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Investigating nanoscale electron transfer processes at the cell mineral interface in Co doped ferrihydrite using *Geobacter sulfurreducens* and a multi-technique approach

DAWN MELISA BUCHANAN[1], JONATHAN RICHARD LLOYD[1], BURKHARD KAULICH[2], LAURA NEWSOME[3], GERRIT VAN DER LAAN[4] AND VICTORIA COKER[1]

[1]University of Manchester
[2]Diamond Light Source Ltd
[3]University of Exeter
[4]Diamond Light Source

Presenting Author: dawn.buchanan@postgrad.manchester.ac.uk

Cobalt is an economically important metal at supply risk due to a limited number of reserves and increasing demand. A 68% increase in total cobalt consumption is forecast between 2015 and 2025 owing to its central role in rechargeable batteries, consequently, alternative cobalt sources are being investigated. Cobalt can be found incorporated in the crystal lattice of ferrihydrite [$Fe^{3+}_{10}O_{14}(OH)_2$] within lateritic ores and ferromanganese nodules, providing new sources for this critical commodity. Dissimilatory metal-reducing bacteria, ubiquitous in the subsurface, can use Fe(III)-oxides as terminal electron acceptors for microbial reduction coupled to the oxidation of organic matter; however, electron transfer processes occurring at the cell-mineral interface require further clarification. Understanding the complex biogeochemical interactions occurring is crucial for the exploitation of these resources and an understanding of the release of Co from these minerals. Synchrotron-based scanning X-ray microscopy (SXM) was employed to assess the variation in metal speciation at the nanoscale through X-ray absorption spectroscopy (XAS) coupled with geochemical data and transmission electron microscopy (TEM).

Geobacter sulfurreducens was used to biotically reduce a synthetic Co doped ferrihydrite in a system emulating enzymatic reduction of Co-Fe-oxides in the environment. Over the course of the experiment, the quantity of solubilised Co fluctuated and TEM demonstrated changes in the mineral morphology. In aggregate, SXM showed a spectral shift to lower photon energies [Figure. 1] and a change in ratio of Co(II):Co(III) from 80:20 to 100:0, signifying biogenic reduction of Co(III) at 72 hours. However, SXM collected at the nano scale detected significantly more Co(II) in areas associated with biomass indicating localised Co(III) reduction from 9 hours onwards. SXM illustrates the nuances of the system operating on the nano scale and demonstrates the need for direct contact between the cells and mineral surface during the enzymatic reduction of Co in these alternative resources.

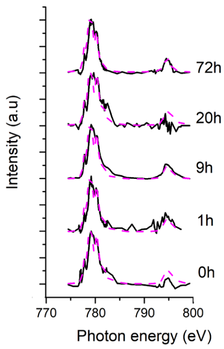

Figure. 1. A spectral summary of the aggregate SXM data during the bio-reduction of Co doped ferrihydrite using *Geobacter sulfurreducens* over 72 hours, where the black line is the gathered SXM data and the pink dashed line denotes the best fit spectra.