Hydrogeochemistry of rare earth elements in an AMD-influenced area

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Abstract The hydrogeochemistry of rare earth elements (REE) in the former uranium mining area of Ronneburg/Germany was studied with emphasis on processes leading to their fractionation. In the acidic groundwater, REE concentrations of up to 8.15 mg/L were measured. Normalisation resulted in site-specific characteristics: Enrichment of middle (and heavy) REE was related to the host rock leaching during former heap operations. The stronger variability of heavy REE was associated with a stronger pH-dependant fractionation compared to light REE and middle REE. A distinctive positive Ce-anomaly reflects the interaction of Ce with Mn-(hydr)oxides as found with LA-ICP-MS.

Key Words rare earth elements, LA-ICP-MS, Ce-anomaly, AMD

Introduction

The study was carried out at the former leaching heap Gessenhalde situated in the former uranium mining area of Ronneburg/Germany (fig. 1). There, between 1971 and 1989 Palaeozoic shales with a low grade uranium mineralization were leached with acid mine drainage (AMD; until 1978) and later on with sulphuric acid (10 g/L; Wismut-GmbH, 1994). A part of the leachate seeped through the lining and caused a contamination of the Quaternary sediments underneath the heap.

In 1989, the leaching was stopped. During the 1990's the Gessenhalde was filled into the nearby open pit Lichtenberg and its basement was remediated. In 2005, in this area the test site Gessenwiese was installed with the purpose of improving strategies of bioremediation and studying the behaviour of metals in the system water-soil-plant. Previously, the geological underground of this site as well as the metal contents of the sediments were described. Especially Cr, Cu, Ni, Mn, U, and Zn in the sediments exceeded reference values (Grawunder et al., 2009). A special group of heavy metals studied at the test site Gessenwiese is the group of rare earth elements (REE) comprising the elements La to Lu. These elements behave chemically coherent. They are often subgrouped into light REE (LREE: La-Nd), middle REE (MREE: Sm-Dy) and heavy REE (HREE: Ho-Lu). After normalisation to a suitable standard as e.g. the Post Archean Australian Shale (PAAS; McLen-

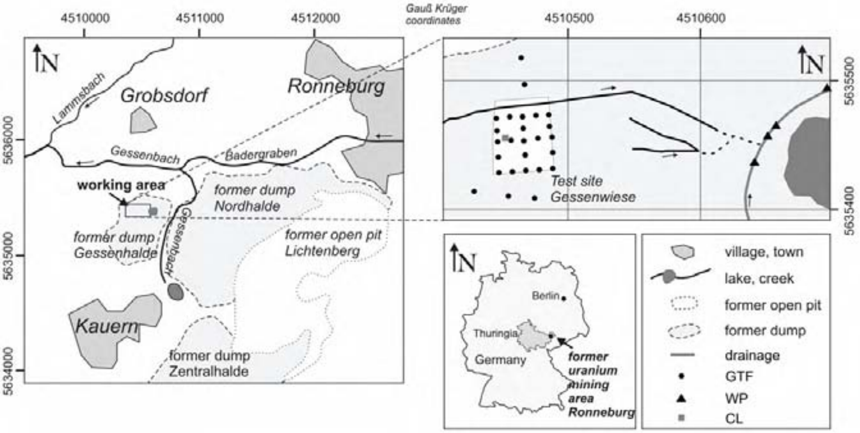

***Figure 1** Location of the working area test site Gessenwiese at the basement area of the former leaching heap Gessenhalde in the uranium mining area of Ronneburg/Germany. GTF indicates groundwater measuring point, WP the sampling points of white Al-flocs and CL the sampling point of the cemented layer*

nan, 1989) fractionations and anomalies among the REE become apparent what makes them suitable tracers for studying processes in the system water-soil-plant. This study aims to rule out factors and processes responsible for the typical features of the PAAS-normalised groundwater REE pattern of the test site Gessenwiese. Therefore, besides water and sediments, secondary precipitations occurring as cemented layers (CL) in various depths and as white flocs (WP) in a surface near drainage were sampled and evaluated in combination with laboratory experiments. The latter ones comprise leaching experiments of shale material similar to the former heap material to evaluate the input REE-pattern from the heap and pH-titrations of groundwater focussing on REE fractionation due to changing pH.

Methods

For groundwater sampling between December 2004 and September 2009, 22 wells were installed within a grid at the test site. Eh and pH were determined in situ using portable instruments (pH320; WTW). Samples were filtered in field to <0.45 µm using cellulose acetate filters (Sartorius). Water samples for element (cation) analysis finally were acidified with HNO_3 (65 %, subboiled) to pH < 2. To evaluate the response of REE fractionation to pH change, the pH of 100 ml of groundwater (in triplicates) was increased with 3.5 % NH_4OH-solution using an automatic titration system (Titrino 716 DMS, Metrohm). Then solutions were centrifuged, sampled and titrated to the next pH. Denotation is pH xx were xx represents the particular pH.

Samples of the white flocs were freeze dried (Christ-Alpha 1—4 LSC) and homogenised. 100 mg of each solid sample (sediments, WP, CL) were digested in a pressure digestion system (DAS, PicoTrace) using strong acids (40 % HF, 70 % $HClO_4$, 65 % HNO_3).

The shale material for batch elutions was crushed to less than 5 mm. For elution 3 to 4 grams of the material were eluted with 10 g/L H_2SO_4 in a ratio of 1:10 (solid: liquid) in triplicates.

The anion concentrations of Cl^-, F^- and SO_4^{2-} in the groundwater samples were analysed by ion chromatography (DX-120, Dionex). Element concentrations in groundwater, digestion and batch solutions were measured with inductively coupled plasma-optical emission spectrometry (ICP-OES; Spectroflame, Spectro) and inductively coupled plasma-mass spectrometry (ICP-MS; PQ3-S, Thermo Elemental until 2007, then X-Series II, Thermo Fisher Scientific).

LA-ICP-MS (laser ablation Microprobe II, Merchantek; inductively coupled plasma mass spectrometry, X-Series II, ThermoFisher Scientific) was used to obtain information on the spatial distribution of heavy metals within the cemented layers (CL). Mineralogical studies were carried out with X-ray diffractometry (XRD; FPM XRD7, Seifert) and microprobe SX50 (Cameca; BSE pictures and EDX).

Results and discussion

The input signal of the heap is mainly controlled by Palaeozoic shales dumped at the heap. Leaching of such shales showed enrichments in MREE and HREE (fig. 2). A further input by AMD used during the leaching between 1971 and 1978 can not be evaluated today. The Quaternary sediments below the heap did not diverge strongly from distribution in the PAAS standard. Only HREE were slightly depleted in some samples (Grawunder et al., 2009). Thin massive cemented layers found at the test site with goethite as cementing agent are enriched in MREE and HREE compared to LREE (CL, fig. 2). Furthermore, at a mixing point of seepage water and surface water in a nearby drainage system (fig. 1) white, X-ray amorphous Al-flocs were sampled. REE patterns showed an increasing enrichment from La to Lu (WP, fig. 2).

The groundwater at the test site Gessenwiese was of Mg-(Ca)-SO_4^{2-} water type, oxic (Eh: 530—630 mV), acidic (pH: 3.2—5.4) and enriched in Al (1—308 mg/L), Mn (5—507 mg/L), Co (0.1 to 20.1 mg/L), Ni (1 to 56 mg/L), and REE (11.4 to 8148 µg/L). After normalisation to PAAS, the patterns revealed four site typical features: i) MREE enrichment compared to LREE and HREE; ii) HREE enrichment compared to LREE; iii) a distinctive positive Ce-anomaly and in some measuring points also iv) a slight positive Gd-anomaly (fig. 2). The concentrations in each measuring point vary, but the REE patterns within nearly all single measuring points were found to be very stable during the sampling period 2004—2009. Furthermore, it was found that REE concentration increases stronger below a pH of 4.5 to 4.7. This pH is assumed not only to be critical for REE concentration in groundwater, but also for fractionation as shown with titration experiments indicating no or less fractionation below pH 4.5. Then, especially HREE fractionate with increasing pH. With regard

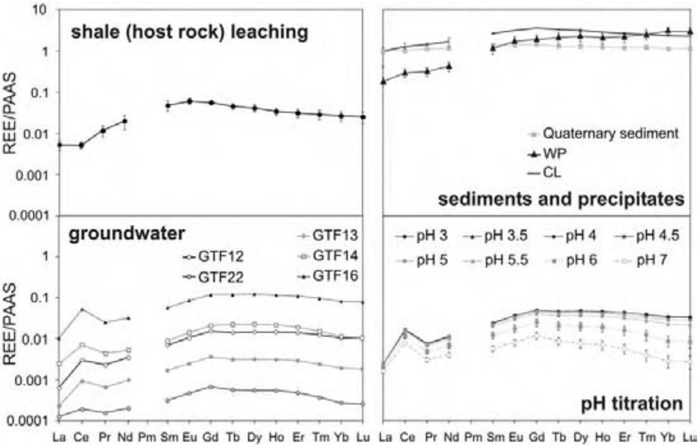

Figure 2 *The shale leaching (upper left) represents the MREE and HREE enriched input signal to the Quaternary sediments below. Those appeared quite similar to PAAS (upper right). Secondary precipitations like goethite cemented layers (CL) or Al-precipitates (WP) were enriched in MREE and HREE, respectively. The REE groundwater concentrations are varying, being generally lower in the southern test site. The patterns are slightly different, but all characterised by the four typical features (see text) (lower left). Groundwater titration revealed stronger pH dependence of HREE compared to MREE and LREE (upper right)*

to other elements, firstly Fe partitions until pH 4.5, followed by Al until pH 5.5. However, sorption to sediments was not considered in this experimental setup, but may play an important role as well. A slight geogenic Gd-anomaly develops with increasing pH. Gd is known to be special among the REE with regard to electron configuration. Titrations experiments of water with higher content of Fe resulted in higher Gd-anomalies. However, distribution coefficients between solution and ferric (hydr)oxides show Gd-anomalies, indicating a higher affinity of Gd to remain in solution (e.g. Bau, 1999). This process is pH dependant, but depends also on the amount of sorbent, in this case ferric (hydr)oxides that are quite common in the sediments of the test site Gessenwiese and proved previously (e.g. Carlsson and Büchel, 2005). Another REE, displaying anomalies is Ce. An indication therefore, was found by LA-ICP-MS studies of a goethite cemented layer (fig. 3). While

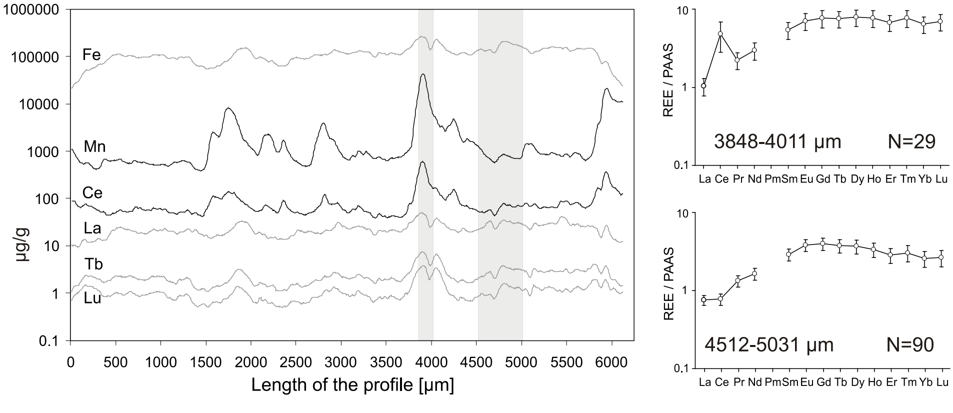

Figure 3 *Distribution of Fe, Mn, as well as La, Ce, Tb, and Lu as representatives of the REE within the cemented layer. Ce was found to correlate with Mn, while the other REE show rather a similar distribution as Fe (left). Measurements of selected segments showed after PAAS normalisation two different REE patterns with a positive Ce-anomaly in Mn-rich segments (right)*

all REE showed a similar spatial distribution as Fe, Ce rather correlated with Mn. Ohta and Kawabe (2001) described the oxidation of Ce^{3+} to Ce^{4+} by Mn-oxides. Mn-(hydr)oxides were found by microprobe studies (BSE, EDX) in thin cracks running through the cemented layer, but are also known to precipitate in the groundwater fluctuation zone (Burkhardt et al., 2009). Thus, rising groundwater table would dissolve these Mn-minerals and the associated Ce due to low pH and cause a stronger Ce-input to the groundwater compared to other REE, resulting in a positive Ce-anomaly.

Conclusion

The REE pattern in the groundwater of the study area was found to be a result of a source-input signal of the leaching process that is modified by recent processes. Increase in pH especially fractionates the HREE. The Ce-anomaly was found to be a result of interaction with Mn-(hydr)oxides; the slight Gd-anomaly was traced back on interactions with Fe-(hydr)oxides. In groundwater, REE have high concentrations making them a useful tracer for environmental studies.

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