Interaction of anaerobic acidophiles with aluminum at the micro-scale

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Bacterial cells have been found to play an important role in the mobility and fate of aluminum in acidic mine waters [1,2]. Through the use of scanning/transmission electron microscopy (STEM) combined with other complementary techniques (SEM, cryo-TEM, HRTEM, EELS) we have studied the interaction of microorganisms inhabiting deep anoxic waters of acidic pit lakes with dissolved aluminum. The anaerobic conditions of these environments allow investigation of geomicrobial interactions that are usually difficult to observe in oxidized environments dominated by Fe(III). Detailed chemical maps obtained in rod-like cells and other structures of possible microbial origin (e.g., spherical particles, bacteriomorphs) show extra- and intra-cellular accumulation of Al. In addition to aluminum, other elements like silica, sulfate and ferrous iron, also present at very high concentrations, are also affected by these interactions and coprecipitate in the cells. Many bacterial rods showed an external nanometric coating of adsorbed Fe(II) and Al on the cell surface and significant presence of Al, Si, and S on the cytoplasm. The chemical and microscopic information obtained suggests the simultaneous precipitation of two amorphous phases, a proto-aluminosilicate with imogolite-like composition and proto-hydrobasaluminite. Geochemical modelling indicates undersaturation with respect to these phases in the bulk solution, suggesting that bacteria may be favouring surface-catalyzed precipitation reactions in microenvironments of higher pH or sorption to cellular exudates (e.g., proteins, lipids). A major question that still needs to be solved is the role played by bacterial cells, either passive or active, since this issue has obvious geomicrobiological implications. In the former case, the microbially-related solids would have been formed by permineralization and mineral replacement of senescent microbial cells. In the second case, the observed features would denote biomineralization by active cells, possibly as a detoxification mechanism, a possibility yet to be explored.

[1] Sánchez-España et al., *Chemical Geology* (2016), **192**, 70-96.
[2] Sánchez-España et al., *Geobiology* (2018), **16(1)**, 88.