

## Microbial reduction of intragrain ferrihydrite in porous glass beads by *Shewanella oneidensis* MR-1

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Microorganisms can reduce Fe(III) either by direct contact between the cell and the oxide surface or by indirect mechanisms not involving contact. These latter mechanisms include "electron shuttling" and soluble Fe(III) complexation with subsequent reduction. Despite of these findings, mechanisms of reduction and particularly how electron transfer from cells to the oxide surface changes at various natural conditions are still poorly understood. The objective of this work was to study bacterial reduction of Fe(III) oxides in intragrain region where restricted sizes prevent direct contact between bacterial and Fe(III) oxide surfaces. Microbiological reduction by *Shewanella oneidensis* MR-1 of 6-line ferrihydrite located in the pores of glass beads (intragrain ferrihydrite) was investigated and compared to the reduction of 6-line ferrihydrite in the absence of beads (free ferrihydrite). We found that the overall extent of reduction of the intragrain ferrihydrite was smaller than of the free ferrihydrite. In the intragrain ferrihydrite suspensions, dissolved Fe(III) was released during the initial stages of the reduction due to nonreductive dissolution of ferrihydrite by organic ligands; no Fe(III) was detected in the free ferrihydrite suspensions. In the presence of phosphate, Fe(II) phosphates of spherical morphology were revealed at the end of intragrain ferrihydrite reduction experiments. The rosettes were surrounded by microorganisms and fragments of extracellular materials suggesting that Fe(II) phosphate formation was influenced by microbial activity.

## Study of the adsorption properties of mineral soils

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The transport and bioavailability of nutrients and contaminants in the environment is mainly controlled by adsorption processes on the soil reactive surfaces. There are many studies of the anion adsorption properties on mineral surfaces [1,2] in which surface complexation models are applied to predict the experimental behaviour. However, due to the complexity of natural systems (presence of different mineral phases, natural organic matter, competing ions, etc.), it is difficult to find studies in which the adsorption properties of soil samples are described with surface complexation models.

In the present study soil samples from two horizons, Ap1 and Bw1, of a mineral soil (Sao Paulo, Brazil) have been used. These samples have a high content of iron oxides but less than 1% organic matter content. Firstly, the acid-base properties of the two mineral horizons were analyzed by means of potentiometric titrations. The surface charge curves were thus obtained in different ionic media, KNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>, over a wide pH range.

Secondly, the phosphate adsorption behaviour on the same horizons was studied. Several experiments were carried out to obtain pH-adsorption edges at different initial phosphate concentrations and adsorption isotherms at different ionic media and pH values. These experimental results can also be compared with previous adsorption data on mineral oxides.

Using surface complexation models which describes the adsorption properties of mineral oxides as a first approach, an attempt has been made to develop a model which is able to predict the sorption behaviour of these soil samples. In order to simplify the interpretation of such complex systems, the possibility of considering the reactive surface of soil samples as constituted mainly by iron oxides, was analyzed.

[1] Antelo, Avena, Fiol, Lopez & Arce (2005), *J. Colloid Interface Sci.* **285** 476-486. [2] Stachowicz, Hiemstra & van Riemsdijk (2008), *J. Colloid Interface Sci.* **320** 400-414.