GONZALEZ A., **POKROVSKY O.S.,** SHIROKOVA L.S. POKROVSKI G.S, JIMENEZ-VILLACORTA F., GONZÁLEZ-DÁVILA M., SANTANA-CASIANO J.M., EMNOVA E.E. (2009) Speciation of Fe adsorbed on and incorporated into soil and aquatic bacteria: XAS structural study. Proceedings of 19th Annual V.M. Goldschmidt Conference, Davos, Switzerland, 21-26 juin 2009. *Geochim. Cosmochim. Acta,* **73,** *No 13,* Suppl. S, p. A453.

Speciation of Fe adsorbed on and incorporated into soil and aquatic bacteria: XAS and macroscopic interaction studies

This work devoted to the interaction of most important oligo-element and nutrient, iron, with surfaces of major planktonic (cyanobacteria) and soil (rhizospheric *Pseudomonas*) microorganisms via physico-chemical characterization of metal adsorption on and incorporation into cells under controlled laboratory conditions. Iron is an essential element, since it is a part of many (co)enzymes, like cytochromes, ferredoxines, nitrogenase and ribonucleotide reductase, which function in vital cellular processes. To understand the first most important step of metal uptake by living cells, the reversible adsorption at the cell – aqueous solution interface, thermodynamic and structural approach was used here to resolve the chemical identity of the complexes formed. Similar to zinc, copper and cadmium (Pokrovsky et al., 2005, 2008), iron can interact with high-affinity (phosphoryl, sulfhydryl) or low-affinity (carboxyl) sites on cell surfaces depending on its concentration in solution. The knowledge of the identity and molecular structure of metal complexes involved in investigated interactions was obtained using in situ XAS (X-ray Absorption Fine Structure, EXAFS and XANES) spectroscopy. In order to assess different mechanism of Fe uptake by aquatic microorganisms, series of rigorously constrained experiments will be conducted on axenic cultures of diatoms, cyanopbacteria and rhizospheric bacteria. From the same type of bacterial strain, *Pseudomonas aurefaciens*, two types of cultures were produced: those containing exopolysaccharaides and growing on sigar-rich media and peptone and cultures poor in the EPS growing on succinic acid. In addition, three typical cyanobacteria (*Synechococcus* sp., *Plantothrix* sp. and *Gloeocapsa* sp.) were used both in assimilation (Fe^{3+}-rich nutrient solution) and adsorption (Fe^{3+} and Fe^{2+} - containing inert electrolyre) experiments. Our experiments 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 event to pH 7 (*P. aurefaciens*) and 10.5 (cyanobacteria). Intracellular Fe storage in the form of Fe(III) phosphate is the most likely scavenging mechanism in case of growth at high 10-100 mg/L of Fe(aq). In case of Fe^{2+} or Fe^{3+} adsorption at pH = 5-8 and 2-6, respectively, mostly Fe(III) isolated octahedral linked to carboxylate, and, probably, phosphoryl groups of the external surface layers were detected. 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 stays in the surface in the form of individual Fe atoms attached to organic moieties. This implies that Fe(III) adsorbed on the cell surface is potentially more bioavialble when follows fcrom physico-chemical thermodynamic equilibrium with Fe(III) solid oxyhydroxides. The decrease of Fe(III) polymerization due to complexation with ligands was also demonstrated by EXAFS spectroscopy for Fe(III) aqueous silicate interaction (Pokrovski et al., 2003) and soil organic functional groups (Karlsson et al., 2008). The main significance of this XAS work lays in the establishing the molecular-level understanding of Fe speciation within typical the aquatic microorganisms, notably the evidence of potential Fe(III) bio-availability despite its tendency to polymerize in Fe-hydroxide supersaturated solutions.

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