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Physical and Chemical Speciation of Iron in the Polar Oceans

Thuróczy, Charles-Edouard

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Chapter 8

Synthesis

1. Major findings

Despite the difficulty of measuring indirectly (titration of empty ligand sites with Fe additions) something that is hardly known (*i.e.* “ligand soup”), and on board a ship, the results obtained during this thesis project proved to be precious for bringing new arguments and hypothesis explaining mechanisms of the Fe cycle in the oceans. Thanks to elaborate equipment and procedures (sampling, filtration, conservation and analyses), the work could be performed in metal clean conditions, without contamination.

1.1. In the Eastern-North Atlantic Ocean

Our results collected during the first expedition (Chapter 3), at a station in the Eastern-North Atlantic Ocean off the coast of Portugal, revealed that unfiltered samples (TDFe concentrations) could be used to distinguish the Mediterranean overflow water (MOW) from other water masses. In addition, we used for the first time the ratio of $[\text{Excess L}]/[\text{Fe}]$ as relative saturation state of the Fe-binding ligands per fraction. Concentration of Excess L shows a potential to bind Fe, a real amount of free ligand sites that is independent of Fe, whereas the reactivity of the ligands is expressed using the alpha factor ($[\text{Excess L}] \times K'$). The ratio of $[\text{Excess L}]/[\text{Fe}]$ is thus a complementary tool to describe the complexation of Fe in seawater. This parameter allows comparisons between stations, and ocean basins. Finally, the fraction <1000 kDa proved to be the most reactive, hence playing an important role in regulating dissolution, colloid aggregation and scavenging processes.

1.2. In the Atlantic sector of the Southern Ocean

In the Atlantic sector of the Southern Ocean (Chapters 4 and 5), high concentrations of unsaturated ligand were measured in upper waters as found at the station in the Eastern-North Atlantic Ocean. This was related to biota with a combination of Fe uptake and ligand production via organic matter, and was especially distinct in HNLC regions. The ligands got more saturated with Fe with increasing depth and reached a constant saturation state at around 450 m depth

characterised by low and constant ratio $[Lt]/[DFe]$ (below 4). This indicates a steady state between ligands and Fe and thus between stabilisation and removal of Fe (scavenging and co-precipitation) towards the seafloor. These dissolved organic ligands have a very strong buffering property, representing a step between sources and export removal of Fe, and their ubiquitous presence reveals the very resistant (refractory) nature of the ligands. Most of the ligands were actually found to exist in the smaller colloidal fraction (<1000 kDa). Along this expedition, we observed for the first time geographical (horizontal) trends in the organic complexation of Fe between different ocean basins by examining the ratio $[Lt]/[DFe]$. These trends in deep waters were attributed to an increasing distance from Fe sources and to scavenging of Fe. Analyses of the complexation of Fe in unfiltered samples confirmed that the particulate fraction ($>0.2 \mu\text{m}$) did not contain reversible adsorption sites (no Excess L), at least not within the measuring detection window established by the use of TAC. Therefore, the particulate fraction only has a role in scavenging and removal processes, as seen everywhere with the increasing concentrations of TDFe with depth.

1.3. In the Arctic Ocean

The conclusions on the speciation of Fe in the Arctic Ocean (Chapter 6) brought some rational explanations on the processes involved in the cycle of Fe. There also, distinct trends in Fe concentrations and ligand characteristics were observed vertically and horizontally, from the shelf seas towards the Makarov Basin in the central Arctic Ocean. The use of the ratio $[TDFe]/[DFe]$ revealed a relative enrichment of particulate Fe towards the bottom at all stations, indicating ubiquitous scavenging and export of Fe towards the deep ocean. As expected and as found elsewhere, the organic ligands became nearly saturated with depth in the Amundsen and Nansen Basins. However, an exception was found at the station in the Makarov Basin. Here the ligands got more unsaturated with Fe towards the bottom. This unexpected change in the saturation state of the ligands between the deep basins was explained by a lower reactivity of the ligands (expressed by $\alpha = [\text{Excess L}] \times K'$) and a lack of Fe sources in deep waters towards the central

Arctic. Despite the high potential of the organic ligands to buffer Fe in the deep Makarov Basin, the inputs of Fe from external sources may not be sufficient to counter balance the continuous scavenging of Fe, leading to a net export of Fe to the sediment.

1.4. In the Amundsen Sea, Southern Ocean

During the final expedition to the Southern Ocean in the Amundsen Sea (Chapter 7), the organic complexation of dissolved Fe in the upper 300 m of the water column has proven to play a crucial role in enhancing the local stock of Fe for phytoplankton blooms that lasted 70 days in 2009. There, the natural fertilisation of Fe of the upper waters was carried out by the upwelling of Circumpolar Deep Water (CDW) beneath the coastal glaciers and by subsequent melting of its basal part and of the surrounding sea-ice. Additionally, sediment resuspension may also represent a source of ligands to the CDW upwelling since higher concentrations of ligands were observed at the upwelling stations near the ice shelves. Thanks to the large glacier source, the organic ligands at the upwelling stations were highly saturated with Fe, hence increased the solubility of Fe, and consequently enhanced the stock of dissolved Fe and its transport towards the coastal polynyas. However, in the coastal upwelling regions, much of the glacial Fe supply (up to 90%) must be lost via scavenging and precipitation due to low buffering capacity of the nearly saturated organic ligands in conjunction with the much higher concentration of particulate Fe. Away from the glacier and towards the coastal polynyas, the organic ligands got desaturated with Fe in surface waters due to the uptake of Fe by the phytoplankton blooms. These relatively unsaturated ligands will most likely complex Fe released after remineralisation and may also be able to dissolve Fe from the particulate phase. Additionally, these unsaturated ligands probably buffer Fe from the continuous glacier/upwelling source, thus keeping a sufficient and more bioavailable stock of Fe to the phytoplankton bloom.

2. The organic complexation of Fe in the oceans: a summary

2.1. The size fractionation

Analyses of the complexation of Fe after ultra-filtration showed that most of the ligands present in the dissolved fraction appeared to be in fact in the smaller fraction (<1000 kDa) as shown by the concentrations of Excess L. Thus, changes of the organic ligands in the dissolved fraction were mainly due to changes of the small colloidal ligands. This smaller fraction was found to be most of the time less saturated with Fe but often slightly stronger ligands than the dissolved fraction, thus highlighting the dominance of small colloidal ligands (<1000 kDa) in controlling the distribution of Fe in seawater. Probably the smaller colloidal fraction was the main pool of ligands.

However, looking at the percentage of dissolved Fe actually present in the fraction <1000 kDa, differences were observed between the oceans. In the station in the Eastern-North Atlantic Ocean, approximately 19% of DFe was present in the smaller fraction (truly dissolved and small colloidal Fe, <1000 kDa). Whereas in the Arctic Ocean, 42-64% of DFe was truly dissolved and small colloidal around the chlorophyll maximum, and up to 74-83% of DFe elsewhere in the water column. In the Atlantic sector of the Southern Ocean, similar percentages were found in the upper waters, with approximately 70-80% of DFe actually present as truly dissolved and small colloidal Fe, and between 50 to 70% of DFe in the deeper waters. Only the upper waters in the Drake Passage were found to be similar to the station in the Eastern-North Atlantic Ocean regarding this proportion, with only 17% of DFe as truly dissolved and small colloidal Fe.

The variability in the percentage of Fe between the different colloidal pools reflects the different environments encountered, in terms of external Fe sources and of the different regimes regarding the primary productivity in surface waters. In the deeper ocean, this variable distribution of Fe over the size fractions is likely related to their residence time, which is influenced by the scavenging rates. In the Arctic Ocean, scavenging is relatively high as seen by the relative enrichment of particulate Fe with depth, and as confirmed by a loss of larger colloidal Fe. There, the larger colloidal Fe represented less than 25% of DFe. These large colloids

probably aggregated and can thus be an initiating step to scavenging. In comparison, scavenging appeared to occur at a lower rate in the Southern Ocean, where the percentage of larger colloidal Fe was higher, up to half of DFe, and even higher at the station in the Eastern-North Atlantic Ocean with up to 80% of DFe present as larger colloidal Fe. The circulation of the water masses might also play a role in these processes, and explain the influence of the missing dimension, the time.

2.2. The processes involved

Stabilisation of Fe in seawater is ensured by organic complexation with natural ligands, which increases the residence time of Fe in seawater, hence enhances its potential bioavailability. The reactivity (alpha value) and the saturation state of the ligands (ratio $[Lt]/[Fe]$ or $[Excess L]/[Fe]$) proved to be excellent tools to explain the distribution and the fate of Fe in the different fractions when associated with the presence and strength of the sources of Fe like continental runoff, melting sea-ice and glaciers or upwelling of deep water. Where sources of Fe were present, the organic ligands got relatively saturated with Fe with increasing depth, whereas where sources of Fe were lacking, the ligands got desaturated with depth revealing a net loss of Fe. Thanks to unfiltered samples, removal processes could be explained. Concentrations of TDFe and the ratio $[TDFe]/[DFe]$ revealed a relative enrichment of particulate Fe with depth and thus removal of Fe via scavenging. Scavenging was found to occur everywhere in all Arctic basins as well as in the Southern Ocean, probably by a permanent rain of particles towards the bottom. The particles with a high affinity to bind Fe will always compete with the dissolved ligands and remove Fe from the water column with the time, unless a source of Fe is present to keep the ligands relatively saturated with Fe. Therefore, the ligands represent a step between the inputs and export of Fe in the oceans. They act as a buffer that controls the solubility of Fe in seawater by their high affinity for Fe, but cannot prevent in the end from the loss via scavenging.

Ligands, sources and scavenging are therefore the three main characters controlling the residence time of Fe in the water column.

3. Discussion on the methods and opened windows on futures investigations

3.1. The organic complexation of Fe in seawater by voltammetry: What about two ligand groups?

The characterisation of the Fe-binding ligands as organic compounds was determined with voltammetric approaches in the middle 90s (Gledhill and Van Den Berg, 1994; Van Den Berg, 1995; Rue and Bruland, 1995). Since then, the knowledge of complexation of Fe in seawater is still predominantly based on results obtained by voltammetry techniques for one ligand group. Nevertheless, the presence of two distinct ligands groups is now widely admitted, with the L_1 siderophore-like ligand attributed to bacterial/microbial activity in upper waters, and the L_2 ligand originating from degradation of organic matter found in the whole water column. However, is the measuring method reliable enough to calculate the concentrations and stability constant of the two supposed ligand groups?

The determination of ligand concentration and stability constant for one group is based on a system with one equation and two unknowns (L' and K' , or three together with the sensitivity S). However, the calculations for two groups of ligands are based on a system with a single equation with four unknowns (L'_1 , K'_1 , L'_2 , K'_2 , or five unknowns together with S). For the same number of measuring points via the titration, the degrees of freedom are lower in the second case, causing higher uncertainties on the determination of the 5 unknowns.

During our project, the titrations were initially done with 11 Fe additions ranging from 0.33 to 8 nM Fe. Later on, 14 Fe additions ranging from 0.2 to 10 nM Fe were used, with more additions in the low range of Fe additions. This simple change improved considerably the fit of the model and reduced the standard error on the estimated parameters for one ligand group due to an increase of the degrees of freedom. Unfortunately, no improvement was seen for the estimation of two ligand groups, with a very weak or even no fit of the two-ligand-model to the data. Another analytical way of determining two groups should be used, with an

increase of the Fe additions in the titration, a much higher sensitivity of the voltammeter in the low range of Fe addition (higher detection limit) and a wider detection window. The use of larger mercury electrode and other added ligand like salicylaldoxime (SA) proved to be useful to further investigate the two supposed ligand groups (Rue and Bruland, 1995; Buck *et al.*, 2007; Buck and Bruland, 2007).

3.2. Filtration, ultra-filtration, unfiltered samples?

So far, filtration and ultra-filtration were used to separate different operationally defined size fractions like the dissolved fraction as $<0.2 \mu\text{m}$, the colloidal fraction (between 10-200 kDa and $0.2 \mu\text{m}$) and soluble fraction ($<10\text{-}200 \text{ kDa}$). Those fractions are operationally defined by the size cut-off of the filters used. In our study, the size cut-off of 1000 kDa allowed distinguishing the larger colloidal fraction (between $0.2 \mu\text{m}$ and 1000 kDa) and the fraction $<1000 \text{ kDa}$ containing small colloidal Fe and the soluble fraction. However, does it reflect the reality? Do we exactly know the effect of filtration? We know that filtration is affected by clogging effects due to aggregation of components on the filter that may be smaller than the size cut-off. Filtration apparently causes disequilibrium in seawater, as found at the station sampled in the Kara Sea of the Arctic Ocean (St. 279) or in deeper waters of the Southern Ocean (St. 128): How to give a rational explanation on the fact that filtration could increase the free ligand sites at these locations other than by concluding that new sites were created by breaking and/or dissociation of ligands, colloids and/or particles during filtration. In order to avoid disturbances generated by filtration and ultra-filtration on the equilibrium in seawater, would it not be needed to develop new separation procedures to study the properties of the ligands in non-disturbed fractions?

Unfiltered samples did bring promising results for concentrations of total dissolvable Fe, and also information that no contribution was given to reversible complexation/adsorption of Fe by the particulate fraction when comparing the concentrations of free ligand sites in both dissolved and unfiltered samples. Unfiltered samples, untouched and close to *in situ* conditions, should be

investigated with more care. The proportion of the different phases in unfiltered samples, like the organic phase, the biota and the mineral phase (refractory), should be estimated for each seawater sample in order to evaluate their influence on the real (*i.e. in situ*) equilibrium of Fe between the different species.

3.3. Inter-comparison and future perspective

The determination of Fe complexation could benefit more from some improvements of the method, calculations and inter-comparison between countries and laboratories. The GEOTRACES program successfully initiated inter-comparison work. This common effort should be continued with collaborations, sharing of the knowledge and development of new research topics and techniques.

Finally, will the organic ligands be affected by a more acidic ocean? What will be then the fate of Fe in the ocean and the impact on the primary productivity? New techniques should be developed to study with care the complexation of essential trace metals in phytoplankton cultures at variable pH in order to predict future impact of the rapid changing climate.

