



Subject offered for a contract starting October 2017

SUBJECT TITLE: Trace metal sequestration in algae and Ocean acidification

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Financing: Doctoral contract with teaching assignment

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Rising atmospheric CO₂ affects the ocean and marine ecosystems through changes in the carbon cycle and through acidification of surface waters. The iron cycle is one of the most important marine dimensions of global climate change. Iron is transported as atmospheric particles from deserts to oceans, affecting ocean biogeochemistry and the climate itself by complex feedback mechanisms (Morel & Price (2003), *Science* **300**, 944-47). It is of particular relevance to anticipate the changes in iron availability to phytoplankton as a result of ocean acidification and to understand how phytoplankton species will adapt more generally with respect to the metabolism of transition metals to this changing environment. This is the purpose of the present project. We propose 1) to characterize the major iron pool associated with model marine micro-algae (the surface iron pool: see preliminary results) and to directly assess the effect of increased pCO₂ on the form and availability of this pool; 2) to decipher the mechanisms of iron uptake by selected phytoplankton species, and 3) to investigate the molecular mechanisms involved in the adaptation of marine micro-algae to acidification, with *Ostreococcus tauri* as a model.

The PhD project will deal with these processes that are expected to change metal speciation and availability. It is of particular relevance to anticipate the changes in iron availability to phytoplankton as a result of ocean acidification and to understand how phytoplankton species will adapt more generally with respect to the metabolism of transition metals to this changing environment. We have preliminary evidence showing that iron binds massively and specifically to the cell wall of diatoms and coccolithophores. Both silicifying and calcifying phytoplankton drive the ocean's biological carbon pump, so if substantial amounts of iron are associated with their cell walls, the biological carbon pump will also directly affect the biogeochemical cycling of iron. In this project we will study the nature of this surface iron in model species of calcifying and silicifying micro-algae (*E. huxleyi*, *P. tricornutum*, *T. oceanica*). In particular, i) we will generate a comprehensive sorption database to fully quantify the relative importance of the main processes involved in the speciation of iron and competing metal ions during sorption and interaction with living organisms.

To that purpose the internship candidate will :

i) Develop a potentiometric titration database with various types of organic matter (organic matter from seawater, phytoplankton cell walls and living organisms) under controlled pH conditions. The changes of the charge of the various types of organic matter will be followed with pH electrodes after addition of base or acid to calculate the overall site density of the organic ligands as well as the chemical nature of the binding moieties by analogy with previous titrations made on known natural ligands and other microorganisms (Plette et al., 1995; Gélabert, 2004). The NICA Donnan model will be used to interpret the protonation behaviour of the organic moieties identified on the organic matter.

ii) Perform Fe titration experiments on the same ligands in batch reactors. The pH will be fixed and the total amount of iron varied to construct sorption isotherms that will be analysed with the NICA-Donnan approach (Weber et al., 2006). Concentration of iron must be low and in the range of those found (0.02-1 nM) in vast oceanic regions. Under such conditions the concentrations are too low to enable the calculation of the amount of Fe bound to the organic matter moieties. We will therefore use iron stock solution with an isotopic composition that is different from the bulk iron solutions in other words a spike that will allow the detection of much lower Fe concentrations (see Zelano et al, 2016 for detailed explanation of the isotopic exchange approach). Ion concentration and spike solutions

of stable Fe isotopes will be monitored by High resolution ICP MS, the total Fe concentration will be varied from 0.5nM to 100 nM and the pH values tested will be 6, 7 and 8 to mimic moderate to strong acidification conditions. The gathered information will be critical for the construction of an accurate speciation model by providing strong constraints on surface complex stoichiometries as well as identification Fe surface precipitates.

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Gelabert, A., Pokrovsky, O. S., Schott, J., Boudou, A., Feurtet-Mazel, A., Mielczarski, J., et al. (2004). Study of diatoms/aqueous solution interface. I. Acid-base equilibria and spectroscopic observation of freshwater and marine species. *Geochimica Et Cosmochimica Acta*, 68(20), 4039–4058.

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Weber, T., Allard, T., Tipping, E., & Benedetti, M. (2006). Modeling Iron Binding to Organic Matter. *Environmental Science & Technology*, 40(24), 7488–7493.

Zelano, I., Sivry, Y., Quantin, C., Gelabert, A., Tharaud, M., Nowak, S., et al. (2016). Study of Ni exchangeable pool speciation in ultramafic and mining environments with isotopic exchange kinetic data and models. *Applied Geochemistry*, 64(c), 146–156.

Collaborations extérieures :

- Dr. Emmanuel Lesuisse Lab Mitochondria, Metals & Oxidative Stress, Institut Jacques Monod, Université Paris Diderot & CNRS.
- Dr. Chris Bowler, Institut de Biologie de l'École Normale Supérieure, Paris
- Dr. Ryszard Lobinski Lab of Analytical Bioinorganic and Environmental Chemistry (LCABIE-IPREM), Pau