

## **SXM analysis of nanoscale electron transfer processes at the cell-mineral interface in Co-bearing Fe/Mn minerals**

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Cobalt is a critical commodity primarily due to usage in rechargeable batteries. This demand, combined with supply risk, has driven a need to find and exploit other geological sources. Cobalt, as Co(III), can be found incorporated into the crystal lattice of minerals such as ferrihydrite [Fe<sup>3+</sup><sub>10</sub>O<sub>14</sub>(OH)<sub>2</sub>] and asbolane [(Ni,Co)<sub>x</sub>Mn<sup>4+</sup>(OOH)<sub>4</sub>•nH<sub>2</sub>O]. These minerals are potential new Co sources in lateritic ores and deep sea nodules. Dissimilatory metal-reducing bacteria, ubiquitous in the subsurface, can use Fe/Mn-oxides as terminal electron acceptors for microbial respiration, coupled to the oxidation of organic matter. However, electron transfer processes occurring at the cell-mineral interface in these systems remain ill-defined. Understanding the complex biogeochemical interactions of bacteria with Co-Fe/Mn-oxides is critical for the exploitation of these future resources. Synchrotron-based scanning X-ray microscopy (SXM) was used to investigate changes in the speciation of metals and organic compounds at the nanoscale through X-ray absorption spectroscopy (XAS) coupled with geochemical data and transmission electron microscopy (TEM).

Enzymatic reduction of Co-rich Fe/Mn-minerals by *Geobacter sulfurreducens* was investigated and release of soluble cobalt was observed during reduction together with changes in mineral morphology. From bulk Mn *L*<sub>2,3</sub>-edge XAS data, the ratio of Mn(IV):Mn(III):Mn(II) changed from 58:17:25 to 30:28:42, indicating biogenic reduction of asbolane. However, from SXM data, collected at the nanoscale, areas associated with biomass experience a higher initial rate of reduction compared to areas not associated with biomass; although, all areas ultimately show the same extent of reduction. These results demonstrate the ability of subsurface reductive processes to release the critical metal Co from mixed mineral phases associated with ore minerals and the necessity for considering the spatial variability of subsurface reductive processes.