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### Zinc interaction with diatom cultures: New insights from XAFS study and stable isotope fractionation

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Marine and freshwater diatoms play a major role in the distribution and transport of many essential and toxic trace elements in surficial aquatic environments. Recently, we characterized the physico-chemical properties of diatom surfaces in metal-free solutions and generated a thermodynamic model of diatoms – solution interface which allowed us to identify the nature and determine the concentration of the major surface functional groups (carboxyl, amine, silanol) responsible for the amphoteric behavior of cell surfaces and their affinity to trace metals [1]. The present study is aimed at the physico-chemical characterization of diatoms interaction with zinc. For this purpose, experiments of metal adsorption on diatom suspensions and electrokinetic measurements in the presence of dissolved zinc have been conducted under controlled laboratory conditions as a function of pH, ionic strength, metal and ligand concentration in solution. These allowed extraction of the kinetic and thermodynamic constants of zinc – diatom interactions for four diatom species.

Further insights on the structural arrangement and speciation of Zn in diatom cultures have been gained by an XAFS study which allows resolving the chemical status (coordination, atomic distances) of zinc adsorbed on or incorporated in the diatoms. Our observations demonstrated that during long-term incorporation into cells and short term adsorption on diatoms surfaces, zinc reduces its coordination number from six (octahedrally coordinated H<sub>2</sub>O in bulk solution) to 4 or 5 (oxygen and nitrogen coordinated complexes). Such an important change of metal local environment produces a significant isotopic fractionation evidenced, for the first time, by measuring <sup>66</sup>Zn/<sup>64</sup>Zn isotopic fractionation between diatoms and Zn-bearing solution using a multi-collector ICP-MS (Neptune) available in LMTG, Toulouse. The results of stable isotope fractionation, consistent with the principles of quantum theory, exhibited an enrichment in <sup>66</sup>Zn on diatom surface and inside the cells ( $\delta^{66}\text{Zn} \geq 0.3 \text{ ‰}$ ).

#### References

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### Zn isotopes fractionation upon sorption and precipitation

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Recent studies have shown a 1.3‰ variation in isotopic composition of Zn (<sup>66</sup>Zn/<sup>64</sup>Zn) in natural marine and continental carbonates, sulfides and Mn/Fe nodules [1-3]. Although these differences are mainly related to different Zn sources, physico-chemical processes such as sorption and precipitation [4] could play a role. Since these processes drive Zn speciation in soils, isotopic variations might indicate past sorption and/or precipitation events in these systems.

The study aimed to measure Zn isotopic composition upon sorption and precipitation in order to quantify possible fractionation. Ferrihydrite and goethite were chosen for sorption experiments since they are known to be ubiquitous and very efficient sorbants in soils. Zincite (ZnO) was chosen for precipitation experiments since this mineral has low solubility and might precipitate during sorption experiments.

Results for sorption indicate that Zn-sorbed ferrihydrite is strongly enriched in heavy isotope relative to solution ( $\Delta^{66}\text{Zn}$  (solid-solution) = + 0.58 ± 0.08 ‰ at 2  $\sigma$  level), whereas Zn enrichment was much lower upon sorption onto goethite ( $\Delta^{66}\text{Zn}$  (solid-solution) = + 0.15 ± 0.08 ‰). The larger Zn fractionation upon sorption onto ferrihydrite could be related to a decrease in Zn coordination number since EXAFS spectroscopy indicated a fourfold coordination for Zn sorbed onto ferrihydrite (Zn-O = 1.95 Å) whereas Zn is octahedrally coordinated in solution. The lower enrichment in heavy isotope for Zn-sorbed goethite is consistent with EXAFS spectroscopy which indicated a sixfold coordination for Zn (Zn-O = 2.09 Å): in this experiment no change in Zn coordination number occurs between solution and solid. In contrast to sorption experiments, results for zincite precipitation indicate that the mineral is strongly depleted in heavy isotope ( $\Delta^{66}\text{Zn}$  (solid-solution) = - 0.52 ± 0.08 ‰ at 2  $\sigma$  level). Despite a slightly stronger fractionation, this result corroborates those obtained for smithsonite synthesis [4].

These results indicate that Zn isotopic composition could be used to trace past sorption and/or precipitation pathways, which are very active during pedogenesis, provided initial Zn isotopic composition is known.

#### References

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