Organic complexation of iron in the West Atlantic Ocean

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ABSTRACT

The characteristics of the dissolved iron (DFe) binding organic ligands were determined during 3 Dutch GEOTRACES cruises covering the length of the West Atlantic Ocean. Adsorptive Differential Pulse Cathodic Stripping Voltammetry (AdDPCSV) with TAC as competing ligand was used to measure Fe binding organic ligands. Although the distribution of DFe is related to its sources, sinks and vertical processes, ultimately it is the solubility of Fe in seawater that determines its concentrations in the oceans. The Fe binding organic ligands increase the solubility of Fe. The total ligand concentration and the excess ligand over Fe concentration showed a decreasing trend from north to south in the surface ocean as well as in the North Atlantic Deep Water (NADW). This trend could be extended further north to the Arctic Ocean, where ligand concentrations were even higher. The Arctic might be a source of ligands to the northern West Atlantic Ocean. We calculated a residence time of 779 to 1039 years for dissolved organic ligands in the NADW. This is 2.5 to 4 times larger than the estimated residence time of DFe in the NADW.

The highest concentrations of excess ligands were found in the surface where the dissolved Fe concentrations were the lowest. This resulted in high ratios of [Lt]/DFe in the surface decreasing with depth to a value close to 2 below 500 m, where more ligands were saturated. Dissolved organic ligands were saturated with Fe in a large part of the southern West Atlantic at mid-depth, where DFe concentrations increased due to hydrothermal activity.

The inorganic Fe concentrations, [Fe′], were surprisingly uniform for the western Atlantic Ocean. Values ranged between 0.2 and 1 pM in the deep Atlantic as well as in the surface, where ligands were unsaturated with Fe. However, in the hydrothermal influenced region, where ligands were (nearly) saturated, [Fe′] was high, possibly larger than the solubility product of the Fe(oxy)hydroxides and thus suggesting either high concentrations of colloidal Fe or particulate Fe. Our results showed that the dissolved Fe concentrations were strictly regulated by a steady state between complexation by ligands and adsorption/precipitation of particles, the extensive hydrothermal influenced area seemed to be an exception.

1. Introduction

Iron (Fe) is a critical nutrient for primary productivity in the oceans. It is an important element in many proteins, enzymes and pigments (Wells et al., 1995). Due to its low solubility, Fe limits phytoplankton growth in large parts of the oceans (de Baar et al., 1990; Martin et al., 1990). Notwithstanding its low solubility, concentrations of dissolved Fe (DFe, <0.2 μm) are higher than predicted by its solubility product alone and vary widely over the water column and across the surface ocean. This variation in DFe concentrations can be explained by i) the chemistry of Fe in the dissolved phase, ii) transport and the proximity of Fe sources, and iii) biological processes (e.g. high DFe at the oxygen minimum) (de Baar and de Jong, 2001; Liu and Millero, 2002; Gledhill and Buck, 2012; Rijkenberg et al., 2012, 2014).

The chemistry of Fe in the dissolved phase is strongly controlled by the physical–chemical speciation in seawater, where colloids and Fe-organic complexes are dominant factors (Gledhill and van den Berg, 1994; Rue and Bruland, 1997; Croot et al., 2001; Thuróczy et al., 2011a,b). Although organic ligands forming Fe-organic complexes play a major role in the solubility and therefore in the distribution and bio-availability of Fe, their identity, sources and sinks are still largely unknown (Gledhill and Buck, 2012 and references herein). Organic ligands can bind 99% of dissolved Fe present in seawater (Gledhill and van den Berg, 1994; Rue and Bruland, 1997) increasing the residence time of Fe in seawater (Archer and Johnson, 2000; Ussher et al., 2004). These organic ligands are thought to be produced in the biological active photic zone, where DFe is low, by bacteria as strong ligands (logK′ > 21.5) called siderophores (a.o. Butler, 2005; Mawji et al., 2008), by grazing (Sato et al., 2007), by viral lysis (Poorvin et al., 2011) and by degradation and transformation of organic materials (Gerringa et al., 2006; Boyd et al., 2010a,b; Gledhill and Buck, 2012). Relatively weak ligands

(logK′ < 21.5) can consist for a part out of terrestrial humic materials (Laglera and van den Berg, 2009) and also for a part out of marine polysaccharides (Hassler et al., 2011). Rivers and sediments are also known to be a source for organic ligands (Croot and Johansson, 2000; Buck et al., 2007; Gerringa et al., 2006). We define degradation and transformation of organic materials as a source of ligands, we define mineralization of organic materials as a loss of ligands.

Most publications report one ligand group (defined by logK′ and [L]) but an increasing number of publications present results of two ligand groups, depending on their binding strength (K′) with Fe. The strong ligand (L1) has a logK1′ between 21.1 and 23.9 (with respect to [Fe^{3+}]) and the relatively weak ligand (L2) has a logK2′ between 19.8 and 22.0 (Rue and Bruland, 1997; Nolting et al., 1998; Cullen et al., 2006; Buck et al., 2007). The overlap in logK′ of L1 and L2 might be because they do belong to different groups but with similar logK′. Another reason of the overlap can be the use of different analytical methods and data treatments (Gerringa et al., 2014; Laglera et al., 2013). Although the recognition of the existence of two ligand classes has allowed significant headway to be made in terms of biogeochemical models (Ye et al., 2009; Tagliabue et al., 2009), firm experimental evidence for this scenario is still lacking (Gerringa et al., 2014). The logK′ of the strong ligand group coincides with that of the siderophores thought to be produced in the upper part of the oceans by bacteria in search for Fe. Concentrations of identified siderophores are far smaller than the measured concentrations of strong ligands. Mawji et al. (2011) could only explain at most 2% of natural complexation from the amount of siderophores found, despite their excellent limit of detection and the wide range of siderophores they could identify. The analytical detection of specific organic complexes such as siderophores is still in its infancy (Gledhill et al., 2004; Mawji et al., 2008, 2011; Velasquez et al., 2011). Strong ligands have also been measured at greater depths (Nolting et al., 1998; Buck et al., in press) although it is not clear whether these are also siderophores. This ambiguity is well illustrated by the lack of consent of for example the logK′ of the siderophore DFOB (desferal), which is relatively low (21.4) according to Witter et al. (2000a) and van den Berg (2006), and relatively high (>23) according to Rue and Bruland (1995) and Croot and Johansson (2000). The logK′ of the weaker ligand group has not been directly linked to specific chemical components. They could be among other humic substances and polysaccharides. Most likely, terrestrial humic substances play especially in coastal areas a role, although they have also been detected at large depth in the oceans. Their presence showed a relationship with Fe solubility in some studies (Tani et al., 2003; Nakayama et al, 2011) but not in others (Heller et al., 2013).

Organic ligands have been measured over the whole water column with concentrations below 500–1000 m remaining quite constant with depth (a.o. Thuróczy et al., 2011a,b). This indicates a high resistance to bacterial mineralisation or a steady state between mineralisation and production. Photochemical oxidation in the surface waters has been assumed to be a sink of organic ligands (Boye et al., 2001; Croot et al., 2004) and is shown to occur in incubation experiments by Powell and Wilson-Finelli (2003) in the Gulf of Mexico. Photoreduction of Fe due to photo-oxidation of the ligands could not be measured in estuarine waters of the Scheldt river (Rijkenberg et al., 2006a) and in laboratory photochemical experiments results differed greatly per model substance, some did not react at all (Rijkenberg et al., 2006b).

The GEOTRACES West Atlantic project produced complete ocean sections with 54 sampling stations of trace elements and several isotopes, transient tracers of global change, microbial biodiversity and metabolism (Fig. 1) (De Corte et al., 2012; Rijkenberg et al., 2014; Bruland et al., 2014; Casacuberta et al., 2014; Dulaquais et al., 2014; Deng et al., 2014; Lamborg et al., in press; Middag et al., 2015). Participating in this West Atlantic GEOTRACES (www.geotraces.org) project enabled us to study the organic ligand characteristics of Fe over this large section at 22 out of the 54 stations and to combine our data with other parameters

indicative of water mass, dust input, and hydrothermal input. It allowed us to investigate processes that determine the distribution of dissolved organic ligands and their role in the distribution and availability of DFe.

2. Materials and methods

2.1. Sampling

Seawater samples were collected during three GEOTRACES cruises along the GEOTRACES GA02 section in the western Atlantic Ocean (Fig. 1a). The first two cruises (64PE319, 64PE321) on the Dutch research vessel RV Pelagia covered the whole Northern Hemisphere between 28 April and 8 July 2010. The third cruise on the British research vessel RRS James Cook (74JC057) covered the Southern Hemisphere between 2 March and 6 April 2011. Seawater was filtered inline (0.2 μm, Sartobran 300 cartridges) from PVDF samplers mounted on an ultraclean titanium CTD (Rijkenberg et al., 2015–in this issue). At 22 out of 54 stations, 12–14 depths were sampled representing the entire water column, with the exception of sampling at station 37 in the Amazon plume, where 4 depths were sampled in upper 75 m, see Fig. 1a.

2.2. Organic speciation analysis

Samples from 64PE319 and 64PE321 were directly measured on board, however, most samples from 74JC057 were frozen and analysed later in the home laboratory. Complexing ligand titrations were used to determine the natural ligand characteristics. In short, different concentrations of Fe were added to 14 subsamples (0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 2, 2.5, 3, 4, 6, and 8 nM Fe) buffered at pH = 8.05 with a 5 mM NH_3/NH_4OH borate buffer. The competing ligand 'TAC' (2-(2-Thiazolylazo)-p-cresol) with a final concentration of 10 μM was used and the Fe(TAC)$_2$ complex was measured after equilibration (>6 h) by adsorptive cathodic stripping voltammetry (AdCSV) (Croot and Johansson, 2000; Croot and Heller, 2012).

The voltammetric equipment consisted of a μAutolab potentiostat (Type II and III, Ecochemie, The Netherlands), a mercury drop electrode (model VA 663 from Metrohm) connected to a Metrohm-Applikon (778) sample changer. To prevent signal noise caused by the motions of the ship, the electrode stand with the mercury drop electrode was mounted on a wooden board hanging with elastic bands in an aluminium frame. All equipment was protected against electrical noise by a current filter (Fortress 750, Best Power).

2.3. Calculation of the ligand characteristics

The sensitivity (S) relates the measured electrical current (nA) to the concentration Fe(TAC)$_2$. Using a straightforward and simple non-linear fit of the Langmuir model in R (Gerringa et al., 2014), we calculated the total ligand concentration ([L_t]) and the binding strength (K′) of the natural Fe-binding ligands together with S. The standard deviation of the fit of the data from the Langmuir model is here given as $SD_{langmuir\ model}$. Using [Lt] and K′, the concentration of DFe bound to a natural Fe-binding ligand [FeL], the concentration of inorganic Fe [Fe′] and the concentration of natural unbound ligand [L′] were calculated using the assumption of chemical equilibrium and the mass balance DFe = [Fe^{3+}] $(1 + 10^{10} + K′ [L′])$ and [Lt] = [FeL] + [L′], respectively by repeated calculations using Newton's algorithm (Press et al., 1986). For the inorganic complexation of Fe by hydroxides an inorganic side reaction coefficient of 10^{10} was used (Hudson et al., 1992; Millero, 1998).

2.4. TAC correction

Surprisingly, the chemical TAC contained so much Fe that the working solution added an extra inadvertent addition of 0.5 nM Fe to the sample. It is therefore important to measure the Fe content in new