



Dissolved and colloidal copper in the tropical South Pacific

Saeed Roshan^{a,1}, Jingfeng Wu^{b,a,*}

^a Rosentiel School of Marine and Atmospheric Science, University of Miami, FL, USA

^b College of Life Science and Oceanography, Shenzhen University, 3688 Nanhai Rd, Shenzhen 518060, Guangdong, China

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Abstract

Copper (Cu) as a bioactive trace metal in the ocean has widely been studied in the context of chemical speciation. However, this trace metal is extremely understudied in the context of physical speciation (i.e., size- or molecular weight-partitioning), which may help in characterizing dissolved Cu species. In this study, we determine total dissolved Cu ($<0.2 \mu\text{m}$) distribution and its physical speciation along the US GEOTRACES 2013 cruise, a 4300-km east-west transect in the tropical South Pacific. The distribution of dissolved Cu is rather uniform horizontally and exhibits a linear increase with depth from surface to 2500–3000 m, below which it varies less significantly both vertically and horizontally. Dissolved Cu shows a strong correlation with silicate (SiO_4^{4-}) in the upper 1500 m, which is in agreement with previous studies in other regions. This correlation is weaker but with higher slope at depths below 1500 m, which supports the sedimentary source hypothesis. Although hydrothermal activity at the East Pacific Rise (EPR) does not show a readily evident impact on the dissolved Cu distribution, high-quality data at 2300–2800 m allow for diagnosing a subtle westward decrease in the background-subtracted dissolved Cu component. This component of dissolved Cu poorly correlates with mantle-derived ^3He ($R^2 = 0.41$), indicating a possible hydrothermal source for dissolved Cu, in contrast to previous studies. For the first time in a major basin, we also determined the physical speciation of dissolved Cu, which shows that Cu species lighter than 10 kDa ($\text{Da} = 1 \text{ g mol}^{-1}$) dominate the pool of dissolved Cu ($<0.2 \mu\text{m}$) below 1000 m with a contribution of $61 \pm 6\%$ (fraction of total dissolved). $39 \pm 6\%$ of dissolved Cu at depths below 1000 m, thus, occurs in the pool of colloidal matter (10 kDa– $0.2 \mu\text{m}$). Moreover, using a suite of molecular weight cutoffs indicate that Cu species are distributed between two distinct molecular weight classes: the lighter than 5 kDa and heavier than 300 kDa classes, which form $53 \pm 6\%$ and $37 \pm 7\%$ of dissolved Cu at 2200–2800 m, respectively. The Cu species with molecular weight between 5 kDa and 300 kDa contribute only to $10 \pm 12\%$ of the pool at 2200–2800 m. These results offer new insights into structure, reactivity and bioavailability of oceanic Cu compounds. As an organic-dominating metal, Cu physical speciation may also shed light on size-reactivity spectrum of dissolved organic matter (DOM) in the deep ocean.

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1. INTRODUCTION

Copper (Cu) is one of the most well-studied trace metals for chemical speciation, particularly the complexation with naturally-occurring organic compounds. It is widely shown that more than 99.8% of dissolved Cu in oceanic water is bound to organic compounds (van den Berg, 1984; Coale and Bruland, 1988; Bruland and Lohan, 2004; Jacquot

* Corresponding author at: Rosentiel School of Marine and Atmospheric Science, University of Miami, FL, USA.

E-mail addresses: sroshan@ucsb.edu (S. Roshan), jwu@rsmas.miami.edu (J. Wu).

¹ Present address: Department of Geography, University of California, Santa Barbara, CA, USA.

et al., 2013; Jacquot and Moffett, 2015). Although Cu is soluble in organic-free seawater, the organic complexation can assist its persistence in seawater in the presence of particles, which could otherwise remove dissolved Cu from seawater (Jacquot and Moffett, 2015). Copper can form strong complexes with organic compounds which can be ubiquitous among both “dissolved” and “particulate” organic matter (DOM and POM) in seawater (Bruland and Lohan, 2004). The partitioning of oceanic Cu between dissolved and particulate forms is of great importance since DOM and POM pass through different biogeochemical routes within the ocean.

While the POM-bound Cu sinks toward the deep ocean and may be in exchange with dissolved Cu through either regeneration or scavenging (Little et al., 2013; Takano et al., 2014; Jacquot and Moffett, 2015), DOM-bound Cu can circulate within the ocean along the oceanic conveyor belt. Therefore, the partitioning of Cu between DOM and POM is crucial in determining the distribution and inventory of dissolved Cu in the ocean. Inasmuch as sedimentary input has been shown to be the major source of dissolved Cu to the ocean (Boyle et al., 1977; Takano et al., 2014; Roshan and Wu, 2015), Cu-binding dissolved organic ligands play an important role in transporting Cu from the sediments to the surface ocean where its biogeochemical characteristics can exert influence on the planktonic community either as a nutrient (Maldonado et al., 2006; Peers and Price, 2006) or a toxic agent (Brand et al., 1986). In the absence of dissolved organic ligands, Cu-binding sites on the sinking organic particles may adsorb dissolved Cu and preclude its transport to shallower zones. Basically, as depicted by Takano et al. (2014), there is a net removal of dissolved Cu through scavenging on sinking particles in the deep ocean (estimated at 2×10^9 mol yr⁻¹). After deposition on the seafloor, a portion of this POM-bound Cu becomes re-solubilized during early diagenesis within the upper layer of sediments. Hence, dissolved Cu-binding ligands may allow for efficient transport of dissolved Cu from the sediment to the surface ocean (Skrabal et al., 2000; Jacquot and Moffett, 2015). As estimated by Takano et al. (2014), dissolved Cu recycling from subsurface to the surface ocean is higher than the sum of atmospheric and riverine inputs to surface (3×10^9 vs. 1.7×10^9 mol yr⁻¹).

Besides the effect of Cu speciation on its transport within the ocean, Cu partitioning between organic and inorganic pools affects its biochemical roles remarkably. While the organic-bound Cu has been shown to be less toxic than inorganic Cu (widely referred to as Cu²⁺; Sunda and Guillard, 1976; Anderson and Morel, 1978), and releasing organic chelators is a defensive mechanism for plankton species to relieve Cu toxicity (Moffett and Brand, 1996), some recent studies have found that organic-bound dissolved Cu is available to marine microorganisms for regulating their metabolic pathways (Annett et al., 2008; Semeniuk et al., 2009, 2015), such as iron transport mechanism in diatoms and involvement in photosynthesis apparatus under low-iron conditions (Maldonado et al., 2006; Peers and Price, 2006). Hence, the chemical form of the oceanic Cu compounds might be a determining factor in

its bio-assimilation. Physical speciation studies can offer complementary and useful information to characterize the major species of this trace metal within the ocean.

Nevertheless, very few studies have attempted to determine the physical speciation of dissolved Cu in the ocean (Wells et al., 1998), while the traditional studies are mostly focused on estuaries (Powell et al., 1996) and rivers (Stolpe et al., 2010). In this study, we determine the distribution and physical speciation of dissolved Cu along a basin-scale transect in the tropical South Pacific, an understudied region for dissolved Cu distributions. As for the physical speciation study, while samples collected from almost every other depth at each station were ultra-filtered using 10 kDa (kilodalton = 1000 g mol^{-1} ; a conventional cutoff for colloidal fraction) ultrafiltration unit, molecular weight cutoffs of 5 kDa, 30 kDa, and 300 kDa were also applied for the depth range of 2200–2800 m for two purposes: (i) Ultrafiltration through different molecular weight cutoffs allows us to benchmark the effectiveness of the ultrafiltration procedure. (ii) The multiple molecular weight study may shed light on the influence of the remarkable boundary exchange processes at the EPR (Lopez et al., 2015; Resing et al., 2015; Roshan et al., 2016; Lam et al., 2017) on the speciation of dissolved Cu. Since concentrations of compounds in filtrates from heavier cutoffs must theoretically not be lower than those from lighter cutoffs, multiple-size ultrafiltration provides a way to assess the quality of physical speciation measurements. Previous studies usually focus on one molecular weight or size cutoff (mainly 10 kDa or 0.02 μm), which may not allow for proper validation of the ultrafiltration method (Wu et al., 2001; Bergquist et al., 2007; Fitzsimmons et al., 2015). Moreover, knowing the generic molecular weight spectrum of dissolved Cu species in the deep ocean may be a valuable information regarding Cu and, generally, DOM speciation and characterization. Such information is currently lacking for most of the biologically-important trace metals including Cu. We will show the molecular weight spectrum of dissolved Cu in the deep ocean, which indicates that dissolved organic compounds with molecular weight in the wide range of 5–300 kDa are not efficient in holding Cu ions. This may provide valuable information if we are to characterize the oceanic Cu species.

We will also discuss the contrasts and similarities between dissolved Cu and SiO_4^{4-} distributions in the tropical South Pacific. These two compounds have been shown to posit a significant similarity in different oceanographic regions (Heller and Croot, 2015; Roshan and Wu, 2015). Our results imply that Cu biotic uptake and retention might posit stronger linkages to SiO_4^{4-} than PO_4^{3-} .

2. SAMPLING AND ANALYSIS

Trace metal-clean seawater samples were collected along the US GEOTRACES 2013 cruise in the tropical South Pacific (Fig. 1) through the procedure detailed elsewhere (Cutter and Bruland, 2012) using Teflon-coated GoFlo bottles. Samples were filtered onboard the ship after recovery through 0.2- μm Acropak capsule filters. A portion of 0.2- μm -filtered seawater was ultra-filtered onboard the ship

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