



## Speciation of Fe adsorbed onto and assimilated by bacteria: XAS structural analysis

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The speciation of iron has been studied in natural waters in order to elucidate the biogeochemical cycle of this element in the environment. One important aspect of Fe biogeochemistry that remains poorly investigated is the speciation of this element within the living organisms, notably bacteria. In this study, iron speciation has been measured using X-ray absorption spectroscopy (XAS) structural analysis in bacterial samples having surface adsorbed or intracellular incorporated Fe. Three typical and abundant cyanobacteria (*Synechococcus* sp., *Planktothrix* sp. and *Gloeocapsa* sp.) and one soil bacteria (rhizospheric *Pseudomonas aureofaciens*) were used both in assimilation (from Fe<sup>3+</sup>-containing nutrient solution) and adsorption (from Fe<sup>3+</sup> and Fe<sup>2+</sup>-containing inert electrolyte) experiments. Aquatic cyanobacteria were selected for their well-known requirement for Fe and *Pseudomonas aureofaciens* was used due to its capacity to produce high exopolysaccharide on the cell surface under environmental stress.

Results of this work demonstrated that Fe uptake during growth of EPS-producing and EPS-poor cultures produces octahedral oxygen environment of trivalent iron with no polymers of Fe-O-Fe structures even at pH 7 (*P. aureofaciens*) and 10.5 (cyanobacteria). Intracellular Fe storage in the form of Fe(III) phosphate is the most likely scavenging mechanism during growth at high concentration (10-100 mg/L of Fe(aq)). Fe(III)-phosphate complexes at the surface and inside the cells were detected for *Synechococcus* sp., *Planktothrix* sp. and *P. aureofaciens*. In contrast, studies with *Gloeocapsa* sp. showed mainly Fe-Alginate structures. Fe(II) were not detected by XANES analysis, being all oxidized to Fe(III) under aerobic environmental conditions. Our results strongly suggest that, in the presence of surface organic ligands, the oxidation of divalent iron does occur but the polymerization of formed Fe(III) oxyhydroxides is completely inhibited and adsorbed iron presents in the form of individual Fe atoms attached to organic moieties. This implies that Fe(III) adsorbed on the cell surface is potentially more bioavailable when follows from physico-chemical thermodynamic equilibrium with Fe(III) solid oxyhydroxides. In addition, the presence of EPS reduces the capacity of binding metal onto the cells and may serve as important screening barrier against metal penetration inside the cell.