16), however, showed a subtle increase in cobalt concentration relative to the surrounding waters (Fig. 2, 3, 8). Five samples were taken within the plume between 3200 and 3500m depth above the well-studied TAG hydrothermal vent site (Fig. 8). A maximum in both dissolved and labile cobalt was observed, constituting a ~37% increase over adjacent depths within the vertical profile for a ~25pM hydrothermal signal over background of which ~16pM is labile cobalt. The presence of labile cobalt in the hydrothermal plume implies that cobalt was released primarily in a labile form and that the vent may act as a local but small source of cobalt to surrounding waters.

Cobalt concentrations in hydrothermal vents have previously been studied at TAG and can be taken as potential mixing endmembers (James et al., 1995; Swanner et al., 2014). Suspended particulate cobalt exhibited a dramatic maximum in the hydrothermal plume (12.5 pM pCo, Fig. 8), a 20-fold increase over the background concentrations (~0.6 pM pCo) as observed in the particulate cobalt ocean section (Fig. 3). The differences between the dissolved cobalt and dissolved iron and manganese within the hydrothermal maximum were staggering: iron concentrations reported in the plume are almost 4 orders of magnitude higher than that of cobalt, and manganese concentrations are 3 orders of magnitude higher (Hatta et al., 2015). These iron and manganese features were observed at adjacent stations as well, while the cobalt feature was confined to the near-ridge region at USGT11-16. These large differences should be considered in light of their respective background concentrations away from the vents: Cobalt concentrations are approximately 1 order of magnitude less than that of iron, and approximately 4-fold less than that of manganese. Thus, even taking the higher relative concentrations of iron and manganese into account, the near-field net hydrothermal source difference between metals was major. Dramatically high concentrations of particulate iron oxyhydroxides were also observed at the vent site (~50nM pFe, Ohnemus and Lam, 2015), which likely controlled the overall modest increase in dissolved cobalt distributions by dominating cobalt scavenging. Evidence for localized scavenging at the vents was also

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observed in negative dCo:P relationships in samples closest to the TAG vent site (see companion manuscript, Saito et al., submitted, their Figs. 6 and 7, bottom depths of station 1116). Interestingly, no similarly dramatic increase in pMn was observed, implying the near-field Co scavenging was related to iron oxide precipitation rather than Mn-oxidizing bacterial activity (Ohnemus and Lam, 2015).

Cobalt comprises a much smaller fraction of crustal material than these other metals, so hydrothermally leached crust may be expected to reflect similar ratios to that found in crustal material. When dissolved cobalt and iron reported above are normalized to manganese, the relative values are consistent with the dilution of hydrothermal fluids measured at Rainbow, one of the vents located at TAG (Fig. 8, (Hatta et al., 2015; James et al., 1995)). This observation is also consistent with the relative concentrations detected just above the Mid-Atlantic Ridge in the South Atlantic where no notable cobalt feature was found amidst pronounced Mn and Fe plumes (Fig. 8, (Noble et al., 2012; Saito et al., 2013)), likely due to the dilution of the hydrothermal cobalt contributions to below the NADW background inventory. The observation of the hydrothermal cobalt signal in the North Atlantic zonal transect but not the South Atlantic zonal transect was likely a result of the targeted and close sampling of a known hydrothermal field, while the South Atlantic transect accidentally observed a large hydrothermal plume without prior knowledge of any nearby potential hydrothermal field sources to the sampling locations. Circulation patterns at vent sites may also be characterized by circulation patterns that are constrained by the bathymetry of the spreading system, creating a local swirling effect that may allow particle reactive metals to precipicate with less lateral advection (Baker et al. 1995). We also observe an interesting trend among these ratios. Where the ratio of Co:Mn increases with dilution (*i.e.* from direct hydrothermal fluid sampling, to intentional plume sampling around a temperature anomaly, to accidental plume sampling with no observed temperature anomaly), the Fe:Mn ratio follows the opposite trend. Vents from different areas are known to be characterized by different source ratios of metals so this comparison may be coincidental. It is also consistent with what would be expected of the relative differences in biogeochemical oxidative removal rates of these metals, where cobalt tends to be scavenged more slowly than manganese and iron. Additionally, it might also be explained by a difference in the relative importance of hydrothermal vs. other sources of dCo and dMn to their respective deep ocean inventories.

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3.4.6 No discernible source of cobalt from Mediterranean Outflow Water

Off the coast of Portugal near the opening to the Mediterranean Sea, Mediterranean Outflow Water (MOW) was sampled at Stations USGT10-01 to USGT10-08 within the Meridional section at a depth range of ~1000-1500m (Jenkins et al., 2015)(Figs 2 and 3). There was no discernible MOW source of elevated cobalt to other Atlantic water masses, similar to a lack of dissolved iron in MOW observed on this transect (Hatta et al, 2015). Previous studies have observed slightly elevated concentrations of these metals (Bowie et al., 2002; Morley et al., 1997), and high aluminum concentrations associated with MOW have been used to help trace the presence of MOW (Measures et al., 2015; Measures et al., 1995). This section also revealed slight increases in Pb concentration coincident with MOW (Noble et al. 2015). Significantly elevated lithogenic particle loads were also identified in these samples (Ohnemus and Lam, 2015) though, suggesting perhaps that any labile particulate cobalt may have already been released or otherwise removed from these particles. Cobalt concentrations were quite uniform within MOW during this expedition, which may be reflective of the short residence time of the Mediterranean Sea of ~100 years (Lacombe et al., 1981).

3.5 Variable Influence of Deep Margin Nepheloid Layers

The role of the sediment-water interface and sediment resuspension in nepheloid layers has long been thought to influence the distributions of trace metals, yet few expeditions have sampled these deep regions, and none we are aware of for dissolved cobalt. The North Atlantic zonal GEOTRACES section provided a useful opportunity to examine these potential interactions, and evidence suggests that the differences in cobalt concentration in deep waters along the margins are more complex than dissolution and release near the bottom: the processes that stir up and create nepheloid layers, which provide increased surface areas for scavenging removal of cobalt, can also promote benthic release of dissolved cobalt. Here we observed a variable influence of nepheloid layers on the distributions of dissolved cobalt (not contributing or removing cobalt), that may be related to particle density and composition.

Along the western margin of the North Atlantic transect, a pronounced nepheloid layer was sampled at USGT11-06 and USGT11-08 (characterized by suspended particulate mass maxima (SPM) of 763 µg/L at USGT11-08, USGT11-06 was not sampled for particles), and a less dramatic but larger nepheloid layer at USGT11-10 (SPM maximum of 40 µg/L, Lam et

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al. 2015, Fig. 9). The bottom two depths at USGT11-06 (~4500 – 4900m) showed slightly (~3 pM) elevated total dissolved cobalt relative to the waters above. This could be due to contributions from different water masses that have experienced differing degrees of scavenging over time and/or release of cobalt from the nepheloid layer sampled therein. The bottom two samples are associated with a higher percentage influence of Iceland Scotland Overflow Water (ISOW) relative to the four shallower samples above (~3500 -4300m), which correspond with a higher percentage of Denmark Straight Overflow Water (DSOW, (Jenkins et al., 2015)). These water mass differences are supported by changes in the $^{206}Pb/^{207}Pb$ isotope signature as well, which gives some indication of the contributions from different water masses due to the isotope signatures captured at their respective outcroppings, both spatially and temporally (Noble et al. 2015). At the BATS crossover station (USGT11-10), several samples were collected near the bottom, and again, a slight increase in labile and total cobalt was observed. A thick nepheloid layer extended several hundreds of meters into the water column but produced a gradual and small decrease in transmittance voltage, unlike the dramatic decrease observed at USGT11-08.

It should be noted that transmittance voltage is not the best indicator of suspended particulate mass due to differential sensitivity to particles of different composition. It does give an indication of the presence of these features, which have been confirmed and characterized more quantitatively by chemical determinations of SPM (Lam et al. 2015). The deepest samples show a slight increase in both the total (8pM) and labile (5pM) concentration approaching the deepest sample, possibly suggestive of some resuspended and redissolved particulate cobalt. This slight increase in dissolved cobalt concentration was accompanied by a strong increase in suspended particulate cobalt (Fig. 9). If this increase were due solely to dissolution of resuspended particulate cobalt, a much stronger dissolved cobalt increase may have been expected at USGT11-08. At USGT11-08, however, where the most dramatic decrease in transmittance voltage was observed, and the highest deepwater concentration of suspended particulate cobalt was observed, there was no significant increase or decrease in dissolved total or labile cobalt. No major differences were observed among the water masses occupying the bottom depths between USGT11-06, USGT11-08, and USGT11-10. These contrary observations suggest a balancing act between the source function of resuspension (benthic release of dCo) and the sink function of the nepheloid layer itself (increased surface area for scavenging, i.e. SPM). It is possible that at USGT11-10, the SPM maximum (40 µg/L) was not high enough to overcome the source from benthic release. At USGT11-08;

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however, the much higher SPM (763 µg/L) may have sufficiently scavenged any cobalt from benthic sources. The composition of the lithogenic particles that dominate these nepheloid layers, are also not particularly good scavengers (Lam et al. 2015), and this composition is likely a key factor driving the differences observed between the wester and eastern margins.

Along the eastern margin, USGT10-09 also sampled a notable, though smaller, nepheloid layer (SPM max of 44 µg/L, Lam et al. 2015), and in this case, a distinct minimum was observed in both total dissolved cobalt and labile cobalt, coincident with a significant maximum in suspended particulate cobalt (Fig. 9). This nepheloid layer, unlike the western margin nepheloid layer, contained particulate manganese and iron oxyhydroxides, which are likely much more efficient scavengers of cobalt than lithogenic particles (Lam et al. 2015). Labile cobalt was undetectable in the deepest sample, suggesting that all cobalt was tightly complexed or that the labile fraction had been scavenged away. This decrease in labile cobalt was also observed at Stations UGST10-10 and USGT10-11, where much smaller nepheloid layers were observed, coincident with relatively small concentrations of resuspended particulate cobalt (Fig. 9). This dramatic difference where some bottom samples along the western margin show slight enrichment while some bottom samples along the eastern margin show strong depletion, both in the presence of notable nepheloid layers and elevated particulate cobalt was intriguing (e.g. compare USGT11-10 to USGT10-09), and demonstrates the chemical diversity of the dissolved and particulate phase interactions. Future characterization of the particle composition in these margin samples and process studies could provide mechanistic explanations for the capacity of particles acting as sources or sinks of cobalt to the dissolved pool.

3.6 Inverse Relationship with Oxygen and Implications for Deoxygenation

In intermediate depths, and particularly within the eastern margin cobalt plume, cobalt and dissolved oxygen showed a significant inverse relationship (Fig. 10). As mentioned in Section 3.4.1, elevated concentrations here are likely driven by a combination of a sedimentary source involving reductive dissolution and advection, as well as remineralization of sinking biological material. Both of these processes are linked to oxygen in an inverse fashion and are the likely explanation for this linear relationship. The low O_2 concentrations also allow for the persistence of high dissolved cobalt through slowed oxidation into manganese oxide particles (Moffett and Ho, 1996). In our previous study of the South

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Atlantic, we discussed the potential for trace metal ocean inventories to increase as a result of ocean deoxygenation (Noble et al., 2012), based on observations compiled by Stramma et al. of deoxygenation within the major oxygen minimum zones across the world oceans over the last 50 years (Stramma et al., 2008). In our South Atlantic work, we made a back-of-the-envelope calculation of the influence of increasing ocean deoxygenation and potential for increasing sedimentary release of cobalt assuming a linear relationship in concert with deoxygenation rates determined by Stramma et al. While this assumption that the linear inverse dCo:O_2 relationship would be constant moving forward in time is simplistic since its mechanistic basis remains unknown, it provides a useful first approximation of potential increases in cobalt ocean inventories.

Here, we apply the same approach to the North Atlantic OMZ to estimate the potential increase in cobalt inventory in the upper 1000m of the North Atlantic that may be attributed to deoxygenation. Within the low oxygen region of the North Atlantic, between 300-800m depth, cobalt and O_2 display an inverse relationship with a slope of -0.56 pmol dCo μmol^{-1} O_2 ($n = 73$, $r^2 = 0.89$), very similar to our findings in the South Atlantic (-0.56, $r^2 = 0.73$, (Noble et al., 2012)). This suggests that a similar chemistry governs the relationship, not an aspect of a preserved coastal dCo:O_2 signature, and could be related to the oxygen needs of manganese oxidation and co-oxidation. Stramma et al. estimated an ocean deoxygenation rate for the North Atlantic OMZ of -0.34 µmol O_2 kg^{-1} y^{-1} over the past 50 yr (Stramma et al., 2008). Together, these relationships can be used to estimate potential future increases in cobalt concentrations within the oxygen minimum zone. An upper 1000m cobalt inventory from USGT11-10 (BATS) across the basin to the most coastal station at USGT10-09 was estimated by summing the estimated dissolved cobalt within each of many trapezoid shaped water parcels, utilizing each depth and the distance between adjacent stations to interpolate cobalt concentrations between stations and between samples. We then estimated the potential impact of deoxygenation rates on the cobalt inventory within the OMZ, and that subsequent impact on the upper 1000m inventory as a whole by using the dCo:O_2 relationship and North Atlantic deoxygenation rate described above. The upper 1000m is utilized because of the low O_2 waters found in the 250-850m depth range, although this calculation could be easily modified for other depth ranges. Extrapolating forward 100 years, using this simple calculation we estimate that the cobalt inventory in the upper 1000m of the North Atlantic could increase by 20% in the next 100 years. These large potential changes in upper ocean inventories may have implications for the ecological balance within this basin. This increase is also two-fold higher

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than the ~10% estimated for the South Atlantic, which is largely due to the two-fold higher rate of deoxygenation reported for the North Atlantic OMZ (-0.34 µmol O_2 kg^{-1} y^{-1}) relative to the South Atlantic OMZ (-0.17 µmol O_2 kg^{-1} y^{-1}, (Stramma et al., 2008)). These results imply a need to consider the influence of changing oceanic oxygen on the biogeochemistries of metals and their influence on marine ecology.

3.7 Relationships of dissolved and labile cobalt with soluble reactive phosphate in the upper Atlantic Ocean

Dissolved cobalt distributions in the oceanic upper water column are influenced by biological processes such as uptake and remineralization (Noble et al., 2008). The nutrient stoichiometry of the aggregate microbial ecosystem can be inferred using a similar approach to that originally used by Alfred Redfield for dissolved and particulate nitrogen and phosphate (Redfield et al., 1963), where linear relationships between dissolved cobalt and soluble reactive phosphate can be interpreted as time-integrated signals of the extent of cobalt utilization by the resident phytoplankton community and their subsequent remineralization from the biological particulate phase. The aggregate slope of this correlation is termed the "ecological stoichiometry" for their inferred biological usage (Sterner and Elser, 2002). An emerging distinguishing feature of cobalt relative to other macro (N and P) and micronutrients (Zn and Cd) is a much larger range in stoichiometries when different oceanic regions are compared (Noble et al., 2012; Noble et al., 2008; Saito et al., 2010) (Baars and Croot, 2015; Bown et al., 2011; Sunda and Huntsman, 1995). The production of large GEOTRACES datasets provides an opportunity to explore this variability in stoichiometry and the processes behind them. Here, we describe broad regional differences in the Co:P relationships in the North Atlantic. A detailed and finer-scale analysis of these relationships and their ecological interpretations are discussed in a companion manuscript (Saito et al. in prep).

When the North and South Atlantic zonal datasets (NAZT and CoFeMUG) were compared in an aggregate scatter plot (Fig. 10), there were two notable differences. First, there is a shift toward lower phosphate concentrations relative to cobalt concentrations in the North Atlantic when compared to the South Atlantic. This is likely due to the lower surface phosphate inventory observed in the North Atlantic relative to the South Atlantic (Noble et al., 2012; Wu et al., 2000), as was evident in comparisons of nitrate+nitrite versus phosphate on these two transects and the higher phosphate axis intercept in the South Atlantic (Fig 10A). Second, there was also an offset in cobalt abundances, with higher total dissolved cobalt in the North

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Atlantic that consistently approached ~150pM in the eastern North Atlantic (Fig. 2), likely due to the higher atmospheric cobalt flux and resultant concentrations in the North Atlantic relative to the South Atlantic. As mentioned earlier, the North Atlantic experiences significant aeolian input from the Saharan Desert compared to the much lower dust inputs to the South Atlantic (Noble et al., 2012), and aeolian deposition is not considered to be a major source of phosphorus. This offset can also be seen in the $dCo:O_2$ plot as a vertical shift (Fig. 10), also likely caused by the higher dust contribution in the North Atlantic and an overall greater inventory.

Dissolved labile cobalt (LCo) also showed linear relationships with phosphate in the North Atlantic (Fig. 11), where labile cobalt is defined as the sum of the free cobalt and the cobalt bound to weak ligands (Saito et al., 2004). To our knowledge, this is the first report of linear relationships between labile cobalt and phosphate. Unlike the frequent observations of excess strong iron binding ligands in oceanic photic zones (Buck, 2007; Buck et al., 2015; Rue and Bruland, 1997), strong cobalt binding ligand concentrations tend to be less than or equal to total Co, allowing frequent detection of labile cobalt in the water column, and the potential for large swings in bioavailability of cobalt. The coherent lower slope of the LCo:P relative to total cobalt in the water column below the upper photic zone is particularly intriguing as it contrasts an apparent steeper and less coherent LCo:P in the upper photic zone. The low labile cobalt in the upper photic zone was expected due to phytoplankton and microbial uptake, reflective of the scarcity of this labile cobalt form and resulting in it comprising a small fraction of total dissolved cobalt there. The correlation labile cobalt with phosphate in the ocean interior (Fig. 11) implicates a remineralization source from decaying phytoplankton material. It is possible that cobalt taken up by phytoplankton and prokaryotic microbes for use in enzymes or vitamin B_{12} is present in a proteinacious form intracellularly that is susceptible to degradation with proteolytic activity upon sinking and results in its release as labile cobalt. This would be in contrast to strongly complexed cobalt that is formed through insertion into corrin rings of the B_{12} precursor by cobaltochelatase enzymes (Bonnet et al., 2010; Rodionov et al., 2003; Saito et al., 2005). This duality in cobalt's chemical forms, having both complexed and labile forms, adds a layer of variability in availability and geochemical cycling that is similar to that of dissolved and colloidal size fractions of iron (Bergquist et al., 2007; Fitzsimmons and Boyle, 2014). This fraction of the labile cobalt is likely a less protected inventory relative to scavenging processes and even though it is a small component of the dissolved cobalt inventory, it could play a major role in cobalt biogeochemical cycling.

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3.7.1 Variation in the depth of the cobaltclines: evidence for dynamic biogeochemistry

Examination of individual vertical profiles, with a focus on several stations from USGT10, further reveals the dynamic nature of cobalt chemical speciation and its influence on cobalt biogeochemical cycling in the photic zone of the North Atlantic (Fig. 12). With the exception of the labile cobalt at station USGT10-06, dissolved cobalt, labile cobalt and phosphate are all drawn down to their lowest concentrations in the mixed layer. By comparing these species to biological and physical proxies such as fluorescence and density, a few subtle differences emerge that are influenced by changes in the mixed layer depth and chlorophyll max. At all 4 stations, the gradient in total cobalt concentrations, or the "total cobalt-cline" coincides with the base of the mixed layer. At USGT10-09, the "phosphocline" and the "labile cobalt-cline" also coincide with the base of the mixed layer. Here, the waters are particularly productive as seen by the intensity of the fluorescence peak, and the three analytes reach relatively high concentrations due to upwelling, potential aerosol inputs (3.4.4), and sedimentary sources from the plume as discussed earlier (3.4.1). The chlorophyll maximum was shallow and pressed up against the base of the mixed layer as a result of the upwelling.

We can compare this to the patterns observed at USGT10-03, where less productivity was observed due to a lack of significant external nutrient sources and correspondingly smaller local sub-mixed layer nutrient inventories (note the scale difference). Here, the total cobaltcline again coincides with the mixed layer depth (77 m), but phosphate and labile cobalt are both drawn down below detection, much deeper, into the middle of the chlorophyll maximum (99m, Fig. 12, (Shelley et al., 2012a)). In the other two stations as well, the chlorophyll maximum is smaller and deeper, and the labile cobaltcline follows the phosphocline, where the total cobaltcline remains coincident with the mixed layer depth, revealing a confluence of processes that are occurring on relatively short timescales. With a short residence time of 0.32 y in the upper water column (upper 100m; Saito and Moffett, 2002), the tug of war between biochemical and geochemical processes within one profile can be seen. This offset between the labile and total cobaltclines suggests that biological processes act quickly enough to complex labile cobalt that enters the chlorophyll maximum at a rate faster than upward mixing. While pigment samples from this transect were lost during freezer failure, making assessment of the biological contributions to these variations difficult, we know that generally the coastal regions of the Atlantic have more eukaryotic phytoplankton

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representation, while the oceanic regions are dominated by picocyanobacteria and picoeukaryotes (Olson et al., 1990), and that picocyanobacteria are sources of metal binding ligands in both open ocean and coastal waters, including for cobalt and copper (Moffett and Brand, 1997; Saito et al., 2005). In the Mauritanian Upwelling, the inventories are higher and productivity is more intense, but the chlorophyll maximum is pressed up against the mixed layer so the differences in rates of uptake, complexation, diffusion, mixing, and upwelling cannot be easily separated.

3.7.2 Loss of cobalt from intermediate and deep waters by scavenging

In addition to the variety of sources that contribute cobalt to the North Atlantic described above, there is evidence for a dissolved sink from the pelagic water column throughout this North Atlantic zonal transect. This is evident in the vertical structure of profiles that, unlike nutrient-like elements such as phosphate and zinc, decrease precipitously at intermediate depths: below ~1000m in the western and northeastern Atlantic profiles and below ~600m on the eastern profiles off of Mauritania (Fig. 2). These changes in vertical structure likely reflect a shift in the balance between long-term scavenging removal processes occurring on horizontally advecting water masses relative to the vertical input of dissolved cobalt from remineralizing sinking particles. These scavenging processes can be observed in aggregate through an examination of the relationship between total dissolved cobalt and soluble reactive phosphorus (dCo:P) across the basin that displayed a downward curl, reflective of a loss of total dissolved cobalt relative to phosphate consistent with a preferential scavenging of total dissolved cobalt (Fig. 13), likely into bacterially-formed manganese oxide particles (Lee and Tebo, 1994; Moffett and Ho, 1996). Examination of the water masses calculated through OMPA analysis (Jenkins et al., 2015) associated with datapoints in dCo:P space showed water masses with unique signatures. In particular, the combined deep DSOW-AABW-ISOW (~ >3000m depth, Denmark Strait Overflow, Antarctic Bottom Water, and Iceland-Scotland Overflow) and CLSW (~2000-3000m, Classical Labrador Seawater) water masses were the major contributors to the North Atlantic scavenged “curl” feature (Fig 13C) implying loss of cobalt relative to phosphate in those water masses during their long-term advection. This cobalt curl feature is also evident in the South Atlantic zonal section as well, largely overlapping with the features observed here (Fig. 13A and 13B). Finally the amount of dissolved cobalt at intermediate depths decreases from the North Atlantic to the South

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Atlantic, consistent with a scavenging loss with thermohaline circulation. The accompanying manuscript (Saito et al. submitted) conducts further statistical analysis and discussion of the scavenging process through a profile-by-profile examination of the dCo:P relationship.

Notably there were also instances where regional circulation influences the otherwise generally "typical" hybrid-type profile structure. For example, vertical structure was notably perturbed at station USGT10-07 where sharp concentration gradients appear coincident with jetting intrusions of water masses as indicated by oxygen concentration, water mass analysis (Jenkins et al., 2015), and SF_6 tracer age (Smethie et al. in prep) (Fig. 14).

4 Conclusions

The dissolved and labile cobalt datasets for the North Atlantic zonal transect reveal numerous sources of cobalt to the North Atlantic. A large plume of cobalt was observed at ~400 m depth within the Mauritanian Upwelling along the eastern margin, which reflect eastern margin dissolved cobalt sources that are concentrated in the OMZ by phytoplankton uptake, export and remineralization and dust inputs. The western margin also displayed an elevated cobalt feature at intermediate depths characterized by ULSW, likely due to the mobilization of cobalt from continental shelf sediments either before or after subduction of the ULSW watermass. Hydrothermal and aeolian sources were detectable but small relative to these larger ocean features. Variable sources and sinks of cobalt were observed in deep margin nepheloid layers, suggesting that particle composition and sediment redox gradients may play an important role and should be taken into consideration in future studies. Using deoxygenation rates and a relationship between cobalt and O_2, we estimate that the cobalt inventory in the upper 1000m of the North Atlantic may increase by 20% in the next 100 years due to ocean deoxygenation, approximately twice that previously estimated for the South Atlantic OMZ region. Differences in the ecological stoichiometry of cobalt observed in the upper water column imply that a wide variety of cobalt utilization regimes exist. The processes of uptake and remineralization exerted control on cobalt in the oligotrophic surface waters of the North Atlantic, demonstrated by correlations with phosphate, and the strong drawdown of phosphate, nitrate, and total dissolved and labile cobalt. When low salinity, coastal, metal inputs and physical processes imposed a strong influence along Line-W, these correlations were obscured, muting the influence of biological processes that operate to couple these species. Combining growing datasets of cobalt coming from the GEOTRACES

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program with future biochemical studies will improve our understanding of the influence of cobalt biogeochemical cycling and its interaction with ocean marine ecology.

Increasing anthropogenic cobalt use due to growth in the economic market for cobalt in lithium batteries and other sources poses the potential to drastically change global oceanic cobalt distributions since the potential environmental impact of cobalt pollution is currently unknown. As such, it is more important than ever to establish a baseline understanding of cobalt distributions in the ocean to provide important insight into its oceanic biogeochemical cycling and to inform potential future impact of industrial use of cobalt on the ocean inventory.

Author contribution

At-sea and laboratory analyses of total dissolved and labile cobalt were conducted by A. Noble. Data analysis and manuscript writing were conducted by A. Noble, M. Saito, and N. Hawco. Particulate sample collection, analyses, and interpretations in the text were conducted by P.J. Lam and D. Ohnemus.

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Figure Captions

Figure 1. Map of USGT10 and USGT11 expedition tracks.

Figure 2. Dissolved profiles of total and labile cobalt for USGT10 and USGT11. Several stations of note are discussed more fully in the text, but some of note include USGT11-10 (BATS), USGT11-16 (TAG), USGT10-09 (Station closest to the Mauritanian coast), USGT11-1 to USGT11-08 (Stations along Line-W). USGT10 was sampled during the fall of 2010, and USGT11 was sampled during the fall of 2011.

Figure 3. (A) Full depth section of total cobalt, (B) full depth section of labile cobalt, and (C) full depth section of particulate cobalt with the meridional section in the right panels and the zonal section in left panels. These ocean sections were created using Ocean Data View. The dissolved sections were created using VG gridding and extrapolated lengths of less than 70 permille in either y or x direction for any of the section representations.

Figure 4. Examination of storage effects and use of gas absorbing satchels for preservation on a vertical profile from Station USGT10-9 collected near Mauritania. "Preserved" samples were kept refrigerated in heat-sealed bags with gas absorbing satchels, while "4 months" samples were only kept refrigerated. The preserved samples showed excellent recovery after four months in cold storage compared with at-sea measurements, while non-preserved samples showed significant loss of dissolved cobalt.

Figure 5. Section of dissolved cobalt and dissolved silicate along the western margin of the North Atlantic (Line-W). Upper Labrador Sea Water, identified generally between 700 and 1500 m depth by OMPA analysis (Jenkins et al., 2015) carries elevated concentrations of cobalt and is depleted in silicate. Elevated cobalt concentrations may be due to interaction of this water mass with sediments along the wide coastal shelf.

Figure 6. Total and labile cobalt show strong correlations with phosphate in the North Atlantic Subtropical Gyre, but this relationship is not observed along Line-W. Along Line-W, strong relationships between (A, B) salinity and total cobalt and (A, C) salinity and labile cobalt were observed in surface waters.

Figure 7. Surface transects for (A-B) the north Atlantic zonal section USGT10 and USGT11 (top panels), and (C) the South Atlantic zonal section CoFeMUG (Noble et al., 2012). (D) Relationships between dCo:dAl and correlations for northeast Atlantic stations USGT10-08 to USGT10-12. (E-F) Comparison of vertical profiles of dCo between the North and South Atlantic zonal sections near the African Coast. Distances of stations to the African coastline

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were ~530km for Tenatso (USGT11-24) and 210 km from USGT10-09 in the North Atlantic, and 1300 km for Station 13 and 790 km for Station 15 from the CoFeMUG Expedition in the South Atlantic.

Figure 8. (A) Manganese-normalized cobalt and iron concentrations in hydrothermal fluid and above the Mid-Atlantic Ridge. Hydrothermally leached crust may reflect ratios of reducible metals that are similar to that found in crustal material. Normalized cobalt and iron values are consistent with what might be expected by dilution of hydrothermal fluids measured at TAG. This is consistent with dissolved data from above the Mid-Atlantic Ridge at 9 ° S as well. The ratio of Co:Mn also increases with presumed dilution (from vent fluids to TAG to 9 ° S), while the Fe:Mn ratio decreases. This is consistent with the expected relative oxidative removal rates of these metals: Co < Mn < Fe. (B) Profiles of dissolved total and labile cobalt above the TAG hydrothermal vent and above the Mid-Atlantic Ridge at 9 ° S. A slight maximum in total and labile cobalt suggests that hydrothermally released cobalt at TAG is primarily labile and that the vent may provide a small, local source of cobalt. (C) Particulate cobalt profile at TAG. The dramatic signal of pCo is notable against the background concentrations, but small relative to those observed for Fe and Mn (see text).

Figure 9. Along the margins, nepheloid layers have differing effects on the dissolved cobalt concentration and composition, suggesting that more complex processes than simple dissolution from resuspended particles. Thick and large nepheloid layers along the western margin (three profiles to the left) appear to have small or insignificant effects on the dissolved and labile cobalt profiles, while a moderate nepheloid layer along the eastern margin at USGT10-09 (profile furthest to the right) appears to have a strong scavenging effect on the dissolved and particularly the labile cobalt. Labile cobalt in the deepest samples here were drawn down below the detection limit. The dramatic differences in the effect of nepheloid layers on the dissolved and labile cobalt concentrations demonstrates great chemical diversity in the dissolved-particulate phase interactions and suggests that these interactions cannot be generalized by phase alone.

Figure 10. Aggregate nutrient stoichiometries between the North Atlantic and the South Atlantic studies. Basin offsets were observed in comparisons between (A) nitrate and phosphate (linear regression for South Atlantic with a slope of 17.4, r^2 of 0.995) and (B) cobalt and phosphate concentrations in the upper water column of the North and South Atlantic zonal sections (North Atlantic stations, 2-400 m, linear regression depths include 54-

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300 m, with a slope of 61.4, r^2 of 0.90; S. Atlantic stations 1-19, 54-300m, same depths for linear regression, slope of 52.6, and r^2 of 0.83). (C) Different slopes and intercepts are observed across many regions of the world oceans that have been studied in the literature (Martin et al., 1989; Noble et al., 2012; Saito et al., 2010). These differences arise from variability in cobalt and phosphate utilization and supply. (D) Linear relationships occur between cobalt and oxygen for USGT10, USGT11, and for previous work done in the South Atlantic.

Figure 11. Co:P ecological stoichiometry observed across different regions in the North Atlantic. A tighter correlation is observed where labile cobalt becomes detectable and the correlation is observed down to differing depths depending on the strength of the processes that affect cobalt and phosphate biogeochemical cycling. Processes that affect both species similarly in time and space will tend to tighten the correlation and deepen the depth to which it is observed (e.g. USGT10-01- USGT10-06). Where scavenging or reductive dissolution may influence the two species differently, the correlation may be more diffuse or not observed at all (CoFeMUG Sta. 8-17).

Figure 12. In the upper water column, labile cobalt is often drawn down above and within the chlorophyll maximum, following the phosphocline. The total cobaltcline appears to be more closely associated with mixed layer depth. Comparing the differences among the stations that do and do not experience upwelling, it is apparent that biological processes are capable of complexing labile cobalt at a rate faster than upward mixing. This is seen by comparing USGT10-03 (located in oligotrophic waters north of the Mauritanian Upwelling) to stations USGT10-12 (located within the Mauritanian Upwelling). At both locations, the labile cobalt is drawn down below detection into the chlorophyll maximum. Station USGT10-03 is located in oligotrophic waters, with a smaller deep inventory of cobalt (~50pM at the chlorophyll max, increasing to ~60 at 200m). Station USGT10-12, however, is located in waters that experience upwelling and have a much larger deep inventory of cobalt (~70pM at the chlorophyll max, increasing to ~100pM at 200m).

Figure 13. Full depth relationships of total dissolved cobalt, phosphate, and AOU. In a comparison with water mass analysis from the NAZT expeditions, clear populations of data by water mass origin were observed in both (A) dCo:P and (B) dCo:AOU space. Data from the Ross Sea is also shown as a potential endmember (Saito et al., 2010). dCo:P relationships and the "cobalt curl" deviance from them were observed in the (C) Western and (D) Eastern

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basins of the Atlantic, and were similar between the North and South Atlantic (South Atlantic data from Noble et al., 2012).

Figure 14. Intermediate depth profile for (A) O_2, (B) labile cobalt (C) total cobalt (D) SF6 age and (E) water mass as a percent for USGT10-07. A strong linear correlation with O_2 is observed (inset). A small but distinct maximum is observed between 400-600m and demonstrates the capability of water mass features to influence the cobalt vertical profile at these depths.

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Figure 1

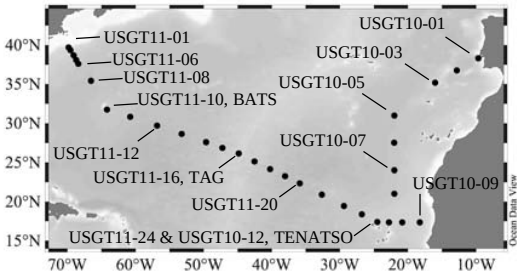

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Figure 2

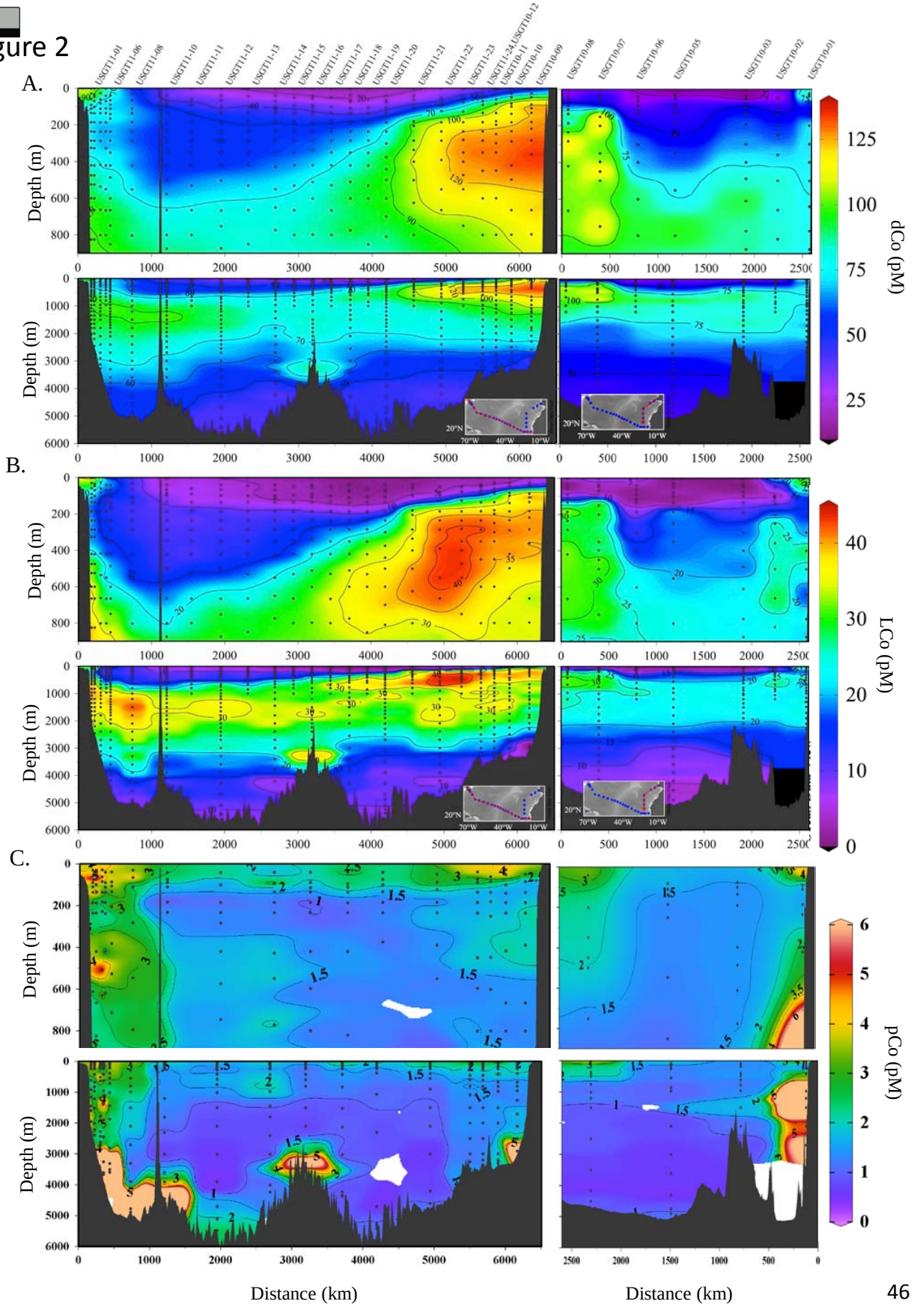

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Figure 3

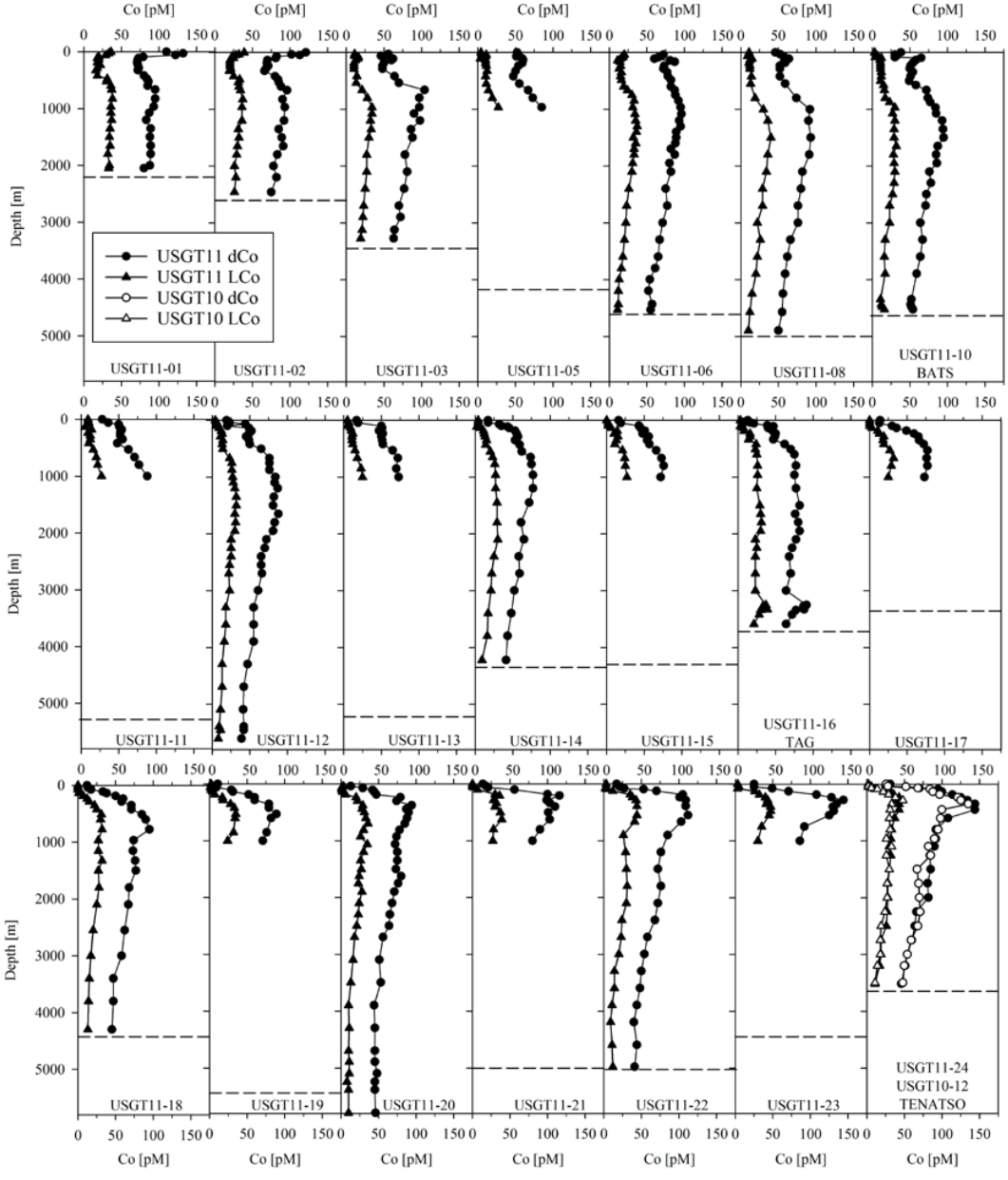

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Figure 3

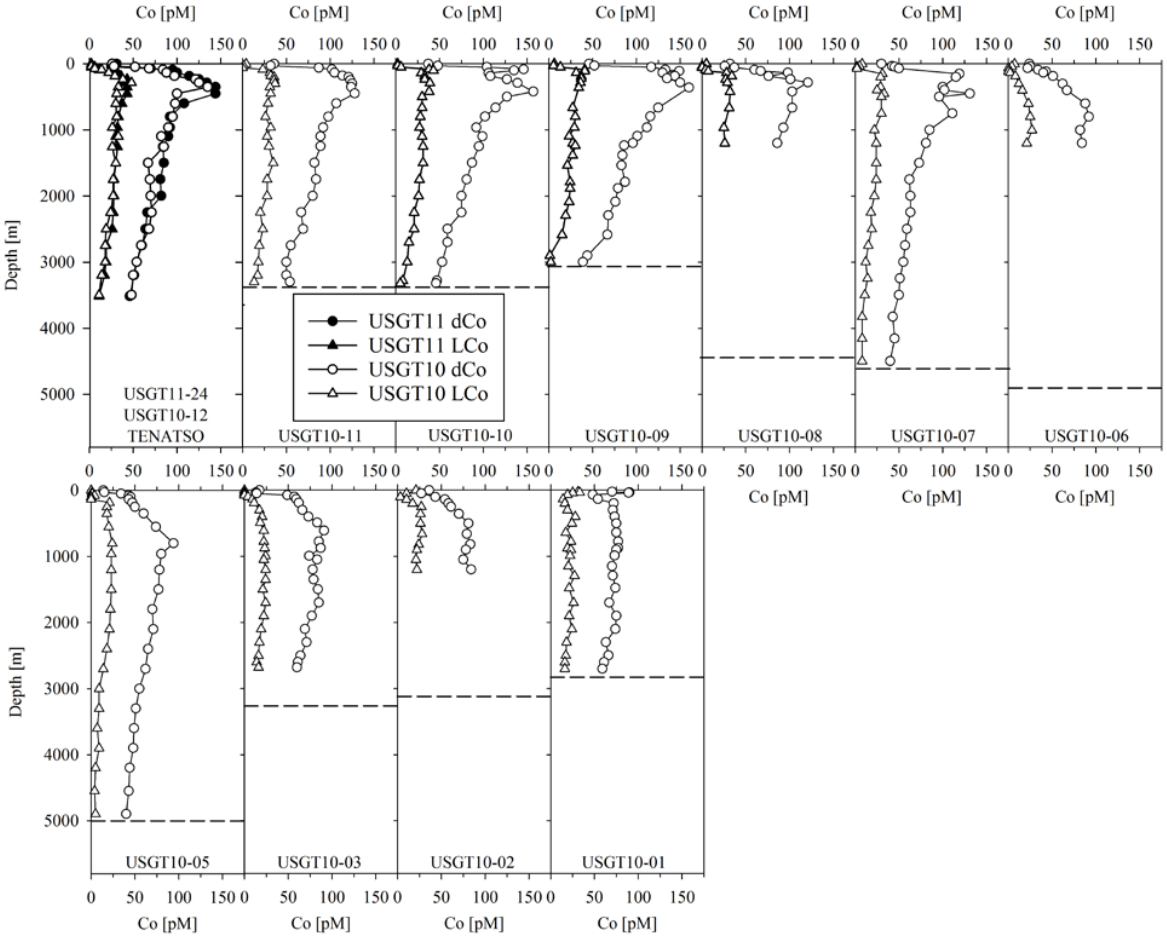

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Figure 4

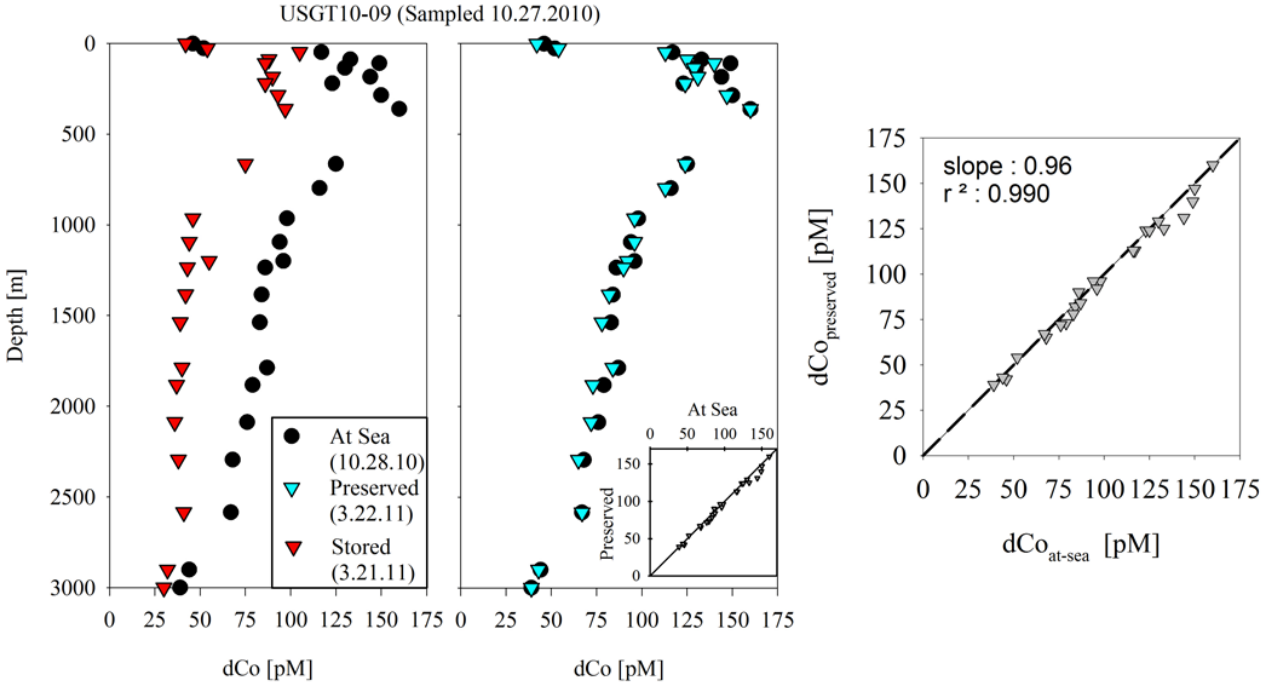

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Figure 5

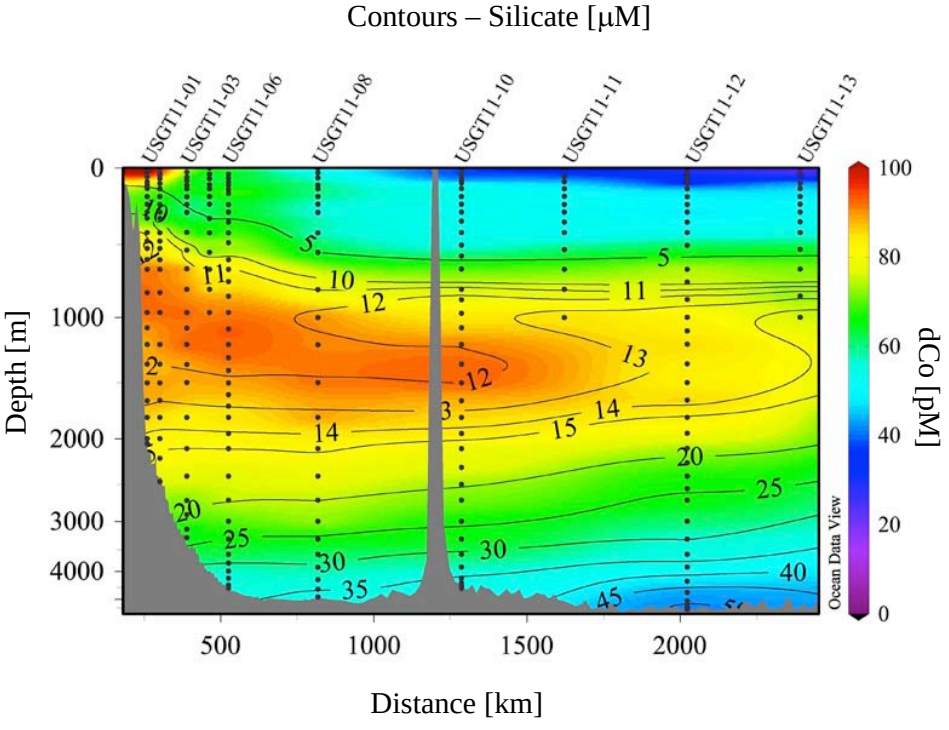

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Figure 6

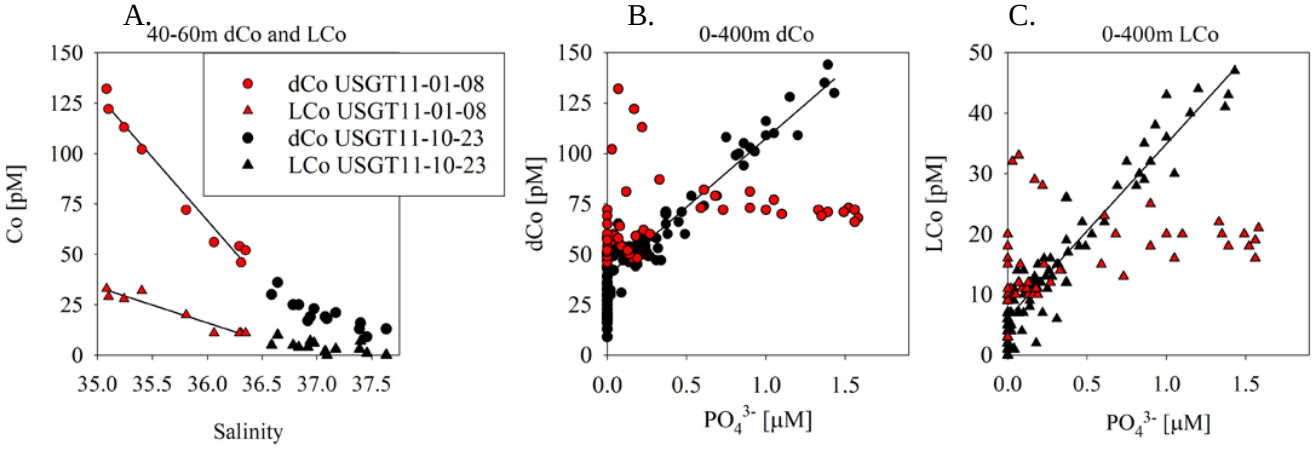

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Figure 7

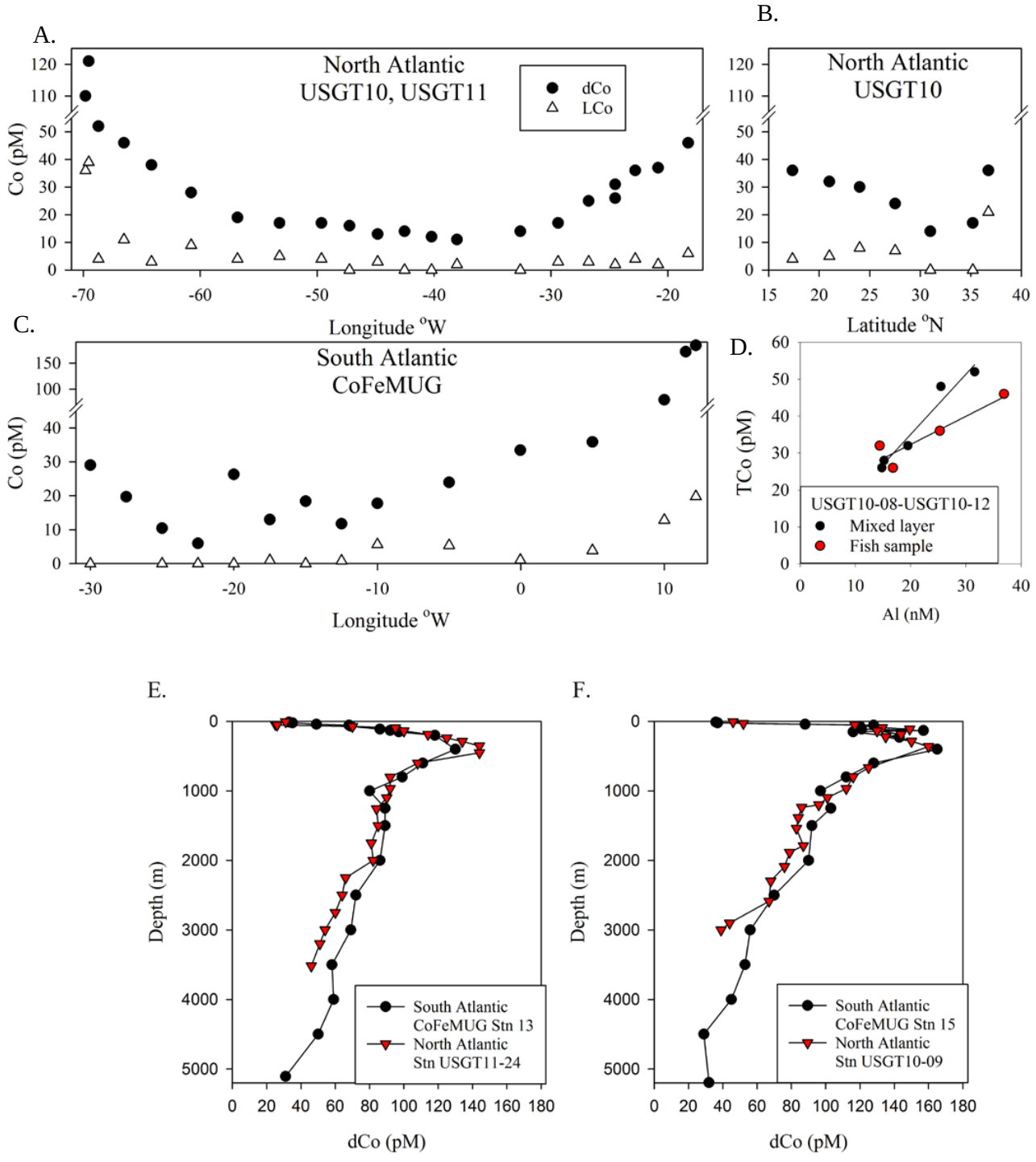

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Figure 8

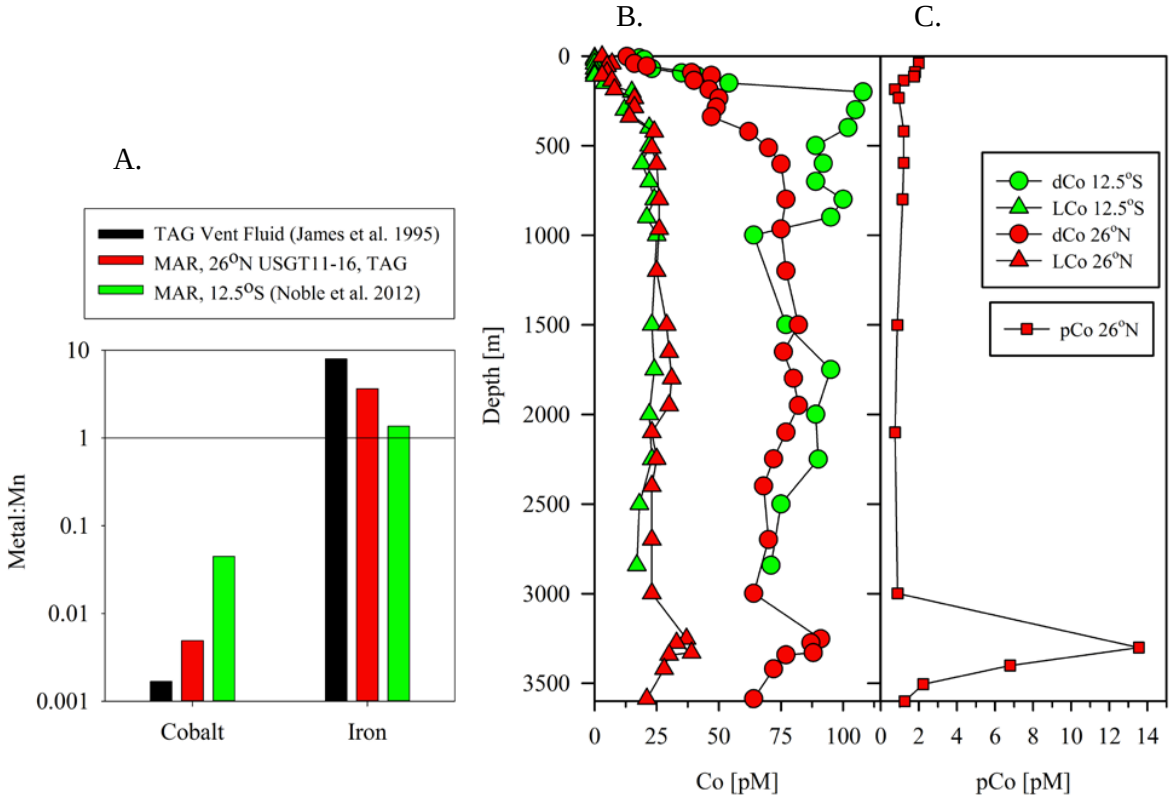

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Figure 9

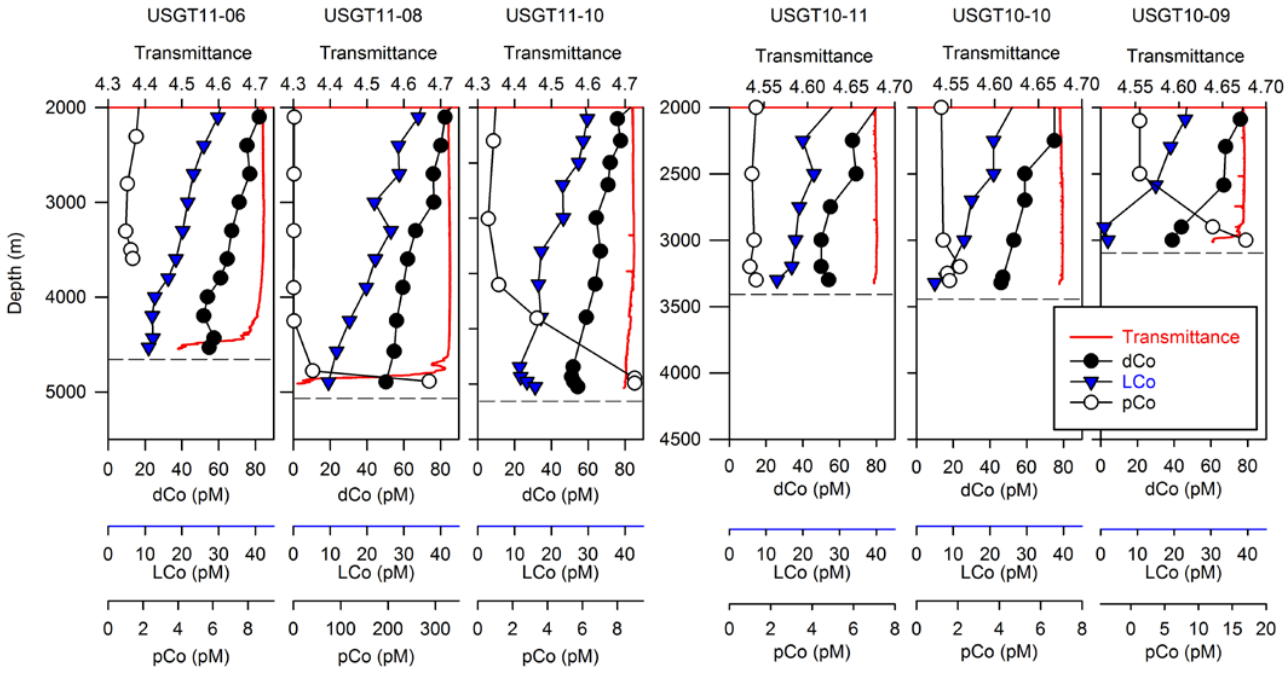

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Figure 10

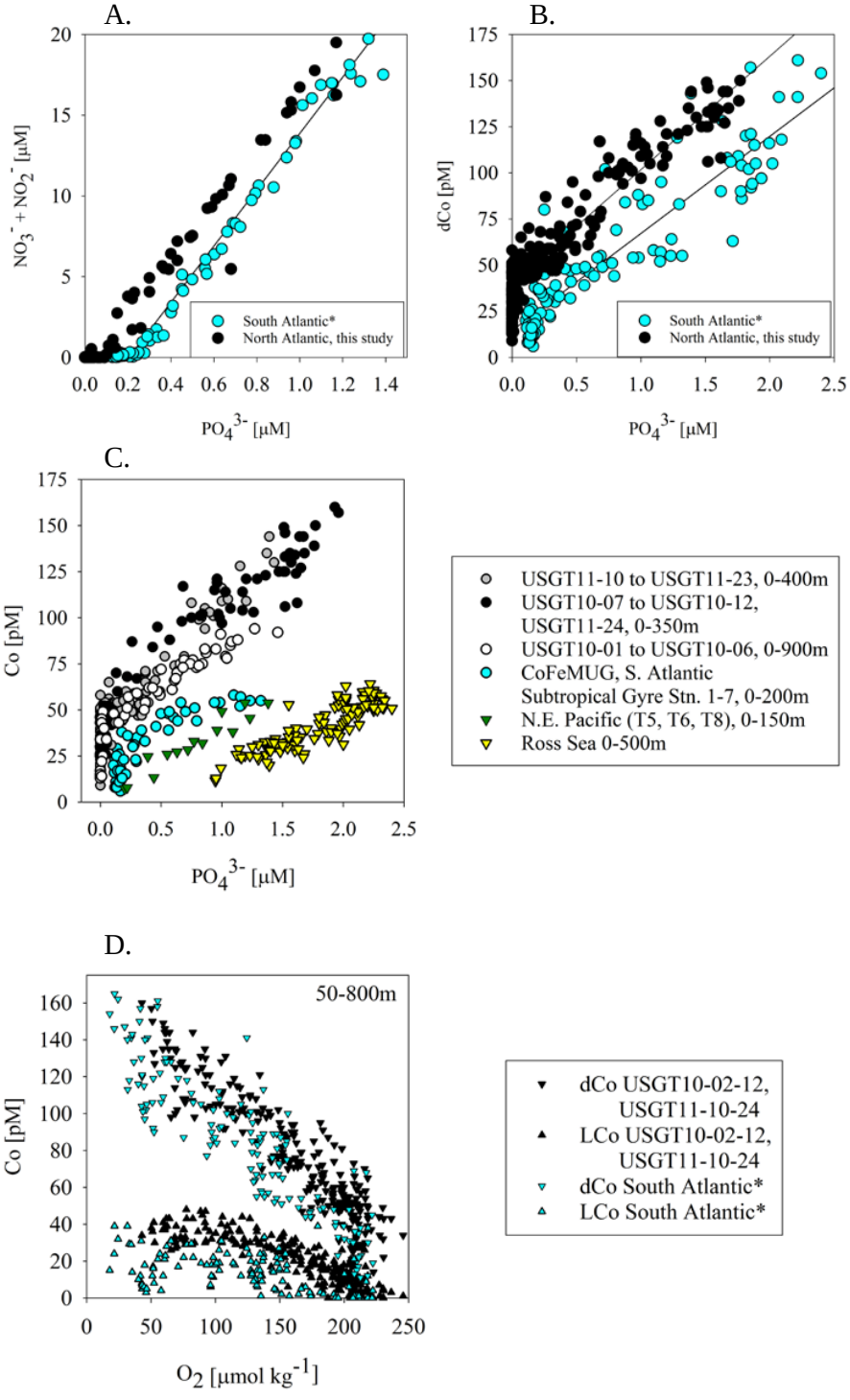

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Figure 11

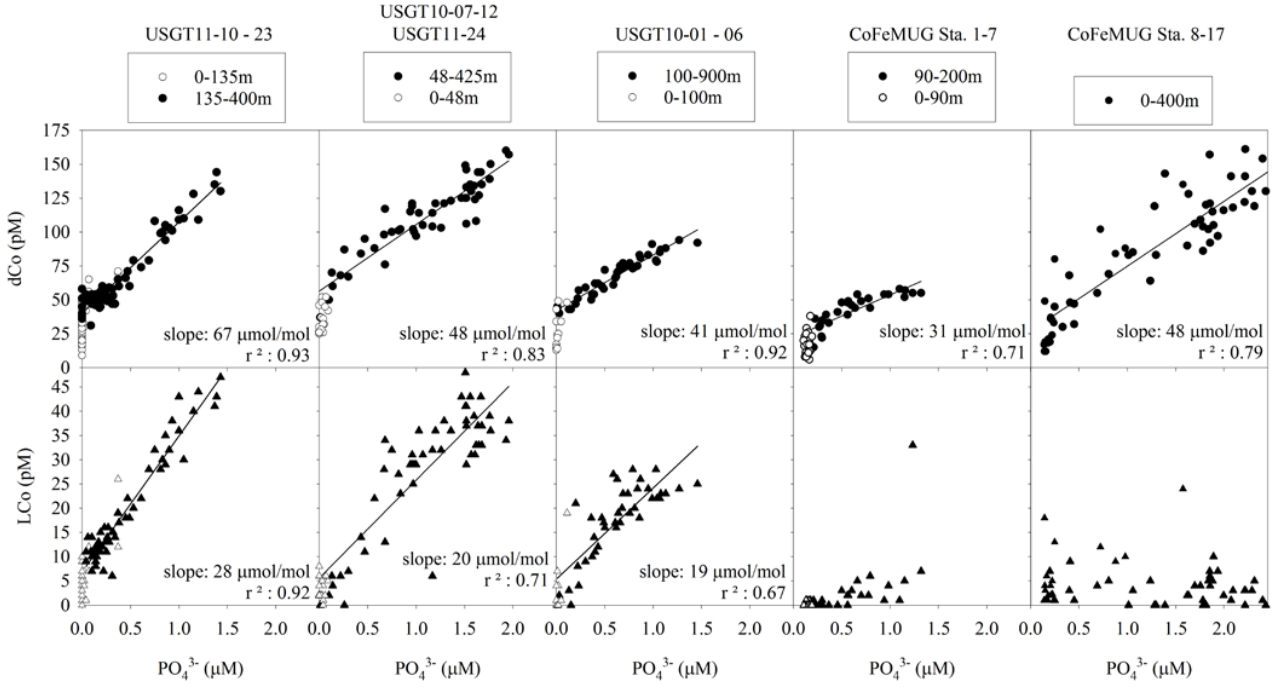

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Figure 12

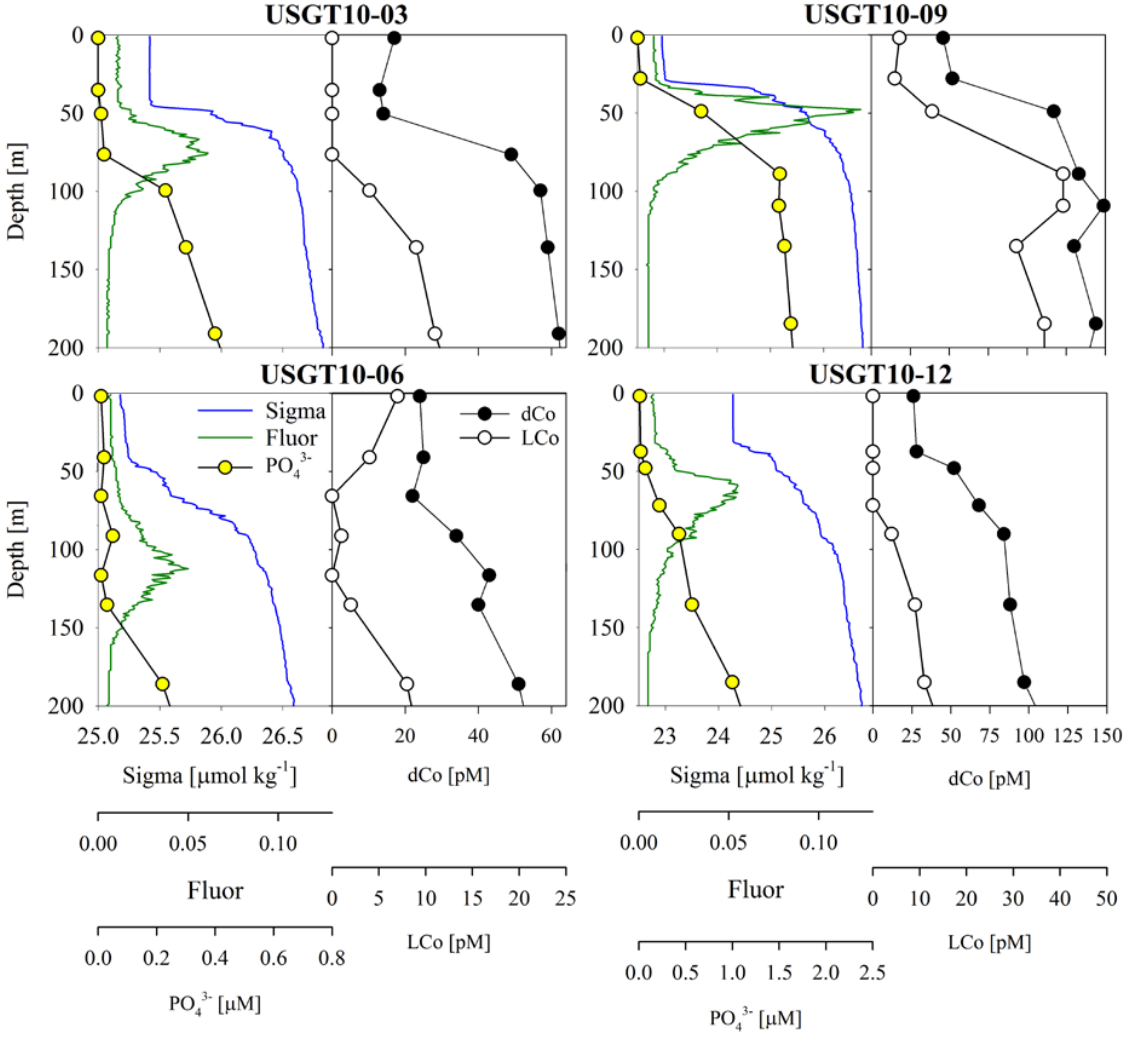

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Figure 13

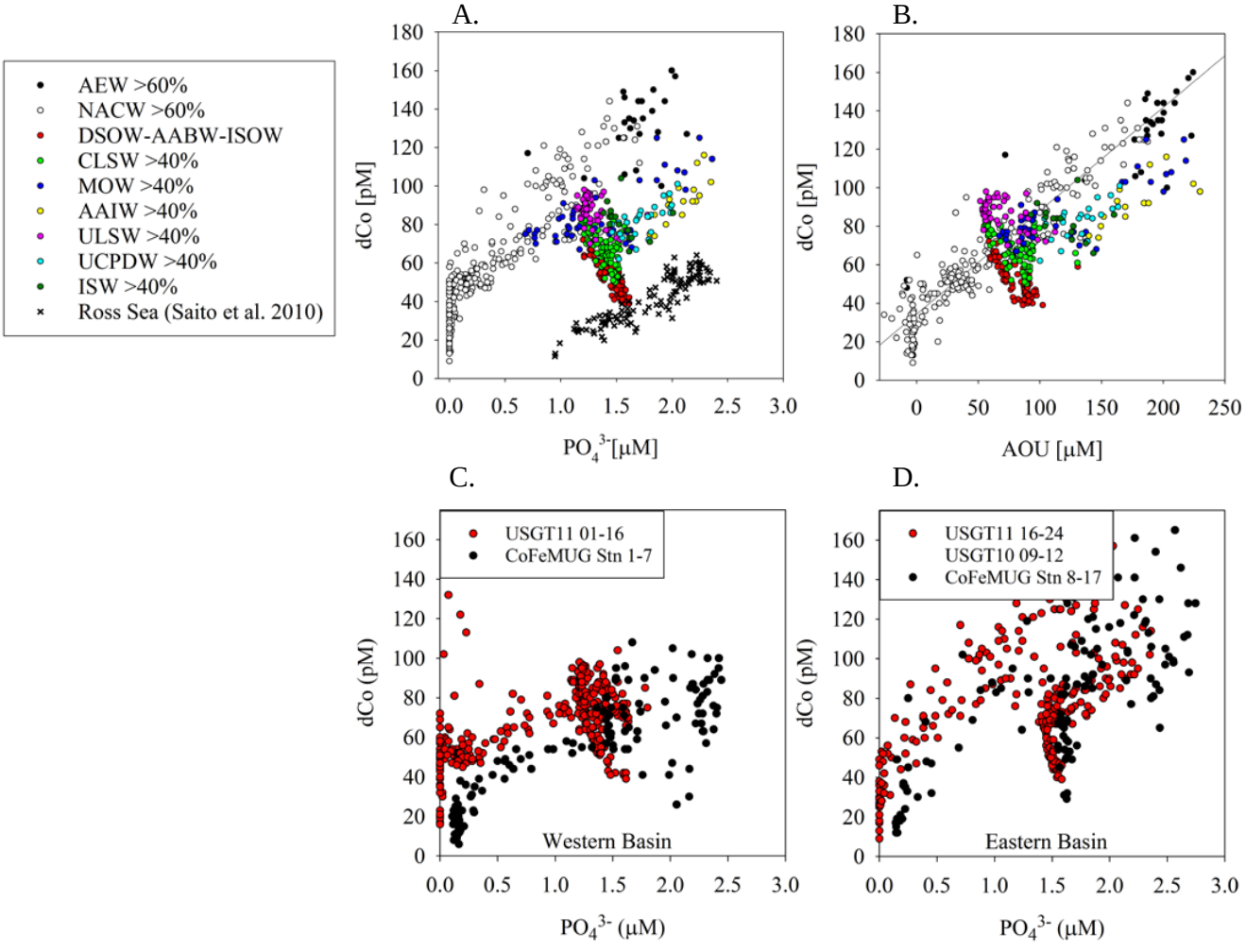

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Figure 14