

## **Investigating the mechanism of microbial reduction of a cobalt-doped asbolane system using Scanning X-ray Microscopy (SXM)**

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Cobalt is a critical metal at supply risk due to the limited number of reserves and increased demand. Currently, cobalt is highly sought after due to its central role in rechargeable batteries for use in electric vehicles and portable devices, in addition to its use in high-tech alloys, therefore new sources of cobalt are necessary. Cobalt can be found within the structure of manganese minerals, such as asbolane  $[(\text{Ni},\text{Co})_x\text{Mn}^{4+}(\text{O},\text{OH})_4 \cdot n\text{H}_2\text{O}]$ , within lateritic ores and deep sea nodules, providing potential new sources for this critical metal. Dissimilatory metal-reducing bacteria, ubiquitous in the subsurface, can use Mn-oxides as a terminal electron acceptor for microbial reduction coupled to the oxidation of organic matter. Understanding the complex biogeochemical interactions of these bacteria with Co-Mn-oxides is critical for the exploitation of these future resources. Synchrotron-based scanning X-ray microscopy (SXM) can be used to investigate the speciation of metals and organic compounds at the cell-mineral interface at the nanoscale, providing information on the electron transfer processes occurring within these systems.

In this study, the enzymatic reduction of Co-doped asbolane by *Geobacter sulfurreducens* was monitored as a synthetic analogue for Co-Mn-oxides within the environment. There was a continual release of soluble cobalt during reduction and electron microscopy demonstrated changes in the mineral morphology during the experiment. Bulk X-ray Absorption Spectroscopy (XAS) at the Mn  $L_{2,3}$ -edge suggested reduction of Mn(III) to Mn(II), with stable proportions of Mn(IV). In contrast, nanoscale imaging using SXM at key timepoints suggested reduction from Mn(IV) to Mn(II) *via* a Mn(III) intermediate, when in close proximity to the cells. These results show the complexity of the cell-mineral interactions at the nanoscale.