

Microbially mediated formation of a new REE enriched Mn-oxide, Ytterby mine, Sweden

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Characterization of a black substance seeping from fractured bedrock in a subterranean tunnel revealed a new, microbially mediated, secondary manganese oxide mineralisation, highly enriched in rare earth elements (REEs). This tunnel is dry and at shallow depth and was built to convert the former Ytterby mine, known for the discovery of yttrium (Y), scandium (Sc) and five rare earth elements, into a fuel deposit for the Swedish Armed Forces. As the type locality of these rare earth elements, the Ytterby mine gave its name to yttrium, ytterbium, erbium and terbium.

Geochemical analysis shows that the substance is enriched in REEs with concentrations one to two orders of magnitude higher than the surrounding rocks. Elemental analysis and X-ray diffraction establish that the main component is a manganese oxide of the birnessite type (general formula: $[\text{Na,Ca}]_{0.5}[\text{Mn(III),Mn(IV)}]_2\text{O}_4 \cdot x\text{Aq}$). There are also minor fractions of calcite, some other manganese oxides, feldspars, quartz and about 1% organic matter, but no iron oxides. Leaching studies (sequential and selective) were performed in order to establish how the minor components are associated with the matrix (in the lattice or merely adsorbed on the outer surface). It shows that the Ytterby birnessite contains about 1% REEs in the lattice, as well as calcium but no sodium.

Formation of birnessite by manganese oxidizing bacteria is well-known (e.g. Tebo et al, 2004). Quantitative PCR shows that the total number of bacteria in the Ytterby substance is in the order 10^{10} cells per g substance while the water feeding the fracture has in the order of 10^6 cells per ml groundwater. qPCR data further confirm that manganese oxidizing microorganisms are present and that the abundance varies with the seasons. Analysis of the precipitated manganese using electron paramagnetic resonance spectroscopy shows that the substance is composed of two or more components, with one part having a biogenic signature. The occurrence of C31 to C35 extended side chain hopanoids among the identified lipid biomarkers provides further evidence of bacterial presence in the depositional environment.

What makes the Ytterby birnessite unique is the incorporation of REEs in the lattice. Work is in progress to understand the process by which REEs are replacing other cations in the lattice and to further investigate the manganese oxidizing bacteria and their REE enriched ecosystem.

References:

Tebo B.M., Bargar J.R., Clement B.G., Dick G.J., Murray K.J., Parker D., Verity R., Webb S.M., (2004), Biogenic manganese oxides: Properties and mechanisms of formation. *Ann. Rev. Earth Planet Sci.* 32, 287-328.