The distribution of dissolved copper in the tropical-subtropical North Atlantic across the GEOTRACES GA03 transect

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Abstract

Dissolved copper (Cu) was determined in the tropical-subtropical North Atlantic Ocean along the GEOTRACES GA03 transect that covers a number of this basin's key regions. In the surface water, dissolved Cu concentration shows a strong shelf input from North American and European continents, and a significant depletion in the productive zone off Mauritania coast. Dissolved Cu concentration in the surface water of the western margin anti-correlates linearly with salinity suggesting an inefficient surface removal of dissolved Cu relative to the rate of lateral mixing in this region. The depletion of dissolved copper near the Mauritanian shore, in contrast, indicates an efficient scavenging of dissolved Cu onto the biogenic particles which precludes the observation of the shelf input. In general, dissolved Cu concentration strongly correlates with silicate. A similar deep water accumulation for dissolved Cu and silicate was observed along the GA03 transect. The Southern Ocean may be the major source of dissolved copper along our transect, because silicate distribution in the North Atlantic is mainly controlled by the Southern Ocean sources through mixing and due to the strong correlation between dissolved Cu and silicate in the Atlantic sector of that basin. However, the ratio of copper to silicate was much larger during our study than that found for the Southern Ocean (Heller and Croot, 2015), suggesting the presence of additional Cu sources in our study region. One of such Cu sources may be from the benthic sediments, as suggested by previous studies. In addition, subsurface enrichment and seaward decrease of dissolved Cu were observed at the western and northeastern part of our transect. Near the Strait of Gibraltar a hotspot of copper was observed within the influence zone of the Mediterranean Outflow Water (MOW). Copper does not show an anomaly within the oxygen

minimum zone (OMZ) off the slope of Mauritania, indicating an insignificant net effect of Cu remineralization relative to scavenging in this region. In this zone, dissolved copper variability, instead, is found mainly near the slopes of Mauritania and Cape Verde Islands, suggesting an influence by sedimentary Cu source. Hydrothermal field on the axis of the Mid-Atlantic Ridge is observed as a sink for the dissolved copper.

Key words: *Copper; North Atlantic; Benthic source*

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1. Introduction

The horizontal and vertical distributions of dissolved copper (Cu) in the ocean have been determined since the 1970s (Boye et al., 2012; Boyle and Edmond, 1975; Boyle et al., 1977; Bruland, 1980; Saager et al., 1992; Heller and Croot, 2014). Nonetheless, there are still a number of regions such as central South Atlantic and South Pacific where few dissolved Cu profiles have been reported. In contrast, the reported surface data cover vast regions of the global ocean (Boyle et al., 1981; Kremling, 1985; Pohl et al., 2011; Rutgers van der Loeff et al., 1997). Dissolved Cu concentration in the surface water of the Atlantic and the Pacific is ~0.5-0.6 nM in the off-shore central regions and increases to above 1 nM near the margins (Bruland, 1980; Pohl et al., 2011) indicating a strong Cu input from the continental shelves. The copper enrichments in the continental margin were observed to be irrespective of the redox condition of the shelf sediment (Heggie et al., 1987; Bruland and Franks, 1983; Donat et al., 1994). Although Cu is an essential micronutrient for marine phytoplankton (Peers and Price, 2006; Maldonado et al., 2006), the dissolved copper depth profiles do not resemble the generic profiles of macronutrients and instead display a monotonic increase with depth. Such a vertical profile is unusual for a biologically-active trace metal. In the Pacific Ocean, copper concentration increases more significantly with depth than in the Atlantic Ocean (Bruland, 1980). Cu in the North Pacific bottom waters is nearly twice as enriched as that in the North Atlantic bottom waters. Boyle et al. (1977) were among the first to analogize the oceanic vertical profile of dissolved copper to ^{226}Ra , the long-lived ($t_{1/2}=1600$ y) radioisotope of radium that has been shown to have a major source from the seafloor sediments (Broecker et al., 1976; Chan et al., 1976; Chung, 1974).

Little et al. (2013) have shown that linear vertical distributions of copper can be explained by “reversible” scavenging. Reversible scavenging was initially hypothesized by

Bacon and Anderson (1982) to model the vertical distribution of dissolved and particulate ^{230}Th . Briefly, Little et al. (2013) suggest that dissolved copper is being pumped from the surface to the deep ocean through the particulate phase and that a partitioning process between dissolved and particulate phases can result in a linear increase of dissolved copper with depth. Boyle et al. (1977), in contrast, have proposed another process in which copper is sustainably supplied from the seafloor and subsequently scavenged in the water column, implying that the benthic sediments are the major source of copper into the ocean, not the dissolution out of the particulate phase. Takano et al. (2014) have determined isotope ratio of dissolved copper with an outstanding precision that allows them to validate Boyle et al. (1977)'s hypothesis that near-bottom enrichment of dissolved copper is emanating from the seafloor sediments.

Within the context of the planktonic life in the surface ocean, copper exhibits a dual role. On the one hand, it has been observed that copper assists the growth of phytoplankton (Peers and Price, 2006; Maldonado et al., 2006). On the other hand, it has a toxic effect at high concentrations (Brand et al., 1986; Anderson and Morel, 1978). It is worth noting that the toxic effect of copper is basically a function of “free” but not “total” dissolved concentration of copper (Anderson and Morel, 1978). The free concentration is a pool of dissolved copper not bound to any natural “organic” compound (van den Berg et al., 1987). Recent studies have shown that the positive role of Cu in the growth of some plankton species increases in the presence of organic ligands (Annett et al. 2008; Semeniuk et al. 2009). Thus, the distribution of dissolved copper, its organic speciation and possibly the processes controlling this element are crucial to understanding its net effect on the biogeochemistry of the ocean.

In this study, we present dissolved copper data in the tropical-subtropical North Atlantic Ocean from the same samples that were previously analyzed for total dissolved copper and

copper organic speciation by Jacquot and Moffett (2015). We try to take advantage of the results reported by Jacquot and Moffett (2015) and the data recently released for the other regions in the Atlantic Ocean to discuss the possible controls on dissolved copper distribution.

2. Sampling and Analysis

Seawater samples were collected on board of R/V *Knorr* during the cruises of U.S. GEOTRACES North Atlantic Zonal Transect in 2010 (October-November) and 2011 (November-December). The cruise in 2010 (hereafter abbreviated as USGT10) started from Lisbon, Portugal and sailed southward to the shore of Mauritania, Africa. It then continued westward and ended at Mindelo, Cape Verde Islands. 12 stations were occupied during this cruise. The cruise in 2011 (USGT11) started from Woods Hole, Massachusetts and sailed southeastward to Bermuda Atlantic Time Series (BATS). After crossing the entire tropical North Atlantic Ocean, the cruise ended at Praia, Cape Verde Islands. 24 stations were occupied during this cruise. Figure 1 shows the cruise track on the map of the oxygen concentration at 400 m depth.

Samples were collected using Teflon-coated GO-FLO bottles mounted on a rosette carousel specifically designed for the U.S GEOTRACES program (Cutter and Bruland, 2012). After recovery of the rosette onboard the ship, GO-FLO bottles were carried into an ISO 5-rated clean van. The seawater samples were then filtered through 0.2 μm Pall Acropak-200™ Supor® capsule filters under ~ 0.4 atm of HEPA-filtered air. The filtered samples were then collected into acid-washed LDPE bottles. Thereupon, samples were acidified to pH=1.7-2.0 using ultra clean 9N HCl (introduced less than 1 pM of copper in 1 L of seawater) and stored at room temperature.

Dissolved copper concentrations were determined with $\text{Mg}(\text{OH})_2$ co-precipitation isotope dilution method (Wu and Boyle, 1997) using a multiple collector high resolution inductively coupled plasma mass spectrometry (Finnigan Neptune®) at the University of Miami. Briefly, 1.8 mL of acidified seawater was spiked with a ^{65}Cu -enriched standard. Ultra clean aqueous solution of NH_4OH was added to the mixture. The mixture was then centrifuged. A small amount of the white $\text{Mg}(\text{OH})_2$ precipitate is retained at the bottom of vial while the supernatant was discarded. Ultra clean HNO_3 was then added to dissolve the precipitate. The solution was then analysed for the isotope ratio of $^{65}\text{Cu}/^{63}\text{Cu}$ using a multi-collector ICP-MS. The concept of isotope dilution was engaged to calculate the concentration of copper in the original seawater sample.

The SAFe seawater standards were determined in order to assess the accuracy of our determination method (Table 1). The procedural blank was prepared in similar manner as samples except using 50 μL Atlantic surface seawater. The method has a procedural blank of ~ 0.05 nM and a detection limit ($3\times\text{SD}$) of ~ 0.01 nM. Silicate concentrations were determined in the same samples by the Ocean Data Facility (ODF) group on the ship using a Seal Autoanalyzer as described elsewhere (Armstrong et al., 1967). Full dataset of this study is appended as the online supporting information. Further information including other trace metals data and the hydrographic settings of these cruises are available on the website of the Biological and Chemical Oceanography Data Management Office via <http://www.bco-dmo.org>.

3. Results and discussion

Figure 2 shows the dissolved Cu distribution during the US GEOTRACES North Atlantic cruises. The most visible feature in the distribution of dissolved Cu is the enrichment of Cu in the bottom waters of the entire transect, with relatively higher accumulation in the eastern side of the Mid-Atlantic Ridge (MAR) than the western side. Horizontal homogeneity of the distribution is the other prevailing feature. Cu also shows a small depletion around the MAR. In the following subsections, each main feature in the dissolved Cu distribution will be interpreted in detail.

3.1 Cu in the surface ocean

Cu concentrations in the North Atlantic surface waters indicate high values near the continental shelves and low values at the central regions, except in the eastern margin off the shore of Africa where copper displays depletion (Fig. 3). The enrichment near the continental shelves is similar to that previously observed in the other marginal regions of the world ocean (Bruland, 1980; Kremling, 1985; Pohl et al., 2011; Saager et al., 1997). A flux of dissolved Cu from the continental shelf that supplies dissolved Cu seaward horizontally along isopycnal surfaces may sustain the marginal-to-central gradient observed in the surface water of our study region, in a way similar to the surface distribution of Ra quartet (223-, 224-, 226- and 228-Ra) that are produced via decay of sediment-residing thorium isotopes (Moore, 2000).

Figure 4 shows a tight correlation ($R^2=0.97$) between dissolved copper and salinity in the western portion of the transect extending from the North America coast to the central gyre of the North Atlantic. This correlation was observed previously by Bruland and Franks (1983) in the

samples collected close to our study locations in the western North Atlantic. Jacquot and Moffett (2015) have noticed a weaker Cu-salinity correlation in this region. Surface concentration of dissolved manganese determined during our survey (Wu et al., 2014) also exhibits a linear relationship with salinity. Mn has been shown to be removed from the surface ocean via oxidation reaction for which a ~10-year residence time can be determined at the typical pH and oxygen concentration of the surface water of the North Atlantic (Von Langen et al., 1997; Wu et al., 2014). This residence time is long considering the remarkable horizontal mixing coefficient in the surface ocean (Zhurbas and Oh, 2004). Therefore, it does not allow us to observe recognizable concavity in the Mn-salinity plot despite the presence of the removal process. Thus, the linearity of Cu-salinity may suggest a long (probably tens of years) residence time of dissolved Cu in the surface mixed layer. The strong complexation of copper by organic ligands observed in these samples may protect dissolved copper against removal from the surface water (Jacquot and Moffett, 2015).

The identical intercepts of Cu-salinity and Mn-salinity linear plots (39.1 and 39.7 as shown in Fig. 4) imply that similar concentrations of Cu and Mn are being mixed from the continental margin into the open ocean. Because Mn is 10 fold more abundant than Cu in the earth's crust (Taylor, 1964), a similar margin end-member concentration of dissolved Cu and Mn would require that Cu is 10 fold more mobile than Mn during their intrusion into the offshore ocean. The Cu-binding organic ligands observed in the sediment pore water near that region may be a process assisting Cu mobilization (Skrabal et al., 2000). Contribution of anthropogenic copper emanating from the continent may also be an explanation to the high continental end-member concentration of dissolved Cu relative to that estimated based on Cu/Mn crustal ratio (Moffett et al., 1997).

The low concentrations of free Cu (i.e. high fraction of ligand-bound Cu) observed near the African margin (Jacquot and Moffett, 2015) may suggest that Cu would be relatively stable and consequently more enriched in that marginal area. However, a depletion of copper is evident in that region (Fig. 3) in contrast to other two margins, North America and Europe. In addition to the natural organic ligands, the amount of suspended particles that remove copper from the dissolved phase may play an important role in controlling the residence time of dissolved Cu in the surface water. Indeed, the Mauritania coast is one of the most productive margins in the world ocean, due to an efficient wind-driven upwelling that feeds the surface plankton community by supplying a remarkable amount of nutrients from the subsurface ocean. The massive algal growth in this region ensures high concentrations of suspended particles in the surface ocean. Such massive production of biogenic particles may be a major sink of dissolved Cu, despite high complexation of copper by organic ligands that stabilizes the dissolved Cu against scavenging removal by sinking particles.

3.2 Cu in the subsurface ocean

Dissolved copper concentration increases almost linearly with depth in the open ocean. Figure 5 shows some open-ocean profiles of this study in the North Atlantic. There are few published data in the South Atlantic (Boye et al., 2012; Yeats et al., 1995) that similarly exhibit this fashion of vertical variability. This unique feature has also been observed in the Pacific by Boyle et al. (1977) and Bruland (1980). Decades ago, Boyle et al. (1977) modeled copper depth profile in the deep Pacific by assuming a benthic flux that balances a constant irreversible scavenging in the overlying water column. While this model did not explain the linear increase of dissolved Cu with depth for the entire water column, the Cu vertical profile is similar to that of ^{230}Th (Bacon and Anderson, 1982). Such linear vertical variability of ^{230}Th was successfully

modeled by Bacon and Anderson (1982) by assuming a reversible type of scavenging without accounting for boundary (e.g. benthic) and lateral sources and vertical mass transport. This reversible scavenging process has provided a clue for Little et al. (2013) to implement a similar model to interpret the dissolved copper vertical profiles. It is worth noting that the reversible scavenging mechanism has also played an important role in depicting the depth variability of many Rare Earth Elements (REEs) like neodymium (Siddall et al., 2008). Recently, Takano et al. (2014) have validated the benthic source of copper which was initially hypothesized by Boyle et al. (1977) by means of the isotope ratio as a novel tool.

3.2.1 General correlation of dissolved copper with silicate

As was first shown by Jacquot and Moffett (2015), copper exhibits a stronger correlation with silicate (SiO_4^{2-}) than macronutrients such as nitrate (NO_3^-) and phosphate (PO_4^{3-}) in our transect (Fig. 6). Our results exhibit a stronger correlation between copper and silicate ($R^2=0.78$) than that estimated by Jacquot and Moffett (2015) ($R^2=0.68$). One might think that the most straightforward clue to follow is to depict the processes controlling silicate in the North Atlantic and to analogize those for copper. Those processes would then be hypothesized to be valid as long as they are in agreement with other studies.

Despite the fact that silicate is a macronutrient and can be remineralized in the water column, its distribution in the North Atlantic has been shown to be mainly controlled by conservative mixing (Sarmiento et al. 2004). Specifically, the negligibility of regenerated component of silicate in our transect (GEOTRACES GA03) allows Jenkins et al. (2015) to take advantage of silicate as a quasi-conservative tracer to conduct an outstanding quantitative water

mass analysis despite the presence of high number of water mass end-members. Brzezinski and Jones (2015) have shown that even dissolved silicon isotopic composition in the GA03 transect is well-coupled to the pattern of the water mass circulation in the North Atlantic. Given that the regeneration process (i.e. dissolution of opal) inputs silicate to the water column with a specific isotopic signature (Demarest et al., 2009), coupling between silicon isotope composition and the pattern of the water mass mixing similarly suggests an insignificant contribution from remineralization.

The insignificant regeneration of silicate in the North Atlantic may be reasonable due to two characteristics of this basin: high efficiency of ventilation in the Atlantic and the lack of diatoms in the plankton community in the surface ocean. The higher rate of ventilation in the entire Atlantic than the Pacific has been proven by means of oceanic water mass age tracers such as ^{14}C (Khatiwala et al. 2012). The rapid movement of water masses in the Atlantic can envelope the effect of in-situ remineralization (or dissolution) of any macronutrient to some extent although we are still able to observe a notable regenerated component in the distribution of other macronutrients such as phosphate in the Atlantic (Duteil et al., 2012). The second fact is about the plankton community composition in the surface of the Atlantic that is mostly dominated by species other than diatom (i.e. the heavily-silicified phytoplankton). This is consistent with the sediment traps results that indicate low flux of opal in the Atlantic relative to the Pacific and the Southern Ocean (Honjo et al., 2008) and also by means of a nutrient/alkalinity analysis (Jin et al., 2006). Note the regenerated silicate has a remarkable component in the Atlantic sector of the Southern Ocean (everywhere around the Antarctica higher than 45°S) as recently modeled by Holzer et al. (2014). This is in fact due to the dominance of the diatoms in that basin (Honjo et

al., 2008; Jin et al., 2006). However, the silicate in the region extending from the lower latitudes of South Atlantic (~45°S) to the North Atlantic is not much affected by in-situ remineralization.

Given that silicate is controlled by mixing in the Atlantic Ocean and, on the other hand, correlates with copper, can we conclude that copper distribution is also controlled by conservative mixing? If so, it would mean that the enrichment of copper in the deep ocean everywhere in the transect (Fig. 2) is due to high concentrations of copper carried by water masses from high-latitude regions to the tropical-subtropical North Atlantic. Indeed, among the major water masses in the deep/bottom of the GA03 transect, the Antarctic Bottom Water (AABW) has far higher silicate than the Iceland-Scotland Overflow Water (ISOW) and the Denmark Strait Overflow Water (DSOW) (Jenkins et al., 2015).

In the scenario of a two-component water mass mixing, the linear correlation between a given property and a conservative property such as salinity (or even silicate as is evident within the region of our study) is considered to imply that the property does not undergo in-situ reactions (either removal or generation) with a rate comparable to or higher than the rate of water mixing. Nonetheless, this approach is not valid when high number of water masses mix within a region. In other words, when more than two end-members are present, the curvature in a plot of a given property against a conservative property does not necessarily reflect that the given property is non-conservative.

Because many water mass end-members were identified in our transect (Jenkins et al., 2015), the relatively strong linear correlation between dissolved copper and silicate (Fig. 6) can only be attributed to three circumstances: (i) dissolved copper strongly correlates with silicate in similar Cu/Si ratios in all of the water mass end-members; (ii) Cu and Si are not correlated in all

end-members with similar Cu/Si ratios, but are correlated in one end-member that is highly enriched with Cu and Si and posits a dominant control on the Cu and Si distribution; (iii) the majority of copper and silicate observed along the transect have been supplied to the water column via in-situ regeneration with a robust Cu/Si stoichiometry ratio. In the latter circumstance, a significant in-situ input from the particulate phase to the dissolved phase (i.e. regeneration) with a constant Cu/Si ratio during the ventilation of water masses can erase any Cu/Si ratio signature of the water masses. As discussed above, because regeneration is insignificant for silicate in our study region, circumstance (iii) may not be the case. To illustrate the possibility of circumstances (i) and (ii), we compare dissolved Cu with ^{226}Ra that has a tight correlation with silicate in the GA03 transect and known major sources (sediment; Charette et al. 2015).

The ^{226}Ra -Si correlation was found to be tighter than that found for Cu-Si (Fig. 6). Charette et al. (2015) proposed that the ^{226}Ra distribution in the GA03 transect is controlled by a sediment input that is coupled with a substantial water mass mixing. The similarity between dissolved Cu and ^{226}Ra vertical profiles implies that copper is also affected by sedimentary processes. Here we avoid a direct linearization between Cu and ^{226}Ra , because of fewer ^{226}Ra samples than dissolved Cu samples and because the depths of ^{226}Ra samples are different from those sampled by GEOTRACES rosette introducing an uncertainty in case of interpolation. However, the ^{226}Ra -Si plot made by Charette et al. (2015) allows for comparing ^{226}Ra with Cu within the context of correlation with silicate. Regarding this similarity between Cu and ^{226}Ra in terms of correlation with silicate, we take the sedimentary source for copper as a hypothesis as long as it agrees with other observations in the Atlantic Ocean.

Heller and Croot (2015) have recently determined copper and silicate concentrations in the Atlantic sector of the Southern Ocean. They have observed a tight correlation between copper and silicate with a Cu/Si ratio more than 2 fold lower than the ratio estimated based on our data (0.014 vs. 0.035). While the Cu-Si correlation in the Si- or Cu-enriched end-member that originates in the Southern Ocean can lead to the correlation observed in the GA03 transect, our data indicate a higher slope of the linear Cu-Si plot (Fig. 6). This may also be inferred by comparing individual concentrations of Cu and Si between the two studies.

Silicate exhibits a mean concentration $\sim 130 \mu\text{mol/kg}$ in the deep Southern Ocean. A dilution of the Southern component water during its northward penetration should result in a $\sim 50 \mu\text{mol/kg}$ concentration in deep/bottom water column of our sampling region. However, dissolved copper concentration is constant at $\sim 3 \text{ nmol/L}$ in the deep ocean between the Southern Ocean (Heller and Croot, 2015) and the GA03 transect. This indicates that in the deep ocean, there are other processes that compensate for the dilution of dissolved copper in the southern component water and maintains an enrichment of dissolved Cu relative to silicate in our study region. The remineralization process is not likely to sustain such enrichment of copper observed in the bottom water of the North Atlantic. Thus, the only additional source of dissolved Cu would be from the benthic sediments that releases copper to the overlying water column dominated by AABW. This conclusion is in agreement with recent studies by Takano al. (2014) and was initially hypothesized by Boyle et al. (1977).

The benthic source of copper has widely been inferred from dissolved copper variability within the sediment pore-waters (Klinkhammer, 1980; Klinkhammer et al., 1982; McKee et al., 1989; Widerlund, 1996). Skrabal et al. (2000) have shown that Cu-binding ligands can be supplied from the sediment and may assist the copper release from the sediment into the

overlying seawater. Fischer et al. (1986) have conducted a sediment trap study for copper that shows a bottomward increase in the flux of particulate copper, implying that copper is continuously being removed from the overlying seawater via the particulate phase. Therefore, benthic flux may be the main process that can sustain the accumulation of dissolved Cu in the deep ocean.

Lam et al. (2015) have observed local enrichments of suspended particulate matter (SPM) near the seafloor along our transect (i.e. benthic nepheloid layer). Since the benthic environment is a major source of copper (as hypothesized above) and that copper is a particle reactive trace metal (Fischer et al, 1986), the sediment re-suspension within the water near the seafloor can affect the water column Cu in two ways. First, as a particle-rich environment, nepheloid layer can extract Cu from seawater and results in local sinks along the transect. Second, the formation of nepheloid layer increases the efficiency by which the sediment-residing Cu can come in contact with seawater, which may result in local Cu enrichments in the bottom seawater along the transect. However, the Cu distribution near the bottom of the transect do not show any recognizable local signals (either positive or negative) and, instead, exhibits a smooth variability superimposable on that of silicate (Fig. 2). Jacquot and Moffett (2015), nonetheless, have found local signals in the distribution of free Cu near the bottom.

In the next subsection, we will take advantage of data determined in a regeneration-dominated zone in order to discern the efficiency of subsurface copper regeneration. We stated above that the degradation of particulate copper may not, individually, maintain the deep accumulation of this element. Our basin-scale survey enables us to further-study the role of this process.

3.2.2 Copper near the shore of Mauritania; effects of OMZ and slope sediments

An oxygen minimum zone (OMZ) is located off the shore of Mauritania, Africa as the result of slow ventilation of the subsurface waters and the high productivity of the surface water induced by efficient upward transport of nutrients via upwelling process (Stramma et al., 2007). In this zone, regenerated component of nutrients can be of substantial fraction of the total nutrient concentration. In addition, since such low-oxygen zones occur near the continental slopes, other redox-driven processes within the sediment can also modify the seawater concentrations for some bioactive elements. For instance, in reducing environment of the eastern tropical North Atlantic OMZ, sedimentary input of iron(II) was observed to enrich the total iron to a value greater than that can be supplied via remineralization process (Conway and John, 2014).

The three easternmost vertical profiles of dissolved copper along the zonal transect are plotted in Figure 7. The profiles of the Apparent Oxygen Utilization (AOU) as an index reflecting the amount of regeneration are also plotted in Figure 7. Despite high values of AOU extending from Mauritania coast, dissolved copper does not exhibit any discernible maxima. Moreover, the horizontal gradient of AOU that decreases seaward does not correspond to that observed for dissolved copper. Station USGT10-10 consistently contains ~0.2 nM lower copper than other two vicinal stations (i.e. USGT10-09 and USGT10-11). Because stations USGT10-09 and USGT 10-11 are located closer to Mauritania and Cape Verde islands whilst station USGT10-10 is located in between station USGT10-09 and station USGT10-11, slope sediments are likely to enrich copper in the water columns close to the continental slopes.

Since copper is also being scavenged and removed from the water column by sinking particles (Fischer et al., 1986), the lack of dissolved copper enrichment within the OMZ does not necessarily suggest that dissolved copper is not being remineralized. Because, to the best of our knowledge, few tools are available to separate the counterintuitive effects of remineralization and scavenging on dissolved copper within a zone where high flux of particles are sinking down the water column (e.g. Mauritanian OMZ), we avoid generalizing that the remineralization is not a possible process for copper. Instead, it is quite possible to state that remineralization of copper is not strong enough to imprint a positive anomaly on its distribution in Mauritanian OMZ. This is at odds to other particle-reactive elements such as iron that displays a pronounced enrichment concurrent with oxygen depletion within the tropical North Atlantic OMZ (Hatta et al., 2015). Jacquot and Moffett (2015) have not similarly observed a positive signal for the total dissolved copper within the OMZ. However, they have found low concentrations of Cu in this zone and enrichments at the stations further offshore zonally (USGT11-18 to 22). The latter observation is not consistent with our results (Fig. 2).

Besides remineralization processes in the water columns, it can be hypothesized that two processes within the slope sediments of Mauritania can modify the dissolved copper concentrations in overlying seawater (i.e. waters within the OMZ). On the one hand, since high flux of particulate organic matter (POM) is being deposited on the slopes and because this organic matter is shown to play a critical role in mobilization of copper from the sediment to the overlying seawater (Skrabal et al., 2000), slope sediments can be considered as a “source” of dissolved copper. On the other hand, respiration of this massive bulk of organic matter being deposited on the seafloor when occurring in an oxygen-limited environment may lead to the utilization of other oxidants such as sulfate (SO_4^{2-} ; Canfield, 1989). Reduction of sulfate

produces sulfide (S^{2-}) which can react with dissolved copper (Cu^{2+}) to make the insoluble precipitate of CuS. Through this process, slope sediments in the reducing environment can be a “sink” for copper or, at least, a barrier to the dissolution of copper from sediment to the overlying seawater. Precipitation of CuS has been shown as a major sink for dissolved copper in the deep Black Sea (Haraldsson and Westerlund, 1988) where the water column acquires a persistent anoxia and consequent sulfide production due to sluggish water column ventilation.

3.2.3 Copper near the North American boundary

Figure 8 shows the copper depth profiles for the three westernmost sampling stations. These profiles display an evident enrichment extending from the boundary at the depth of ~500 m. Given that the regeneration may have a minimal effect on dissolved Cu concentration in this region and even within the OMZ as discussed in section 3.2.2, the two circumstances that can cause such mid-depth enrichment are lateral mixing from a Cu-enriched location or a direct input of dissolved Cu from continental slope sediments. The water mass analysis shows that the North Atlantic Central Water (NACW) is the predominant water mass at ~500 m depth on the western boundary (Jenkins et al., 2015). This water mass originates in the north of the GA03 transect and carries the saline water at the mid-Atlantic gyre center to the lower thermocline equatorward. Since the center of the gyre is far from the continental margins and consequently may acquire a minimal surface dissolved copper (~0.5 nM), it is unlikely that such high copper emanates from the NACW end-member located near the surface of mid-Atlantic gyre. Moreover, given the uniform NACW influence at the depth of ~500 m along the GA03 transect extending from the west to the center (nearly similar mixing fractions as quantified by Jenkins et al.(2015)), copper enrichment should also be observed in the central portion of the GA03 transect. However, a seaward decrease of dissolved copper was observed (Fig. 8). Therefore, this copper enrichment is

likely to result from the Cu source at the continental slope of the North America. This is in agreement with the processes in the eastern continental margin (see section 3.2.2) that also posits the copper distribution explainable within the context of proximity to the continents. Jacquot and Moffett (2015) have observed a similar enrichment near the slope of western boundary. They have, however, found a local depletion at USGT10-08 and marked enrichment in stations further away from the North America, which is not in agreement with our results (Fig 2).

3.2.4 Copper near the Strait of Gibraltar; effects of European continental margin and Mediterranean Outflow Water

The GA03 transect comprises a leg extending from the European to African margins. Station USGT10-01 is the closest sampling station to the Strait of Gibraltar through which heavily-saline Mediterranean Outflow Water (MOW) enters the North Atlantic. Figure 9a shows the three profiles of dissolved copper for the upper 2000 m of the water column at stations USGT10-01, USGT10-03 and USGT10-05. All the data points falling within the upper 500 m of the water column exhibit an enrichment extending from the continental margin of Europe. A hotspot of ~2.4 nmol/L dissolved copper is also evident at ~ 800 m at station USGT10-01.

However, this high dissolved copper does not remain visible at other two proximal stations (USGT10-05 and -07).

Two processes may result in this high copper. First, since the MOW has its highest impact on station USGT10-01 among all stations occupied along the GA03 transect (Jenkins et al., 2015), the MOW may be a controlling factor in this enrichment. Trace metals such as zinc and ^{228}Ra have similarly been shown to acquire a significant enrichment in this zone (Roshan and Wu, 2015; Charette et al., 2015). According to the salinity profile plotted in Figure 9b, the MOW influence zone at station USGT10-01 extends from 500 to 1500 m depth.

The copper enrichment is found in the upper portion of the MOW (Fig. 9). The dissolved copper concentrations reported for the Western Mediterranean exhibit an approximately constant $\sim 2\text{ nM}$ value at this depth range (Boyle et al., 1985). This is about two folds higher than dissolved copper concentration determined in this depth range in the central North Atlantic ($\sim 1\text{ nM}$), indicating that the Western Mediterranean water may also play a role in the observed 2 nM Cu enrichment. In addition, similar to the other two marginal areas, continental slopes can also be a source of dissolved copper that can further-concentrate Cu to above 2 nM as observed at station USGT10-01 (Fig. 9a). Assuming central North Atlantic and Western Mediterranean Sea (WMS) to be two major end-members, from salinity we estimate that North Atlantic and WMS contribute to the waters located at 800 m of USGT10-01 with $\sim 30\%$ and $\sim 70\%$ fractions, respectively. Applying these mixing fractions on dissolved Cu in the end-members (1 nM for North Atlantic and 2 nM for WMS) entails that the mixing of the North Atlantic with the WMS would result in a dissolved copper concentration of $\sim 1.7\text{ nM}$. This concentration is much lower than observed $\sim 2.4\text{ nM}$, indicating that another source of dissolved copper must be at play.

The depth range that may be influenced by the MOW, according to salinity (Fig. 9b), extends from 500 m to 1500 m. However, high concentration of copper in USGT10-01 is only visible at depths between 500 m and 850 m. The depth variability of light beam transmittance as an index for the presence of particles is plotted in Figure 9b. Transmittance similarly displays a minimum in the aforementioned depth range indicating a high population of particles. These particles may be re-suspended via the flow of MOW over the Strait of Gibraltar's slope sediments. Given that the sediment is one major source of copper as discussed throughout this paper, these sediment-sourced particles can be a factor contributing to the high concentration of Cu observed at station USGT10-01 (Fig. 9a). This local enrichment of total dissolved copper was not observed by Jacquot and Moffett (2015).

3.2.5 Copper within the TAG hydrothermal plume

Hydrothermal activity is a seafloor process known to modify the seawater composition of many trace metals (Von Damm et al., 1985; German et al. 1991). The basin-scale transect of GEOTRACES GA03 encompasses an active hydrothermal vent (TAG) located at the axis of the Mid-Atlantic Ridge (MAR). During our survey, this hydrothermal field has been shown to be a moderate source for some trace metals such as iron (Hatta et al., 2015; Fitzsimmons et al., 2015), manganese (Wu et al., 2014), and zinc (Roshan and Wu, 2015). However, the results of this study indicate a sink for dissolved copper. Figure 10 shows the vertical variability of dissolved copper at a station near TAG (USGT11-16) for the depth range between 2650 m to 3650 m. Dissolved Cu is almost a mirror image of dissolved Fe (Fig. 10). German et al. (1991) have shown high particulate copper concentrations through the near-field surveys, indicating a particle-associated removal for copper. This removal may be due to CuS precipitation since substantial amount of sulfide (S^{2-}) is also sourced from the hydrothermal vents (Von Damm et

al., 1985). The depletion of excess Cu-binding ligand in these waters (Jacquot and Moffett, 2015) can increase the efficiency of this removal process.

4. Conclusion

A high-resolution set of dissolved copper data were determined for a basin-wide transect in the tropical-subtropical North Atlantic occupied during the US GEOTRACES 2010&2011 (GEOTRACES GA03). Dissolved copper shows a stronger correlation with silicate than with other macronutrients. Similar to silicate, copper acquires high concentrations in the bottom of the North Atlantic which corresponds to the influence zone of the AABW. However, the Cu/Si concentration ratio is two times larger than that observed in waters closer to the origin of AABW in the Southern Ocean. We hypothesized that such an increase in Cu/Si may be mainly controlled by an input from the sediments beneath the flow path of the AABW from the Southern Ocean to the North Atlantic that allows the Cu concentration to remain relatively constant as the silicate is diluted.

We also observed an enrichment of dissolved copper in the surface water near the continental margins, except the productive zone off Mauritania. The dissolved Cu data in the surface water extending from the Woods Hole, Massachusetts to the central region of North Atlantic indicate a strong linear relationship with salinity. This linear correlation may suggest a relatively long residence time of dissolved Cu relative to the time scale of water mixing in the surface of the western North Atlantic. Considering that manganese is a 10-fold more abundant than Cu in the earth's crust, the similar intercept of the Cu-salinity line to that of Mn-salinity

may indicate a higher mobilization of copper during the sourcing from the continent or an impact by human activities.

At the mid-depths, dissolved copper displays enrichments at the North American and European margins, but not the African margin. In the European margin, near the Strait of Gibraltar, dissolved copper displays a hotspot at ~800 m which coincides with a minimum of light transmittance. At the mid-depths near the shore of Mauritania, Africa, dissolved copper does not exhibit an anomaly associated with a persistent oxygen minimum, indicating an insignificant net effect of subsurface remineralization on the distribution of dissolved Cu. This is also consistent with our hypothesis that the deep accumulation of dissolved copper is mainly controlled by benthic sediment inputs. Horizontal variability of dissolved Cu at the mid-depths of the African margin appears to be more explainable within the context of proximity to the continental slopes. The active hydrothermal field on the axis of the Mid-Atlantic Ridge is also observed as a sink of dissolved copper, likely due to CuS precipitation.

Although this study along with some other studies such as Boyle et al. (1977) and Takano et al. (2014) emphasize the benthic input as the sustainable source of copper, further studies related to particulate phase of oceanic copper is needed to further validate it. Little et al. (2013) have also found it possible to resemble the observed distribution of copper through reversible scavenging process. These two hypotheses posit a profound difference regarding the role of the particulate phase. The former studies assume that copper is sourced from the sediment with particle scavenging as a major sink that can keep the oceanic content of copper in steady state. Therefore, measurements of particulate phase of copper must show a persistent increase in the flux of particulate copper with depth. In contrast, reversible scavenging mechanism assumes that copper is sourced from the sinking particle in a reversible manner which leads to a linear

type of vertical variability. Thus, through this mechanism, the particulate flux of copper must decrease with depths.

Ohnemus and Lam (2015) have found Cu as the element with the most unique particulate distribution along our transect. Particulate Cu concentration shows the lowest similarity with other elements including both lithogenic-dominated ones such as iron and aluminum, and biogenic-dominated ones such as phosphorous. This may be consistent with the cycling proposed in this paper where Cu is sourced from the benthic sediments and removed by scavenging onto the particles. Besides Cu, none of the trace metals whose particulate concentrations are studied by Ohnemus and Lam (2015) have been shown to undergo such oceanic cycling, which may consequently result in the uniqueness of particulate Cu.

It is worth noting that the reversible scavenging model for copper has been studied in an ocean without considering mixing (Little et al., 2013). In the future, when more basin-scale measurements of copper are available through prominent oceanography programs such as GEOTRACES, conducting the three-dimensional high-resolution biogeochemical modeling will be substantially helpful in our understanding of copper oceanic cycling. Even in the case of coexistence of the two aforementioned processes, the advanced biogeochemical modeling coupled with observational dissolved and particulate Cu data can help in assessing the contribution of each process in shaping the global Cu distribution.

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Table 1. Total dissolved copper concentrations determined from SAFe seawater standards in comparison to the consensus values.

Seawater Standard	Cu (nmol L ⁻¹)	
	This work	Consensus value†
SAFe S n= 24	0.51 ± 0.04	0.52 ± 0.05
SAFe D2 n=28	2.35 ± 0.09	2.28 ± 0.15

† As of May 2013

Figure Captions

Figure 1

Dissolved O₂ distribution at 400 m depth from the WOCE dataset with sampling locations shown as black filled circles for the USGT10 and red filled circles for the USGT11. Stations near the Bermuda-Atlantic time series and Mid-Atlantic Ridge are labeled on the map as BATS and TAG, respectively.

Figure 2

Dissolved Cu distribution within the upper 1000 m (top) and full depth range (bottom) in the tropical-subtropical North Atlantic determined during the US GEOTRACES 2010 and 2011 cruises. The contours in the bottom panel show the silicate distribution ($\mu\text{mol/kg}$) as determined during the same surveys.

Figure 3

Distribution of dissolved copper in the surface of the North Atlantic (20-40 m) indicating enrichments near the North American and European continental margins but depletion near the shore of Africa.

Figure 4

Dissolved copper (red squares) and manganese (blue squares; Wu et al., 2014) against salinity for the surface samples collected along the western leg of the USGT11 including USGT11-01 to USGT11-16. A linear relationship is evident.

Figure 5

Depth profiles of dissolved copper for stations located more offshore in the central regions of the North Atlantic.

Figure 6

Dissolved copper against silicate indicating a relatively strong linear correlation. The equations resulted from the linear fitting on all the data and two different ranges of silicic acid concentrations are written in the chart area.

Figure 7

Vertical profiles of dissolved copper for the USGT10-09, USGT10-10 and USGT10-11. The profiles of AOU are also plotted which show a substantial utilization of dissolved oxygen. Note USGT10-09 and USGT10-11 are close to Mauritania and Cape Verde Islands.

Figure 8

Vertical profiles of dissolved copper for the three westernmost stations along the USGT11 including USGT11-01, USGT11-02 and USGT11-03 within the top 2500 m in comparison to the open-ocean profile USGT11-18.

Figure 9a&b

Vertical profiles of dissolved copper in the USGT10-01, -03 and -05 (a). The salinity and transmittance profiles for USGT10-01 are also plotted (b). USGT10-01 is the closest station to the Strait of Gibraltar where MOW has the highest impact. The shaded area highlights the depth range of subsurface Cu enrichment at USGT10-01.

Figure 10

Vertical distribution of copper and iron near the hydrothermal field of TAG on the axis of the Mid-Atlantic Ridge. Iron data are determined by Wu and Roshan (included in Fitzsimmons et al. (2015)).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9a&b

Figure 10