



Subject title:

What is the redox speciation of contaminants at the surface of heterogeneous colloids in aquatic and urban environments?

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Host lab/ Team : **IPGP - Team ACE – UMR 7154**

Financing: Doctoral contract with or without teaching assignment

Presentation of the subject:

Scientific context. Accurate prediction of the biogeochemical behavior of trace elements (TE; e.g. As, Cr, U, Cu) in natural systems is of major concern because of the severe threats they cause to human health, aquatic life and the environment. Environmental TE transport, bioavailability and/or toxicity are known to be controlled by their speciation. However, TE speciation determination is hampered by the occurrence of colloids, which are ubiquitous, small (1-nm to 1- μ m-size), highly heterogeneous and reactive organic, inorganic particles or organomineral assemblages towards TEs. Understanding and predicting colloids-TE interactions is also particularly challenging for redox sensitive TE, whose toxicity and biogeochemical behavior is primarily dictated by their oxidation state. Therefore, new knowledge is required for accurate prediction of TE speciation in natural systems. The study of colloidal dynamics in urban environments is particularly interesting, given the presence of a large number of these TE due to human activities (brake pads, air pollution, roofs and buildings...) and the risks for water and soil contamination.

Objectives. This project will investigate the binding mechanisms of some redox-sensitive elements (for example Cr(III/VI), Cu(0/I/II), Ce(III/IV) and U(IV/V/VI)), with heterogeneous colloids composed of natural organic matter (NOM), metal oxides (e.g., iron or aluminium oxides) and/or clay minerals. Especially, the project aims at answering the two questions:
1. How and where redox reactions proceed at the surface of heterogeneous colloids?
2. Onto which constituting phase of colloids TE final oxidation state will bind?

Methodology.

Task 1. Kinetic and equilibrium investigation of TE-colloid binding. In this task, we will investigate the effects of different parameters on TE-colloid binding in order to gain a better understanding of their behavior in complex environments. Batch reaction experiments will be carried out under different physico-chemical conditions (redox potential, pH, presence of organic molecules, etc...) and the solutions will be analyzed after filtration by ICP-MS, in order to determine overall TE-colloids binding versus time.

Task 2. TE surface speciation onto heterogeneous colloidal assemblages. This task aims at better understanding the dynamics of contaminants at a colloidal scale. It will determine the distribution of TEs on colloids with different sizes as well as on different phases constituting colloids. Suspensions prepared in task 1 will be analyzed using advanced metrology tools such as (i) coupling colloid size fractionation (asymmetrical flow field flow fractionation, A4F) and ICP-MS for elemental composition or (ii) time-of-flight ICP-MS used in single particle mode (spICP-ToF-MS). The combination of these approaches will simultaneously allow the physical characterization of colloids (i.e., size, degree of aggregation), the determination of the composition of colloids and the co-elution of TE with these colloids. In addition, TE distribution onto heterogeneous colloids will be determined by electron microscopy (scanning transmission electron microscopy with electron energy loss spectroscopy, STEM-EELS).

Task 3. Elucidation of TE redox speciation and reaction mechanisms. Understanding the risks of TE contamination requires a better understanding of their speciation and the associated reaction mechanisms. Therefore, synchrotron X-ray absorption spectroscopy (XAS) will be used to determine the redox speciation of TE onto heterogeneous colloids, as well as their local environment (i.e. type of surface binding sites on both organic and inorganic phases of the colloids). In addition, time-resolved XAS analysis, will allow to monitor reaction kinetics, in order to decipher the reaction mechanisms.

Context of the thesis.

PhD will be based mainly at IPGP (Jussieu, Paris), with occasional stays in Lyon (INSA Lyon, Villeurbanne). The PhD candidate will participate to the larger project funded by the French National Research Agency (ANR) "COLOSSAL". Therefore, in addition to the thesis co-supervision, the work will give rise to numerous national collaborations (Géosciences Rennes for A4F-ICPMS; SOLEIL and ESRF synchrotrons for XAS analysis; National Institute of Agronomy (INRAE), Bordeaux, for organic matter characterization; Institute of catalysis and solid chemistry of Lille, for data analysis of time-resolved spectroscopy; Institute Jean Lamour, Nancy, for STEM-EELS analysis) and even international collaborations (Karlsruhe Institute of Technology, Germany, for geochemical calculations; University Laval, Canada, and Duke University, USA, to collect and analyze samples from other city observatories; Golden Colorado School of Mines, USA, for further colloids characterization; Indian Institute of Sciences, India, for mineralogical determination).

Scientific background of the candidates. To be successful, the candidate should be a chemist or a geochemist with knowledge in aqueous solution chemistry and, if possible on the solid-liquid interface. The candidate should have skills in lab experiments, analytical chemistry, spectroscopy and/or electron microscopy. He/She should demonstrate its capability to work in a team and have good communications skills in English (both oral and written).

Application.

The **application file to be sent before May 17 at 12:00 am** to the supervision team consists of a detailed CV and a letter of motivation, to be completed with the transcripts of the bachelor's degree, master's degree (or equivalent diploma), including the ranking and number of graduates, and one or two letters of recommendation.

Shortlisted candidates will defend the subject and their scientific file/profile in July 2024 in front of a jury from the STEP'UP Doctoral School.