

## 4.2.12

### Cadmium complexation by bacteriogenic iron oxides from a subterranean environment

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This study quantifies the metal sorption characteristics of subterranean bacteriogenic iron oxides (BIOS) and their organic phase (intermixed intact and fragmented bacteria). A Cd<sup>2+</sup> ion selective electrode was used to generate high resolution metal sorption data as a function of increasing pH. A multi-site Langmuir model, along with a linear programming regression method (LPM), were applied to fit experimental data. This approach found two discrete Cd<sup>2+</sup> binding sites for the BIOS with average  $-\log_{10}$  equilibrium constants ( $pK_{S,j}$ ) of  $1.06 \pm 0.19$  and  $2.24 \pm 0.28$ . Three discrete sites were obtained for the bacterial fraction, with  $pK_{S,j}$  values of  $-0.05 \pm 0.12$ ,  $1.18 \pm 0.02$  and  $3.81 \pm 0.16$ . This indicated that the BIOS surface had a lower affinity for Cd<sup>2+</sup> than that of the bacteria.  $pK_{S,j}$  values for the BIOS were similar to those of reported for pure iron oxide phases, while the organic fraction  $pK_{S,j}$  spectrum was consistent with previous spectra for intact bacteria. Individual binding site densities of  $0.04 \pm 0.01$  and  $0.05 \pm 0.02$ , and  $0.29 \pm 0.05$ ,  $0.11 \pm 0.01$  and  $0.09 \pm 0.02$   $\mu\text{moles/mg}$  of BIOS, corresponded to the iron oxide mixture and bacteria fraction respectively. These values indicated high concentrations of strong affinity Cd<sup>2+</sup> complexing groups on the bacterial surface. Comparison of total site densities of  $0.08 \pm 0.02$  and  $0.48 \pm 0.06$   $\mu\text{moles/mg}$  of BIOS for the mixture and the bacterial phase respectively, suggested a non-additive character for the BIOS surface reactivity. This was emphasized by a higher affinity for Cd<sup>2+</sup>, as well as an increase in total site concentration observed for the bacterial phase. LPM was able to distinguish between the BIOS mixture and its organic fraction Cd<sup>2+</sup> complexation characteristics. This approach is therefore a useful tool for the study of natural sorbent materials controlling metal partitioning in contaminated and pristine environments.

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### Adsorption of ferrous ions onto *Bacillus subtilis* cells

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In this paper<sup>1</sup>, the adsorption of ferrous ions onto *Bacillus subtilis* was measured under anoxic conditions as a function of pH for various Fe(II)/bacteria ratios. Acid-Base titrations of the bacterial suspension were also performed. The titration data could be fitted using a simple three-site model, where the three sites had pK values of  $pK_1 = 4.41$ ,  $pK_2 = 6.69$ ,  $pK_3 = 9.10$ . The adsorption data for Fe(II) could be fitted with a single site model, involving the type 2 sites ( $pK_2 = 6.69$ ). More generally, we determined the ranges of acceptable parameters for one and two-site models, and found that the type 1 sites ( $pK_2 = 4.41$ ) contributed to very little Fe(II) adsorption. Our work is particularly interesting for the following reasons:

- understanding the adsorption properties of major redox elements in the earth's crust onto bacterial surfaces is of importance for various biogeochemical processes, including the dissolution and precipitation of Fe(III) minerals.

- our experimental data is highly reproducible, which allowed us to perform a particularly meaningful modeling analysis.

- our modeling analysis methods are simple but their conclusions can likely be generalized to the adsorption of other cations onto bacterial cells. In particular, our work demonstrates that the search for a "best fit" for a single adsorption isotherm can be misleading. It also indicates that the general belief that carboxylic groups (corresponding to type 1 sites) are the dominant reactive sites for adsorption is not obviously consistent with batch adsorption experiments. This apparent discrepancy with results obtained using other techniques still needs to be resolved.

#### References

- [1] Châtelier X. and Fortin D. (2004) *Chem. Geol.*, submitted.