

## REE-Enriched Mn-Oxide Precipitates in Water-Bearing Fractures in the Ytterby Mine, Sweden

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### Abstract

The Ytterby mine, Sweden, is known for the discovery of eight elements, including yttrium and five of the rare earth elements (REE). The mine was in operation from 1750 to 1933 and was after closure used as a storage depot for fuel from the 1950s to 1995. A tunnel was opened in the 1950s through the bedrock into the mine to allow access to the storage depot. Recent water monitoring campaigns (2012–2015) in the mine revealed a black substance (denoted YBS) in some fractures opening into the tunnel.

Analysis of the YBS (elemental analysis, phase analysis by XRD, SEM with energy dispersive X-ray spectrometry, IR- and EPR-spectroscopy, preferential leaching at pH 4) showed that the main mineral component of the YBS is the manganese oxide birnessite. Also minor quantities of other less well defined manganese oxides were found, as well as silicates (quartz grains, possibly feldspar grains) and calcite. Birnessite has typically the composition  $M_x(Mn^{3+}, Mn^{4+})_2O_4xAq$ , with M=Na,Ca and x=0.5. The birnessite component in YBS had a  $Mn^{3+}/Mn^{4+}$  ratio of 1.04/0.96 with M = 0.42 Ca + 0.03 (REE+Y), 0.03 Mg and 0.03 other metals. All of these metals were firmly associated with the structure, since no release was observed at pH 4, except for significant fractions of the total Na, Mg, Ca-contents. Thus, REE+Y correspond to 1% of the total YBS mass and up to 3% of the metal content in the birnessite phase. This corresponds to an REE enrichment factor of the order  $10^6$  (YBS-birnessite/fracture water). Birnessite with a substantial fraction of REE in the lattice has not previously been reported.

The formation of birnessite is a microbial process. Identification of the microorganisms present in the Ytterby system is in progress.

Key words: Mine water geochemistry, manganese oxide precipitation, birnessite, rare earth elements

### Introduction

The Ytterby mine located on Resarö in the Baltic Sea, Sweden, is known for the discovery of five of the rare earth elements (REE), as well as yttrium, scandium and tantalum (Enghag 1999). In the 1750s quartz and feldspars, were mined from Ytterby as raw materials used for the production of porcelain, and by 1933 the mine was closed. The mine, which is a single shaft with a depth of some 145 m, was used for storage of fuel from the early 1950s until 1995. A tunnel was opened through the bedrock into the upper part of the shaft, 29 m below ground surface but above the fuel storage level and 5 m above sea level.

A black soft precipitate with an oily appearance was observed, seeping from some of the fractures in the tunnel, during monitoring campaigns in 2012 and 2014, see Figure 1 (Sjöberg 2012; Sjöberg 2014). Analysis of this precipitate, which was also observed to occasionally produce gas bubbles, was the objective of the present study, focusing mainly on its mineralogical composition. Of particular interest was the investigation of associated trace elements and organics in this unusual environment with potential sources of REE as well as uranium and thorium in the bedrock.

A detailed description of the project is given by Sjöberg et al. 2016.



**Figure 1** Photo of the precipitate (YBS)

### Geology/hydrology

The bedrock in the Ytterby area is part of the crystalline basement of the Baltic Shield. Isotopic age determination of pegmatite from the region indicates an age of approximatively 1795 Ma (Romer and Smeds 1994). The pegmatite in the mine is bordered by amphibolites as well as gneiss. Some 50 minerals have been identified in the pegmatite, including 15 containing REE (Sundius 1948, Brotzen 1959).

The hydraulic conductivity in the bedrock in the mining area is of the order  $3 \times 10^{-8}$ m/s, corresponding to an inflow of water to the shaft of some 9 m<sup>3</sup>/day (Rydström 2001). The inflow comprises infiltrating precipitation, as well as intruding shallow groundwater, and deep groundwater to the lower parts of the mine shaft.

### Methods

The black precipitate (denoted YBS) from the tunnel leading to the mine shaft was collected during water sampling campaigns in 2012-15 using sterile equipment and stored in glass bottles prior to analysis. Water was collected in polyethylene bottles from fractures, the mine shaft and shallow groundwaters from several sampling holes near-by the mine. Samples were filtered (0.2 µm) and pH, temperature and conductivity were measured in the field. Samples for element analysis were acidified and stored in a fridge prior to analysis.

#### *Solid YBS characterization*

Analysis by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry was carried out (Stockholm University) in order to get compositional information, as well as a visual picture of the YBS.

Mineralogic phases were determined by X-ray diffractometry (XRD) (Stockholm University and Swedish Museum of Natural History).

Structural information was also obtained from infrared and electron paramagnetic resonance spectroscopy (Örebro University and Linköping University).

The various procedures and analyses are described in detail in Sjöberg et al. 2016.

### *Element analysis of YBS and water*

Solid samples of YBS were washed and dried and digested following different procedures. The digested YBS samples and the water samples collected in the field were analyzed at four different laboratories (by ICP-MS, ICP-OES; ALS Scandinavia, Sweden; Activation Laboratories Ltd, Canada; Örebro University, Sweden and Friedrich Schiller University, Germany).

### *YBS leaching*

A leaching test was performed in order to establish how minor components of the YBS were associated with the major matrix:

Exchangeable, carbonates, fresh hydroxides - leaching at pH 4 with 0.11 M HAc

### **Results and discussion**

The composition of the YBS (one of the four analyzed samples, also used in the leaching test) is given in Table 1.

**Table 1** Concentrations and leachable fractions at pH 4 of major components and trace elements above the 0.02%-level.

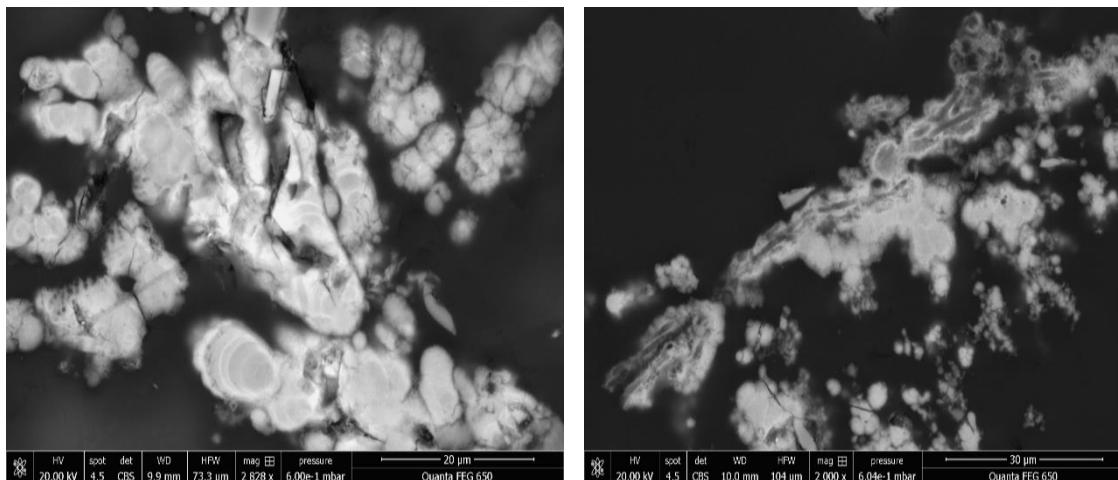
	YBS mg/kg	Leachate pH4 %		YBS mg/kg	Leachate pH 4 %
Na	320	44	Al	750	0
K	411	4	Si	2480	0
Mg	3590	47	V	471	0
Ca	60750	22	Mn	354065	2
Sr	635	20	Fe	790	0
Ba	1860	<1	Cu	1310	0
Y+REE	11410	0	Zn	421	0

The leachable fraction at pH 4 corresponds to exchangeable and adsorbed metals, as well as carbonates. The major component in the remaining YBS is Mn with 83.5% of the total mass of metals plus Si, followed by Ca (11.2%), REE+Y (2.7%), Na+K+Mg+Sr+Ba (1.1%), Al+Si (0.8%) and V+Fe+Cu+Zn (0.7%). The Al+Si-fraction can be attributed to silicate and quartz grains in the precipitate that is largely an oxide of Mn(III) +Mn(IV).

Scanning electron microscopy images (SEM) of YBS, Figure 2, show dendritic shrub-like or microspherolitic botryoidal morphologies with concentrations of Mn of 82-86%, Ca 8-13% Mg <2% and all other elements (besides O) <1%. Mn/Fe-ratios are above 100, comparable with the analyses, Table 1, giving Mn/Fe = 448. Individual quartz grains can be seen in some images, as well as calcite particles, not part of the Mn-oxide matrix.

A biogenic origin is indicated from the electron paramagnetic resonance spectroscopy that confirms the presence of a biogenic MnO<sub>2</sub> component having a spectral width of 600 Gauss, and an abiotic component with a spectral width of 1800 Gauss (Sjöberg 2014).

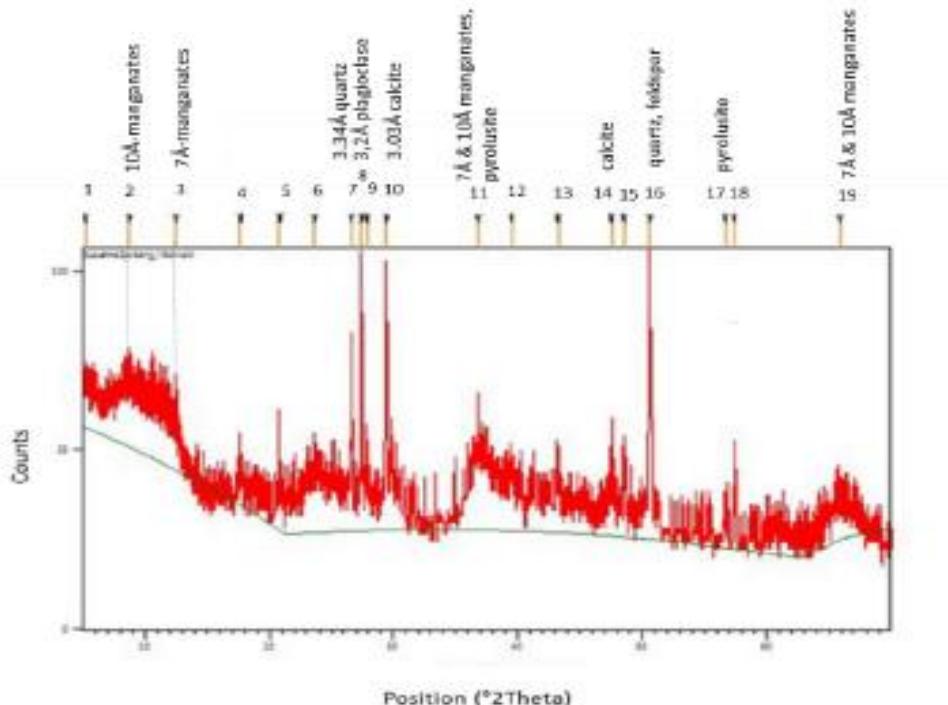
The infrared spectrum only shows one weak absorbance peak at 1630 cm<sup>-1</sup> (possibly C=O), as well as a pronounced absorbance below 800 cm<sup>-1</sup> indicating a dominating metal oxide, but no distinct C-H peaks.



**Figure 2** SEM images of the YBS

Carbon isotopic analysis has previously indicated that dried YBS contains about 1.8% carbon, including ca 0.6% that is organic ( $\delta^{13}\text{C}$  of -24.73; Sjöberg 2014). Leaching with an alkaline solution did not release the organic carbon (no humic acids), but solvent extraction and lipid extraction indicate that the organic carbon fraction contains a range of lipids which indicate that the YBS contains a biogenic fraction (work in progress).

X-ray diffractogram, Figure 3, confirms that YBS consists of some 80-90% of a manganese oxide of the birnessite type (typically  $M_{0.5}[\text{Mn(III),Mn(IV)}]_2\text{O}_4 \times \text{Aq}$ , where M usually is Na or Ca). There are also minor fractions of calcite, some other manganese oxides (manganates), as well as feldspars and quartz but no distinct iron oxide phase.



**Figure 3** X-ray diffractogram of the precipitate (Sjöberg 2014)

Concentrations, with omission of the leachable fraction (pH 4), and corresponding number of atoms/mol, assuming 2 manganese atoms in the birnessite unit, are given in Table 2. Two different cases are compared:

I: All of the manganese (except the leachable fraction) constitutes the birnessite phase

II: Only 90% of the non-leachable manganese constitutes the birnessite phase, with 10% in other non-defined manganate phases.

**Table 2** Composition of the proposed birnessite phase calculated from the concentrations of non-leachable major components and trace elements above the 0.02%-level

	YBS mg/kg	YBS mmol/kg	YBS atom/mol (I)	YBS atom/mol (II)
Mn	347560	6330	2	2
Ca	47380	1180	0.37	0.42
REE+Y	11410	85.5	0.025	0.030
Mg	1900	78.3	0.025	0.028
Na+K+Sr+Ba	2940	37.2	0.012	0.013
V+Fe+Cu+Zn	2990	50.4	0.016	0.016
Total			2.45	2.50

I: 98% of total manganese in birnessite

$M_{0.45}(Mn^{3+}, Mn^{4+})_2O_4 \times Aq$  with  $Mn^{3+}/Mn^{4+} = 0.94/1.06$

$M = 0.37 \text{ Ca} + 0.025 \text{ (REE, Y)} + 0.025 \text{ Mg} + 0.028 \text{ other metals}$

$\text{REE+Y} = 2.7\% \text{ of the metals, } 1.1\% \text{ of the total mass}$

II: 88% of total manganese in birnessite

$M_{0.50}(Mn^{3+}, Mn^{4+})_2O_4 \times Aq$  with  $Mn^{3+}/Mn^{4+} = 1.04/0.96$

$M = 0.42 \text{ Ca} + 0.030 \text{ (REE, Y)} + 0.028 \text{ Mg} + 0.029 \text{ other metals}$

$\text{REE+Y} = 3.0\% \text{ of the metals, } 1.1\% \text{ of the total mass}$

The composition according to assumption II is close to the ideal composition, however with 0.03 (REE+Y) in the structure.

The source of manganese is the groundwater; there are no accumulations of discrete manganese minerals in the bedrock surrounding the mine. The source of REE is obviously the REE-rich minerals in the pegmatite.

Some water data are given in Table 3, representing present oxic conditions with substantial in-flow of precipitation and shallow groundwater into the mine and the water-bearing fractures above the groundwater level (from the 2015 campaign, Förster 2015). All of GW 2, Shaft and Fracture waters have presently a Ca-carbonate signature and a high pH. Groundwater GW 1, from a sampling hole close to the Baltic Sea, has a Na-carbonate signature with a higher sulfate level. Considerably higher concentrations have been recorded of all the major species, including manganese, in deep groundwaters in the area (Augustsson et al. 2009) as well as in the shaft (anoxic conditions with little inflow of surface water). However, no older records showing past levels of REE in the mine or in the groundwaters are available. Therefore, data in Table 3 may not be representative of the conditions during the early years of the tunnel, when precipitation of birnessite was initiated. However, an enrichment factor, defined as [Concentration in solid YBS]/[Concentration in solution], [Lit/kg] would be of the order  $10^6$  when calculated using present day concentrations.

**Table 3** Present water chemistry in shallow groundwaters and fracture water

	GW 1 mg/l	GW 2 mg/l	Shaft mg/l	Fracture mg/l
pH	8.17	7.95	8.29	8.30
Cl <sup>-</sup>	10.5	10.5	24.4	15.3
SO <sub>4</sub> <sup>2-</sup>	51.7	21.5	29.7	29.4
HCO <sub>3</sub> <sup>-</sup>	240	21.5	29.7	29.4
DOC	8.2	6.6	8.0	4.2
Na	102	34.2	19.3	28.4
K	3.08	1.75	4.83	1.54
Mg	3.81	5.51	7.99	7.71
Ca	13.4	51.0	59.7	53.4
Mn	1.31	1.09	1.80	2.77
REE+Y	0.0011	0.0018	0.0028	0.0068

GW 1, GW 2: Shallow groundwater within 50 m from the mine

Shaft: Surface water in the shaft

Fracture: Water in fracture with YBS precipitate

## Conclusions

The black precipitate discovered in Ytterby mine tunnel fractures is mainly birnessite, together with other manganese oxide phases not yet specified. In addition minor fractions of quartz, feldspars and notably calcite, not associated with the birnessite were found. The birnessite appears to have a biogenic origin, as indicated by the morphology (SEM) and by the presence of some 0.6% organic carbon, containing lipids and no humic substances. An arbitrary composition can be assessed as M<sub>0.5</sub>(Mn<sup>3+</sup>,Mn<sup>4+</sup>)<sub>2</sub>O<sub>4</sub>xAq, where M = 0.42 Ca + 0.030 REE,Y + 0.028 Mg + 0.029 other metals, with a Mn<sup>3+</sup>/Mn<sup>4+</sup> - ratio of 1.04/0.96. The REE fraction appears to be a structural component in the birnessite and not only adsorbed and easily exchangable. What makes the YBS-birnessite unique is the REE-enrichment: Ca 3% of the metal content, corresponding to 1.1% of the total mass.

Work is in progress to assess the formation process, where REEs are replacing sodium and largely calcium in the lattice, and to identify if manganese oxidizing bacteria are involved in the formation of this REE enriched birnessite.

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