

Iron chemical speciation in a more acidic ocean

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Introduction:

Increasing atmospheric levels of CO₂ is responsible for the process of ocean acidification (OA), leading to a wide range of effects on the chemistry of seawater: increase pCO₂, decrease pH, decrease of the carbonate ion concentration and changes in trace metal speciation. The latter could strongly affect primary production, phytoplankton abundance and phytoplankton community [1]. Trace metals, including bio-essential elements such as Fe, Cu, Co or Zn, are distributed under a variety of chemical forms (Figure 1), inorganic and organics, and each of these forms has a different mobility/bioavailability. A lower pH will result in changes in their biogeochemical cycle by affecting their redox state, solubility, inorganic or organic speciation, thus affecting their residence time (e.g. by favoring its removal through adsorption onto particles/colloids). Amongst these bio-essential elements, iron is of particular interest: it is currently the limiting nutrient in 40% of the world oceans and any change in its chemical speciation and bioavailability may have profound implication to atmospheric CO₂ levels [2]. Preliminary work have shown that, in presence of well defined ligand, only the inorganic fraction of Fe (called Fe') is bioavailable and bioassays in natural seawater performed at lower pH resulted in lower biouptake of Fe, thus predicting an increase stress of Fe in future oceans. At the current seawater pH of 8.1, Fe is mostly present as Fe(III), Fe(II) being rapidly oxidized in oxygenated water. Fe(III) is however poorly soluble [3] and is only maintained in the dissolved fraction at low nM levels, thanks to extensive complexation with various organic compounds [4] [5]. While inorganic Fe(III) solubility and Fe(II) oxidation rate are predicted to increase and slow down respectively, it is however largely unknown how Fe(III) complexation with organic compounds will be affected, and thus how Fe' will vary.

Project Summary:

This PhD project is aiming to gain insights into Fe speciation in seawater at pH values predicted to occur within an ocean acidification context. Fe speciation (stability constant and ligand concentration) is best estimated by titrating the original sample with increasing amount of iron and analysis by the voltammetric method of CLE-AdCSV (Competitive Ligand Exchange – Adsorptive Cathodic Stripping Voltammetry). This method is based on the addition of an electroactive complexing agent that competes with natural ligands for Fe(III) complexation. While a recently CLE-AdCSV optimized method works [6] well at current pH values of c.a. 8.1, it is not suited for lower pH values because of decreasing sensitivity. The main part of this proposal will therefore consist in finding a suitable Fe ligand to be used in the CLE-AdCSV method for the speciation of Fe in marine waters at lower pH (7 to 8). The complexation of that ligand will need to be calibrated against a known ligand (e.g. EDTA) and once optimized, the new method will be used to assess any changes in the organic complexation of iron in acidified samples collected in various part of the marine systems, from estuaries, coastal waters and open oceans to assess if a consistent trend is

emerging. Controlled acidification will be obtained by varying dissolved $p\text{CO}_2$. Additional work may include the effect of temperature and/or any changes related to other bio-essential (or toxic metals) such as Cu, whose free metal ion concentration could increase significantly with lower pH [7], thus possibly increasing its toxicity. Depending on the results and interest of the student, implications of the finding will be assessed through modeling using a global biogeochemical model. There will also be opportunities to collect samples and gain sea-experience during weeks long cruises.

We are looking for a motivated student with a strong chemical background and ideally a MSc in Oceanography, who enjoys analytical chemistry and laboratory work. She/he will benefit from numerous training and placement opportunities that will enhance his/her CV. The student will develop strong interdisciplinary skills through specific training programs, research seminars and an emulating research environment with world-leading experts in Fe biogeochemistry.

Competitive tuition fee, research costs and stipend (slightly more than £14,000 - tax free) are funded by the NERC Doctoral Training Partnership "Understanding the Earth, Atmosphere and Ocean" (DTP website: <http://www.liv.ac.uk/studentships-earth-atmosphere-ocean/>) led by the University of Liverpool, the National Oceanographic Centre and the University of Manchester. The studentship is granted for a period of 42 months. Further details on eligibility, how to apply, deadlines for applications and interview dates can be found on the website. EU students are eligible for a fee-only award.

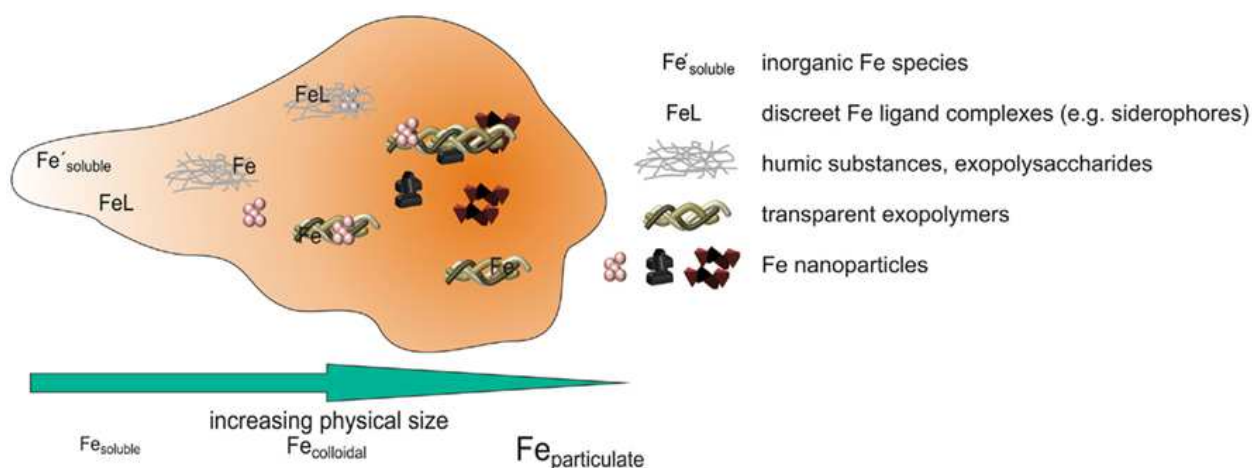


Image 1 Caption – Schematic representation of chemical forms under which dissolved iron has been so far identified in seawater. Taken from [4]

References

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