

## **RARE EARTH ELEMENT PATTERNS RELATED TO BIOREMEDIATION PROCESSES IN A SITE INFLUENCED BY ACID MINE DRAINAGE**

*Dirk Merten, Anja Grawunder, Martin Lonschinski, Christian Lorenz and Georg Büchel  
Friedrich-Schiller-University, Institute of Earth Sciences, Burgweg 11, 07749 Jena, Germany*

### **Abstract**

Tremendous values of up to 8 mg/L total REE (Rare Earth Elements) are observed in ground water affected by Acid Mine Drainage (AMD) in a former uranium mining area of Eastern Thuringia, Germany. The distribution of REE is applied to study processes in (bio)remediation of AMD. Normalization of REE concentrations in water to Post Archean Australian Shale (PAAS) shows strong enrichment of middle and heavy REE and for the case of the former leaching dump "Gessenhalde" also a characteristic positive Ce anomaly. For the case of AMD, REE patterns are representative for the seepage location and can be used to identify (former) waste rock dumps as a source of contamination. The cycling of heavy metals in the system soil – water – biota was investigated. On a former leaching dump planting experiments with and without the addition of microbes were performed. Sequential extraction reveals high bioavailability of heavy metals making the site interesting for studying bioremediation. Hydrochemical analyses of soil water and ground water revealed large heterogeneity in distribution of heavy metals. The remobilisation of earlier formed hardpans is the most probable reason for the observed contamination of ground water and seepage water.

### **Introduction**

The uranium mining area of Ronneburg and Seelingstädt, Eastern Thuringia (Germany) produced about 200 kt of uranium in the years 1946 – 1990 (Jakubick et al., 1997). These extensive mining operations resulted in, among other things, large open pit mines and waste rock piles. Rain infiltrated into the dumps only partly covered and seepage water with a pH below 3 and high metal load was observed. The seepage contaminated surface and ground water and the valley sediments.

During the active mining period (1971-1990) low graded ore substrate containing radionuclides was leached on the ancient leaching heap "Gessenhalde" with Acid Mine Drainage (AMD) and sulphuric acid (Beleites, 1992). The leachate containing high concentrations of heavy metals and radionuclides infiltrated through the barrier soil and was retained in the glacial sediments underneath. Precipitating Fe-minerals contain large amounts of heavy metals and radionuclides due to coprecipitation (Carlsson, 2005). The risk of remobilisation of heavy metals has to be minimized. Bioremediation could be a cost-effective means for decontaminating these slightly and heterogeneously contaminated sites.

A subarea of the former leaching heap is used to investigate the processes of mobilization and immobilisation of radionuclides on the field and on the laboratory scale using rare earth elements (REE). Below a pH of 5.1, REE act as conservative tracers in the aqueous phase and can be used as fingerprints for specific element compositions. Fractionation of REE is an important indicator for several bio-geochemical processes (Merten et al., 2005). These include the sorption of heavy metals/radionuclides to microorganisms and plants or the active uptake by them. Furthermore, processes such as forming and dissolution of specific minerals and other reactions dealing with AMD are another field for identification by REE patterns (Merten et al., 2004).

The investigations comprise geological and hydrochemical conditions on the testing area, analyses of soil, groundwater, seepage water and planting tests with and without the addition of microbes.

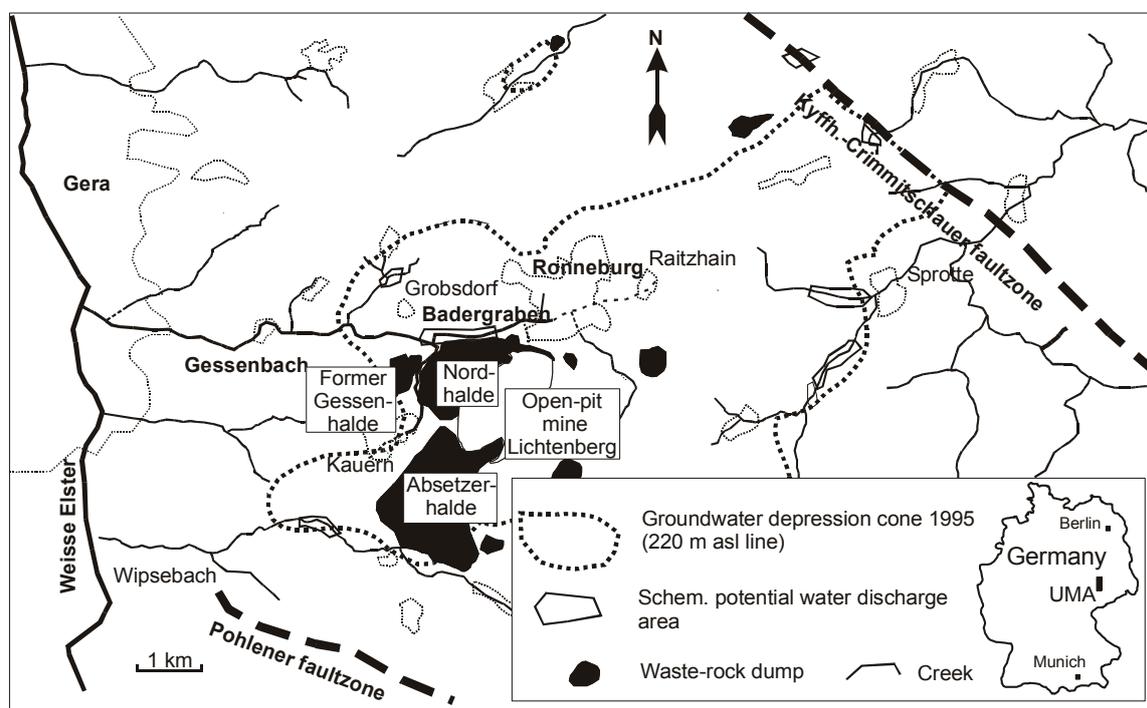
### **Methods**

Surface water samples (100 ml each) were collected at the western boundary of the former waste rock dump "Nordhalde" (still being present during investigation time), at the northeastern boundary of the former dump "Gessenhalde" and along the Gessenbach creek. Groundwater samples were taken from groundwater wells installed on the former leaching dump „Gessenhalde“. The water samples were filtered in the field using cellulose acetate filters (Sartorius, Germany) with a pore size of 0.45 µm. The pH, electrical conductivity, redox potential and temperature of the unfiltered samples were measured in the field using portable instruments pH320, LF320 and an external thermocouple (WTW Wissenschaftlich Technische Werkstätten, Germany). An aliquot of 100 µl HNO<sub>3</sub> (65 %, Baker Ultrex, USA) was added to 50 ml of the water samples for stabilization.

Sequential extraction was performed according to the scheme described by Zeien and Brümmer (1989). In brief, 2 g of air dried soil were eluted sequentially with 1 M NH<sub>4</sub>NO<sub>3</sub>, 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 6.0), 0.1 M NH<sub>2</sub>OH-HCl + 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 6.0), 0.025 M NH<sub>4</sub>-EDTA (pH 4.6), 0.2 M NH<sub>4</sub>-Oxalatebuffer (pH 3.25) in the darkness and finally 0.1 M Ascorbic acid in 0.2 M NH<sub>4</sub>-Oxalatebuffer (pH 3.25).

To determine the total content of metals about 100 mg of the dried and ground soil samples were digested using 4 ml 40% HF and 4 ml 70% HClO<sub>4</sub>, both of Suprapur quality (Merck, Germany) in a pressure digestion system (DAS, PicoTrace, Germany). About 100 mg of biomass (plants and microbes) was digested with nitric acid (65%, subboiled) in a microwave assisted pressure digestion system (Mars 5, CEM, Germany). A hardpan layer

was sampled on the former leaching dump “Gessenhalde” and for different values of pH the elution of elements into deionized water was investigated. All solutions were analyzed for their element content by inductively coupled plasma mass spectrometry (ICP-MS; PQ3S and XSeriesII, ThermoElectron, Germany) and inductively coupled plasma optical emission spectrometry (ICP-OES, SpectroFlame, Spectro, Germany).



**Figure 1. Northern part of the former uranium mining site Ronneburg, Germany (1950-1990) (UMA: uranium mining area Ronneburg).**

## Results and Discussion

The seepage water from the (former) dumps can be characterised as Mg-Ca-SO<sub>4</sub><sup>2-</sup>-type, being typical for AMD. Seepage water G16 had a pH between 3 and 5.5, total dissolved solids (TDS) in the range of 4-5 g/L and high redox potentials of typically 400-500 mV. The seepage waters in the western part of the Nordhalde, concentrated in the seepage leakage Q4, were also highly mineralized (TDS about 10 g/L), with an even lower pH (2.0-3.6) and also high redox potentials.

The total REE concentration in seepage water Q4 North varied between 1600 and 3000 µg/L in 1999 to 2001. Such high REE concentrations in seepage waters are only found in areas affected by AMD. After normalising REE concentrations in seepage waters to Post Archean Australian Shale (PAAS) (Taylor and McLennan, 1985) an enrichment of middle REE (Sm to Dy) and especially of heavy (Ho to Lu) REE as compared to the light ones (La-Nd) is observed. For the seepage water of the Nordhalde (Q4 North), sampled over a period of two years, the shale normalized REE patterns look the same, although the concentration differs significantly (Fig. 2). For sample Q4 North the enrichment of heavy REE over the light ones expressed as (Lu/La)<sub>SN</sub> is calculated to be 42±2 (N=4). It is interesting to note that the REE patterns show variations in the range of only a few % relative standard deviation and thus within the analytical error, although the sampling period covers about two years. This has also been shown for two other seepage water sampling sites of the Nordhalde sampled between June and September 2001 (Merten and Büchel, 2004). It was also reported by Verplanck et al. (2004) for sulphate-rich AMD that REE do not fractionate at pH below 5.1. Thus, under acidic conditions REE can be used as conservative tracers and REE patterns can be used as fingerprints of acid mine drainage from waste rock dumps contaminating surrounding valley sediments, creeks and groundwater.

For the former leaching heap “Gessenhalde” heavy metals including REE are distributed very heterogeneously. Total REE concentrations of up to 8 mg/L were determined in groundwater samples. However, the most characteristic feature is a positive Ce anomaly observed in most water samples from the former leaching heap. Cerium is immobile at oxidising conditions since CeO<sub>2</sub> is precipitated. This process was likely to occur during oxidative leaching of the uranium ores. Precipitated Ce is now remobilised. The formation of the positive Ce anomaly and also the enrichment of middle and heavy REE can be monitored by elution of secondary precipitates found in a hardpan layer. With decreasing pH, an increase in the total REE concentration, Ce anomaly and also enrichment of middle and heavy REE is observed. Thus, by the use of REE patterns secondary minerals can be identified as source for the contamination of ground and soil water still observed at the former dump.

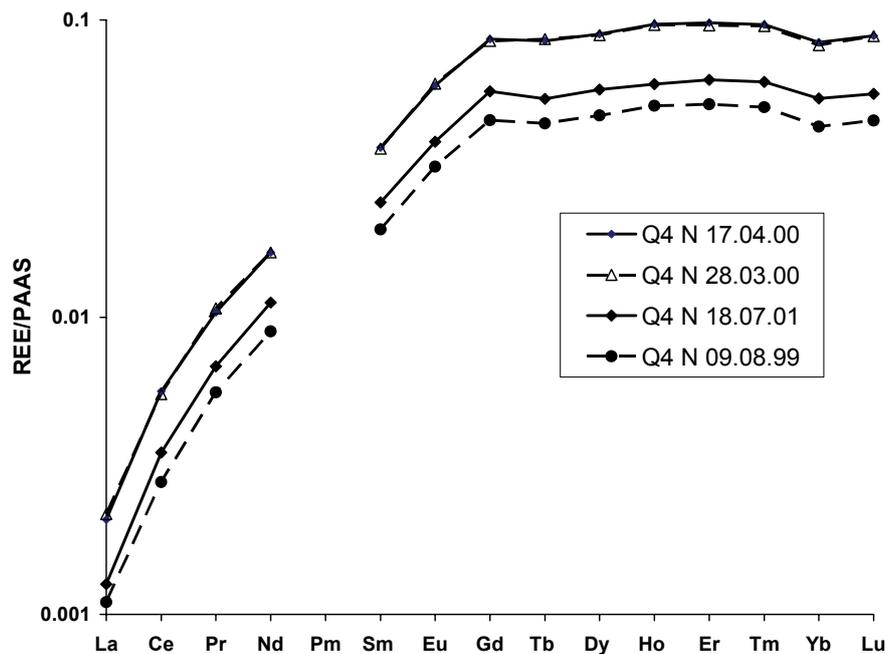


Figure 2. REE patterns of the seepage water site Q4 North (Q4 N) sampled over a period of about two years.

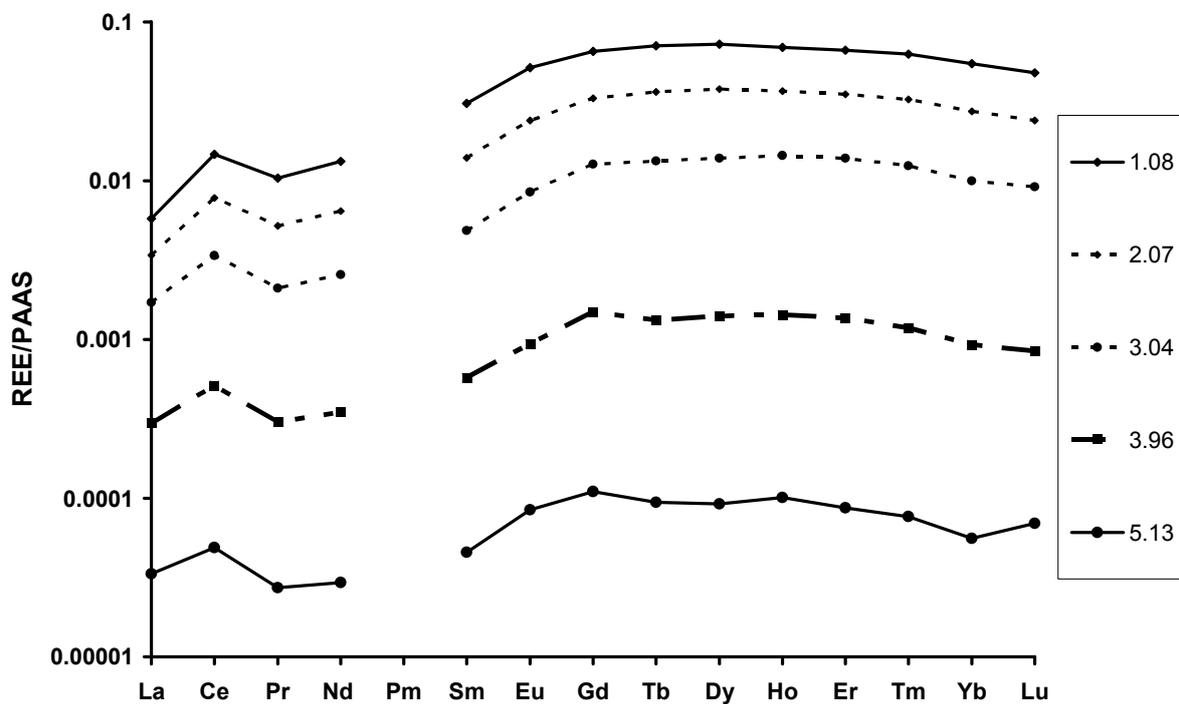
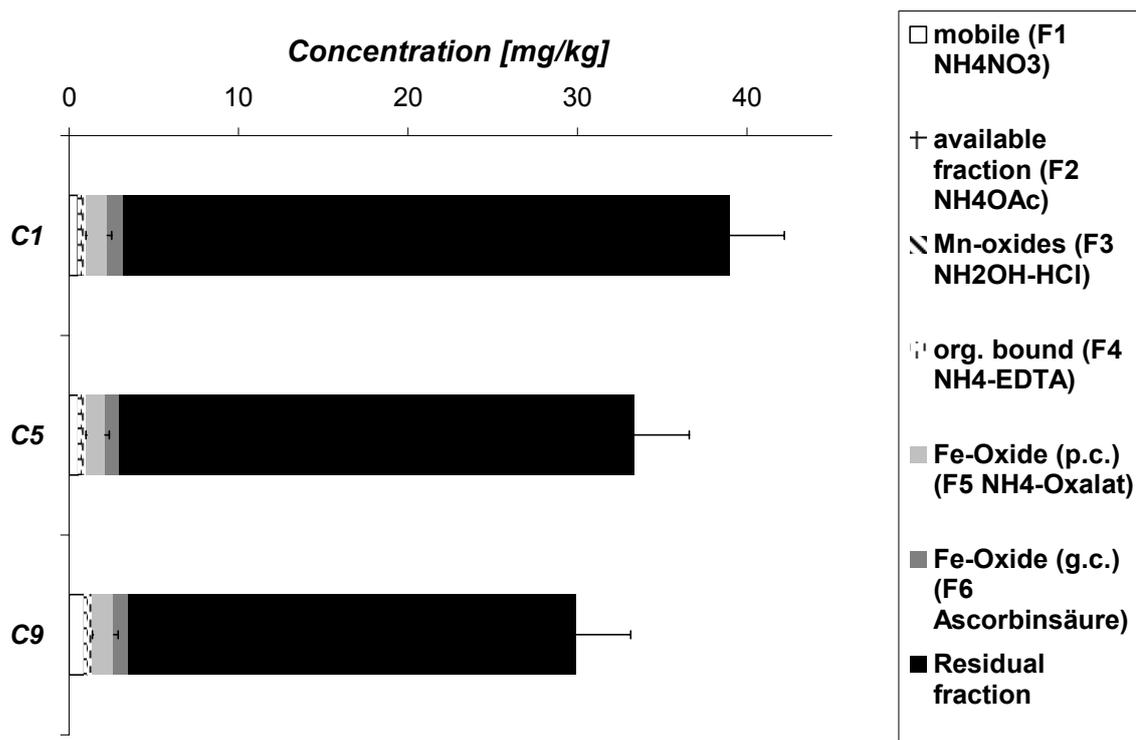


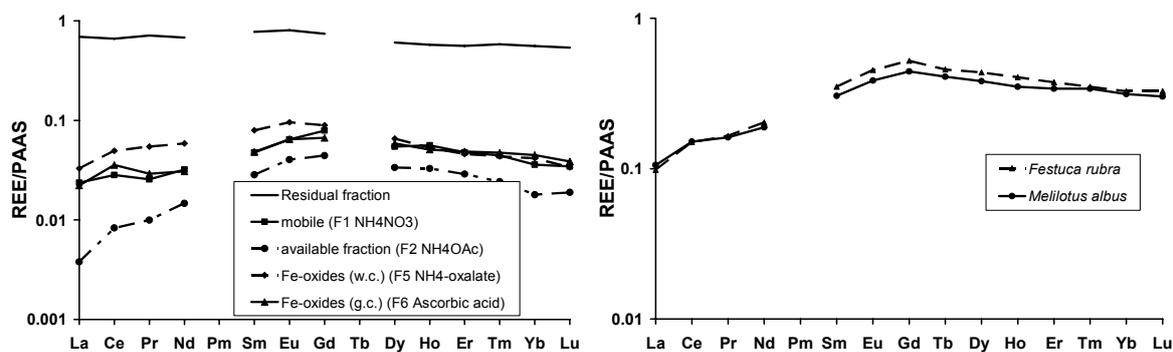
Figure 3. Elution of REE from a hardpan material in the pH range 1 to 5.

For the investigation of bioremediation the binding of heavy metals in the soil substrates used for planting experiments has to be determined. For this purpose a sequential extraction scheme was applied. As can be seen from Figure 4, La is mainly bound in the residual fraction, accessible only by a digestion. The next important fractions are good and poorly crystalline Fe-oxides. However, a significant portion of La is also found in the mobile fraction and thus is bioavailable, making the site attractive for bioremediation studies.



**Figure 4. Binding characteristics of La in soil from an untreated plot (Control) from the test field site on the former uranium leaching heap "Gessenhalde" as obtained by sequential extraction.**

When looking on the REE patterns of various fractions of the sequential extraction (see Fig. 5 left) and comparing them to the REE patterns found for the roots of *Festuca rubra* and *Melilotus albus* (see Fig. 5 right) grown on the investigated soil, it becomes obvious that the residual fraction is not of influence for the distribution of REE in plant roots, although it is the major fraction for REE.



**Figure 5. REE patterns in selected fractions from sequential extraction (left) and REE patterns in roots of *Festuca rubra* and *Melilotus albus* (right) grown on the corresponding soil.**

In contrast the REE patterns of the mobile, the available fraction and also the fractions bound to Fe-oxides are rather similar to the REE patterns found in the plant roots. Since both plant species show the same REE patterns in roots, it seems probable that REE were not strongly fractionated during root uptake, making sequential extraction a useful tool to study the transfer of heavy metals from soil to plants.

## Conclusions

REE patterns can be used to identify seepage water sites as the sources of contamination of surface and ground water and valley sediments. The main reason for the still observed contamination is the remobilization of heavy metals from secondary precipitates. Due to the low pH of soil water and groundwater, REE are mobile and bioavailable, making them useful tracers in bioremediation studies.

### **Acknowledgements**

This work was supported by the German Federal Ministry for Education and Research (BMBF) under grant no. 02S8294.

### **References**

- Beleites M. (1992). Altlast Wismut: Ausnahmezustand: Umweltkatastrophe und das Sanierungsproblem im deutschen Uranbergbau.- 1. Aufl., Brandes und Apsel, Frankfurt (Main).
- Carlsson E., Büchel G. (2005). Screening of residual contamination at a former uranium leaching site, Thuringia, Germany. *Chem. Erde* 65 S1, 75-95.
- Jakubick A.T., Gatzweiler R., Mager D., Robertson A.M. (1997). The Wismut waste rock pile remediation program of the Ronneburg mining district, Germany. *Proceedings Fourth International Conference on Acid Rock Drainage*, held in Vancouver, B.C./Canada, May 31 - June 6, 1997; Vol. III, 1285-1301.
- Merten D., Büchel G., Kothe, E. (2004). Studies on microbial heavy metal retention from uranium mining drainage water with special emphasis on rare earth elements. *Mine Water Environm.* 23, 34-43.
- Merten D., Geletneky J., Bergmann H., Haferburg G., Kothe E., Büchel G. (2005). Rare earth element patterns: A tool for understanding processes in remediation of acid mine drainage. *Chem. Erde* 65 S1, 97-114.
- Taylor S.R., McLennan S.M. (1985). *The Continental Crust: Its Composition and Evolution*. Blackwell, Oxford, UK, 312 p.
- Verplanck P.L., Nordstrom D.K., Taylor H.E., Kimball B.A. (2004). Rare earth element partitioning between hydrous ferric oxides and acid mine water during iron oxidation. *Appl. Geochem.* 19, 1339-1354.
- Zeien H., Brümmer G.W. (1989). Chemische Extraktion zur Bestimmung von Schwermetallbindungsformen in Böden. *Mitt. Dt. Bodenkundl. Ges.* 59, 505-510.