



Copper speciation and distribution in the Atlantic sector of the Southern Ocean



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ABSTRACT

The distribution and speciation of dissolved copper (Cu) was investigated in the Atlantic sector of the Southern Ocean in austral autumn of 2008 as part of the IPY GEOTRACES expedition ZERO & DRAKE. Distribution measurements focused on two transects across the major frontal systems along the Zero Meridian and across the Drake Passage whereas speciation work was investigated in the Drake Passage and the ice covered Weddell Sea. Along the two transects the dissolved Cu concentration exhibited a gradient in the surface with Cu values increasing poleward. Vertical profiles of Cu showed in general monotonic increases with depth, which correlated slightly with silicate but poorly with phosphate. Benthic sources of Cu were observed along the Zero Meridian transect and close to the Antarctic Peninsula for the Drake Passage. Dissolved Cu (DCu) appears to be removed from surface waters through adsorption/complexation by particulate matter. Speciation measurements on DCu indicated a relatively uniform distribution of 25–50 nM of L₂ (log K ~ 11.8) class ligands. No L₁ class ligands (log K > 13) were detected in any of the samples examined. Estimates of free Cu (pCu = 13.5 to 12.5) showed only small variations in the upper water column and was generally uniform in deep waters. These findings indicate that there is insufficient free copper to account for the rapid reactivity of superoxide (O₂⁻) with Cu in these waters (Heller and Croot, 2010c) suggesting that the organic Cu complexes present in seawater can undergo rapid redox reactions.

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1. Introduction

1.1. Aim of this study in the Southern Ocean

Information on the distribution and speciation of trace metals is of critical importance for understanding what are the key drivers affecting the physiology and community structure of phytoplankton in the open ocean (Sunda, 1994, 2012). The element copper (Cu) is toxic to most phytoplankton but is also a required element as it is an important component of respiratory proteins and oxidases (Baron et al., 1995). The toxicity of Cu to phytoplankton is strongly dependent on the concentration of free copper (Cu²⁺) and not the total Cu concentration (Anderson and Morel, 1978; Sunda and Lewis, 1978) and indeed such studies were instrumental in the development of the free ion association model (FIAM) (Campbell, 1995). The concentration at which toxicity occurs though, is species specific, with eukaryotes such as diatoms (Wei et al., 2014) and coccolithophorids (Walsh and Ahner, 2014) in general more tolerant than small cyanobacteria, including for example

the globally important species *Synechococcus* (Brand et al., 1986) and *Prochlorococcus* (Mann et al., 2002) whose growth rates are sensitive even to the low concentrations of free copper (Cu²⁺) found in the environment (pM to nM). Elevated free Cu in seawater can competitively inhibit the uptake of other essential metals such as Mn (Sunda et al., 1981; Sunda and Huntsman, 1983, 1998) and once internalized can decrease photosynthetic rates (Baron et al., 1995) and disrupt enzyme function through binding to thiol groups (-SH) or via reactions with oxygen species to form the damaging hydroxyl radical (Staubert and Florence, 1987). Most phytoplankton however do require Cu for some key redox functions: e.g. plastocyanin (Peers and Price, 2006), multicopper oxidase (MCO) (Kustka et al., 2007) and superoxide dismutase (SOD) (Wolfe-Simon et al., 2005).

In this work we examine both the distribution and speciation of dissolved copper along two transects across the major frontal zones in the Atlantic sector of the Southern Ocean at the Zero Meridian and across the Drake Passage. Data is also reported from the ice covered Weddell Sea region. This work was conducted as a contribution to activities in the International Polar Year (IPY) and the GEOTRACES program (www.geotraces.org). The expedition ANTXXIV-3 on the German icebreaker *Polarstern* began on the 10th of February 2008 in Cape Town, headed south along the Zero Meridian, traversing the Weddell Sea and finally crossing the Drake Passage before arriving in Punta Arenas,

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Chile, on the 16th of April. The overall objective of this cruise was to examine the distribution and speciation of key elements and their isotopes in the Southern Ocean (Baars et al., 2014; Baars and Croot, 2011; Bluhm et al., 2011; Croot et al., 2011; Heller and Croot, 2010c; Klunder et al., 2011; Middag et al., 2011a,b, 2013; Rutgers van der Loeff et al., 2011; Thuróczy et al., 2011). The overall aim of the work presented here was to improve our understanding of the biogeochemical cycling and speciation of copper in the Southern Ocean.

1.1.1. Dissolved copper in the Ocean

Copper can be supplied to the surface waters of the ocean by a variety of natural pathways: (1) riverine inputs, (2) atmospheric deposition, (3) resuspension of material from the underlying sediments, (4) diffusion from sediments, (5) upwelling and mixing from deep water and (6) hydrothermal vents. Presently the exact magnitudes of each of these potential fluxes are not known to any degree of certainty. Additionally today, significant anthropogenic Cu fluxes to the coastal and open ocean occur from the aerosol deposition of material from industrial processes (Jordi et al., 2012) and from the use of Cu based anti-fouling paint for protecting marine equipment (Karlsson et al., 2010). Estimates of the residence time for copper in the ocean range from 2 to 50 years for surface waters (Boyle and Edmond, 1975) and 1500 to 5000 years for deep waters (Bewers and Yeats, 1977; Boyle et al., 1977) based on only riverine supply. Later studies have indicated that residence times are most likely much shorter, as riverine supplies are relatively insignificant inputs to the coastal margin (Martin and Thomas, 1994) and estimates based on the supply of Cu from sediments suggest short residence times (~650 years) with respect to scavenging (Balistrieri et al., 1981; Balistrieri and Murray, 1984).

1.1.2. Copper speciation in seawater and cellular homeostasis

Understanding the speciation of trace elements in the ocean is critical in interpreting the links between the bioavailability and uptake of an element, and its impact on the physiology and growth of organisms. The speciation of many bioactive trace metals in seawater is controlled by the availability of specific metal complexing organic ligands. According to the assumptions in FIAM, and the subsequent biotic ligand model (BLM) (Campbell et al., 2002; Hassler et al., 2004), the complexation of trace metals lowers the biological availability of that element. However exceptions to the FIAM and BLM are possible, most notably in the case of vitamin B₁₂ for Co (King et al., 2011), iron binding siderophores (Butler, 2005) and Cu binding chalkophores (Yoon et al., 2011), as these complexes are taken up directly by specific extracellular transporters. Thus organic complexation may also play an important role in the biogeochemical cycling of these elements in the upper ocean. For most elements, measurements of organic ligand concentrations are highest in the euphotic zone (Bruland et al., 1991), suggesting a recent biological source.

Dissolved Cu(II) is the thermodynamically favored form in seawater and has been found to be efficiently complexed by strong organic ligands, of unknown functionality, which are believed to be biologically produced (Coale and Bruland, 1988; Croot et al., 2000; Moffett et al., 1990; Sunda and Huntsman, 1991; van den Berg, 1984; van den Berg et al., 1987). The inorganic speciation of Cu(II) in seawater is dominated by carbonate complexation (Powell et al., 2007) and for Cu(I), by chloride complexation (Byrne et al., 1983). Complexation is of particular importance for Cu, as it is both an essential micronutrient and also extremely toxic. The organic complexation of Cu was found to greatly reduce the free copper concentration to below 1 pM in most open ocean waters and unpolluted coastal waters (Moffett, 1995, 1997), a level at which most phytoplankton are not Cu stressed (Brand et al., 1986). In seawater two ligand classes are typically identified by their conditional stability constants, though it is likely that there is a continuum of ligands present. The strong ligands (ligand class 1) are found at concentrations slightly in excess of the ambient copper concentration in seawater and have conditional stability constants of about $10^{12.5} \text{ M}^{-1}$

or higher whereas the stability constants of the weaker ligands (ligand class 2) were found to range from 10^{10} to 10^{12} M^{-1} . Field and laboratory work found a strong link between the strong complexation of copper and the presence of the cyanobacterium *Synechococcus* (Moffett, 1990, 1995, 1996). These works have also shown that if there was no organic complexation of Cu the growth of *Synechococcus* would be significantly inhibited in ambient open-ocean seawater. Too much complexation can also be a problem as Cu deficient cells are less able to transport Fe due to the involvement of multi copper oxidases (MCOs) in Fe uptake (Annett et al., 2008; Guo et al., 2012; Maldonado et al., 2006). Thus maintenance of cellular homeostasis for Cu is crucial and cells appear to rely on two general mechanisms: (i) storage of the Cu as metallothionein (Davis et al., 2006) or phytochelatin (Ahner et al., 1994, 1995; Wei et al., 2003) or via (ii) an active efflux mechanism as observed for *Synechococcus* (Croot et al., 2003) and *Emiliania huxleyi* (Walsh and Ahner, 2014). It is not yet known whether the metal is effluxed from the cell as a metal–ligand complex or if the metal and ligand are effluxed via separate pathways. The release of metabolites that complex Cu may occur either as an active or passive process (Croot et al., 2000). Several studies have indicated that copper stressed phytoplankton release ligands containing thiol functional groups (Dupont et al., 2004b; Laglera and van den Berg, 2003; Leal et al., 1999) which potentially bind Cu as Cu(I) (Leal and Van den Berg, 1998).

1.2. Frontal systems in the Southern Ocean

The location of the various frontal systems throughout the entire Southern Ocean were summarized recently (Sokolov and Rintoul, 2009) based on sea surface height data. The description of the physical oceanography of the Southern Ocean in the Atlantic sector is described in more detail in two related publications arising from the ANTXXIV-3 expedition (Bluhm et al., 2011; Croot et al., 2011). The following provides a brief description.

The northern boundary of the Southern Ocean is the Subtropical Front (STF) which separates the warm, salty temperate surface waters from cold sub-Antarctic waters (Orsi et al., 1995; Whitworth and Nowlin, 1987). South of the STF the Antarctic Circumpolar Current (ACC) flows in an eastward direction, and is dominated by two major fronts, the Subantarctic Front (SAF) and the Antarctic Polar Front (APF) (Orsi et al., 1995; Whitworth and Nowlin, 1987). The zone between the STF and the SAF is referred to as the Subantarctic Zone (SAZ), and surface water (Subantarctic Surface Water – SASW) stratification in this region is controlled mainly by temperature. Biological production has been suggested to be limited by silicate not only in the SAZ, but also across the ACC (Pollard et al., 2002).

The cold surface water in the APF, termed the Antarctic Surface Water (AASW), reaches all the way to the Antarctic Continental Shelf (Orsi et al., 1995). Below the AASW is a saltier and more nutrient-rich water mass called Circumpolar Deep Water (CDW) (Orsi et al., 1995). The CDW is derived from North Atlantic Deep Water (NADW) and covers most of the area from the APF to the Weddell Gyre (Veth et al., 1997). In this region biological production is not limited by the macronutrients, nitrate and phosphate but instead by iron (Croot et al., 2004; de Baar et al., 1995) as has been clearly shown in mesoscale iron enrichment experiments in this region (Croot et al., 2005; Gervais et al., 2002; Hoffmann et al., 2006). The area between the SAF and the APF is referred to as the Polar Frontal Zone (PFZ) (Pollard et al., 2002; Whitworth and Nowlin, 1987) where salinity is equally as important as temperature in regulating surface water density and stratification, but primary production has been shown to be limited by silicate availability (Pollard et al., 2002).

Along the Zero Meridian a further front, the Southern Polar Front (SPF), is found south of the APF at 56° S. Veth et al. (1997) found at 6° W, that the main current is flowing parallel to the America–Antarctica Ridge and that the SPF coincides with the average northern slope of the ridge and the ACC–Weddell Gyre Boundary Front. The

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