Microbial biomineralization and redox transformation of As and Fe in an acid mine drainage

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Bulk chemical and mineralogical data (bulk XANES, EXAFS and XRD) showed that indigenous bacteria living in the As-rich Carnoulès Acid Mine Drainage ([As] = up to 350 mg.l-1) play an important role in the nature and composition of the solid phases that sequester arsenic at the site: some bacteria oxidize Fe(II) but not As(III) and promote the precipitation of a rare ferric arsenite sulfate oxy-hydroxide mineral, called tooeleite (Morin *et al*. 2006), while other bacterial species catalyze As(III) to As(V) oxidation leading to the formation of amorphous As(V) rich ferric oxy-hydroxides (Morin and Calas 2006).

In order to better document the interactions between microbes and Fe and As redox processes in the Carnoules AMD, we combined Scanning Transmission X-ray Microscopy (STXM) and Transmission Electron Microscopy (TEM) to collect near-edge x-ray absorption fine structure spectra (NEXAFS) at high spatial and energy resolution and to perform high resolution imaging at the submicrometer scale, following procedures described previously (Benzerara *et al*., 2006**).** Spectromicroscopy was performed at the C K-edge, Fe L2,3-edge, and As L2,3-edge offering the possibility to locate living and/or mineralized bacterial cells and to characterize Fe and As oxidation states in the vicinity of those cells. Many precipitates were found associated with extracellular organic polymers. Moreover, some As-Fe precipitate show a vesicular appearance that we interpret as microbial cell's products. TEM was used to image the same areas, providing higher resolution images and complementary crystallographic and chemical information through electron diffraction and EDX analysis. This approach offers a unique opportunity to assess at the submicrometer scale the various and heterogeneous geochemical activities of complex microbial communities in acidic environments.

References

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Sedimentary phosphorus speciation and its relation to the CNS and bottom water in an estuary influenced by anthropic activities

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Phosphorus element plays a key role on the biogeochemical cycles in estuaries. Phosphorus is one of principal nutrients to the organic matter production in the acquatic system and its excess contribute to eutrophization process. This study focus on the sedimentary phosphorus speciation in the Santos Estuary, a strongly impacted coastal area located at São Paulo State – Brazil, where accommodates the largest harbour of Latin America with an important industrial pole which include 5 fertilizer industries, urbain poles with respresentative domestic wastes and some mangrove vegetation along the system. During the summer period, the tourism activities contribute to the nutrient inputs to the acquatic environment. In this study, the sedimentary concentrations of bioavaiable-P (P-bio) varied from 1,78 to 9,36 μmol g^{-1}, iron oxihydroxides-P (P-Fe), from 1,09 to 37,68 μmol g^{-1} , authigenic-P (P-auth), from 0,37 to 10,64 μmol g^{-1}, fluorapaptite-P (P-FAP) varied from 0,94 to 7,21 μmol g^{-1} and organic-P (P org) varied from 0,37 to 10,50 μmol g^{-1}. The organic carbon (Corg) varied from 0,14 to 6,26 %, total nitrogen (TN) varied from 0,01 to 0,55 %, total sulfur (TS) varied from 0,01 to 2,11 % with high concentrations in the internal part of the port channel decreasing in direction to the Santos' Bay. The TN and TS were highly correlated with C org and P org ($r > 0,87$, $p<0,01$), indicating that S org is the second pool of reduced S in the sediments, after S content associated to pyrite. Organic speciation of C, N, S and P were higher during the summer, while the inorganic ones were higher during the winter, due to the different intensities of mineralization process in these two marked seasonal periods at this region. In general, the sedimentary parameters show high positive correlations with the bottom hydrochemical characteristics as observed for dissolved inorganic phoshporus (DIP) ($r > 0,77$, $p< 0,01$). There was negative correlations with dissolved oxygen ($r = -0,69$, $p <0,01$) in relation to sedimentary parametres. The sedimentary sulphur concentration increased when the water reduced conditions were present in the environment as occured during the summer, facilitating the phosphorus liberation. On the other hand, there were significative percentages of P-Fe (around 40 -53 %) in relation to total P and this is correlated to the C/N and C/S. The C/N (>6) and C/S (> 10) molar ratios showed that the continental organic matter input probably had high content of humic substances that could be sequestrate iron oxihydroxides bound phosphorus.