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Acid-base activity of live cells, dead cells and cell wall components

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Bacteria are present in almost every natural environment. While performing metabolic reactions, such as metal reduction/oxidation, bacteria may change the alkalinity or the acidity of the environment. Bacteria can also interact with dissolved components, such as metals and nutrients, by adsorption or uptake. Once metals are complexed at the cell walls, they can become nucleation sites for mineral precipitation via counter adsorption of anions. The interaction between the bacteria and their environment takes place via the cell wall. The cell walls of bacteria are three-dimensional complex structures composed of different macromolecules. These macromolecules contain carboxylic, phosphate, hydroxyl and ammonium groups. The acid-base properties of these functional groups play an important role in metal binding and are being investigated in order to understand and quantify metal complexation to bacterial cells. In addition to the available functional groups in the cell walls, metabolic activity may also control the metal binding to live cells [1].

Acid-base titrations are a powerful technique to characterize the pH-dependency of functional groups on surfaces. In a previous study we have shown that protonation and deprotonation of the functional groups are not the only process controlling the acid-base activity of live cells of *Shewanella putrefaciens*, a facultative anaerobe Gram-negative bacterium [2]. In the present study we compare the acid-base activity of live and dead cells, to distinguish between protonation/deprotonation reactions and metabolic processes. We characterize the metabolic responses to external pH changes by monitoring the build-up in solution of fatty acids, amino acids, phosphate and cations. The acid-base activities of the cell membranes and lipopolysaccharides are also measured and compared to the buffer capacity of whole cells.

References

[1] Urrutia Mera M., Kemper M., Doyle R. and Beveridge T.J. (1992) *Applied and environmental microbiology* **58**, 3837-3844.
[2] Claessens J., Behrends T. and Van Cappellen P. (2004) *Aquatic Sciences*, in press.

2.3.31

Interactions of Fe^{2+}, Zn^{2+}, and H_4SiO_4 at clay/water interface: Distinguishing competitive sorption, coadsorption and surface oxidation phenomena

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The mechanisms of Fe(II) sorption on montmorillonite in anoxic conditions is investigated through Mössbauer spectroscopy and original analytical chemistry experiments. The whole sorption of Fe(II) is found to be caused by several mechanisms taking place at the same time on the montmorillonite edge surfaces. The relative importance of these mechanisms is dependent on the pH. In the alkaline pH range, a Si-Fe precipitate forms from pH equal to ~9.5, with Si/Fe ratio comprising between 1 and 2. In the acid pH range, clay surfaces have high affinity for Fe^{2+} sorption. Sorption mechanism is responsible for the net release of 2 H^+ per Fe^{2+} adsorbed and is thought to be a two-step mechanism including a pure sorption step followed by a surface oxidation step, as shown by Mössbauer experiments. The oxidation of Fe^{2+} into Fe^{3+} and the structural fit between the montmorillonite octahedral layer and Fe^{3+} should explain the high affinity of clay for Fe^{2+} sorption. Sorbed Fe^{2+} is also shown to replace structural Mg^{2+} or previously sorbed Zn^{2+} on the clay edges at pH 5.82. If a sufficient concentration of H_4SiO_4 is available via clay dissolution, Fe^{2+} and H_4SiO_4 can be sorbed together (cooperative sorption), leading to the formation of a surface precipitate in the acid and neutral pH range. These results will be discussed in term of structural-based clay – solute interaction modeling as a function of pH-range.

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