Prospects of rare earth elements and other heavy metals as tracers in acid rock drainage (ARD) at the former uranium mining site of Ronneburg, Thuringia

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Between 1950 and 1990 the Ronneburg mining district in the eastern part of Thuringia (Germany) was one of the largest uranium mining sites in the world. Since 1990 the remediation of the mining site is realized with the aim to reduce the concentrations of radionuclides and heavy metals in groundwater and surface waters. The remaining waste rocks mainly consists of black shales, metabasaltic rocks and carbonate of Ordovician to Devonian age, containing up to 7 wt% sulfides, 5–9 wt% organic carbon, 30-60 ppm uranium and a series of trace elements including rare earth elements (REE).

Aim of this study is to investigate the influence of acid rock drainage (ARD) of waste rock dumps on valley sediments, groundwater and adjacent creeks. High concentrations of SO_4^{2-}, Al, Ca, Cu, Fe, Mg, Mn, Ni, U, Zn, and REE were found in the seepage water. Utilizing REE concentrations (up to 3 mg/l total REE) normalized to shale, flow paths of seepage water in the surface water and in shallow groundwater of the valley sediments were detected.

1 Introduction

1.1 Background

The Ronneburg mining district (Fig. 1) in Eastern Thuringia (Germany) was one of the largest uranium mining sites in the world. Between 1950 and 1990 about 216000 t of uranium were produced in the eastern part of Germany. After the USA and Canada the former GDR was the third largest uranium producer in the world (BARTHEL 1993). About half of the production (113000 t) originated from the underground and the open pit operations near the city of Ronneburg. By the end of 1990 the mining legacy consisted of (i) a complex underground mine covering an area of 74 square kilometers with 40 shafts and about 3000 km of mine workings, (ii) the Lichtenberg open pit mine with an open volume of about 84 Mio. m³, (iii) 16 waste rock dumps with about 200 Mio m³ of partly acid generating waste rock, and (iv) about 1000 ha of contaminated areas.

Starting in 1990 the remediation projects are mainly aimed at reducing the radiological and chemical exposure of the public and the environment (GATZWEILER et al. 1997). One of the remediation topics is backfilling the former waste rock dumps into the open-pit mine of Lichtenberg. The passive flooding of the mine was initiated in 1998 and is expected to be completed between 2003 and 2005. The investigation area "Gessental" valley is expected to be the main discharge area for the flooding water in the future (GELETNEKY 2002; UNLAND et al. 2002).

1.2 Rare earth elements

REE (La-Lu) show smooth but continuous variations of their chemical behaviour as a function of their atomic number. After standardization to PAAS (Post Archean Australian Shale) (TAYLOR & MCLENNAN 1985) they can be used as tracers in ground water and surface water (JOHANNESSON 2000). Furthermore, they are suited to study processes such as dissolution, sorption, complexation (ASTROM 1993), (co)precipitation (BYRNE & KIM 1993) and especially water-rock interaction (WORRALL et al. 2001). The use of PAAS-normalized REE in flooded mines (WOLKERSDORFER 2002) and in acid rock drainage (MERTEN et al. 2002) show examples for their successful application as environmental tracers.

2 Geology

The uranium deposit of Ronneburg, Thuringia, Germany, is a strata-controlled, structure bound deposit. It consists of uranium concentrations in small scale brittle structures which form stockworks within or immediately adjacent to carbonaceous, pyritic black shales. The Paleozoic host rocks mainly consist of argillaceous and siliceous black shales with intercalations of dolomitic and phosporite nodule beds (Silurian "Graptolithenschiefer"). The main black-shale horizon lies below Ordovician carbonaceous sandy shales and overlies Silurian carbonate rocks ("Ockerkalk"). Some Devonian metabasaltic dikes and sills cut the metasedimentary rocks (DAHLKAMP 1993). The rocks contain up to 7 wt% sulfides, 5-9 wt% organic carbon, 40–60 ppm uranium and a series of trace elements.

The intensively folded and faulted, incompetent and competent rocks have high density small scale brittle structures (fissures, joints, faults). Permian and Tertiary supergene oxidation processes associated with mobilization and precipitation of trace elements created an oxidation and cementation zone. The irregular distribution and size of the ore bodies is controlled by major and minor faults. The uranium ore appeared near the surface in the southern part and down to 1000 m deep in the northern part of the Ronneburg mining district.

3 Investigation Area

The creek "Gessenbach" is the main drainage system in the Western part of the former uranium mining area. The Gessental valley is located between the cities of Ronneburg and Gera. Near the city of Ronneburg it is influenced by two former waste rock dumps called Gessenhalde and Nordhalde. The Gessenbach creek and its tributary Badergraben follow the valley in western direction (Fig. 1, Fig. 2).

The Gessental valley will be one of the main discharge areas of mine water in the post-flooding situation.

4 Hydrochemical Results

1.3 General Hydrochemistry

The hydrological situation of the Gessental valley is dominated by the existence of the former dumps and by the groundwater depression cone of the underground mine. The seepage waters in the western part of the Nordhalde (Q4, Q16 in Fig. 2) are highly mineralized (el. conductivity about 12 mS/cm), have a low pH (2-3.5) and high redox potentials (about 570 mV). This water has high concentrations of Fe, Ca, Mg, Al, Mn, SO_4, Si, Cu, Zn, Ni, Cd, Cr, U and REE. Discharge measurements in the Gessenbach creek showed that the amount of seepage water flow-

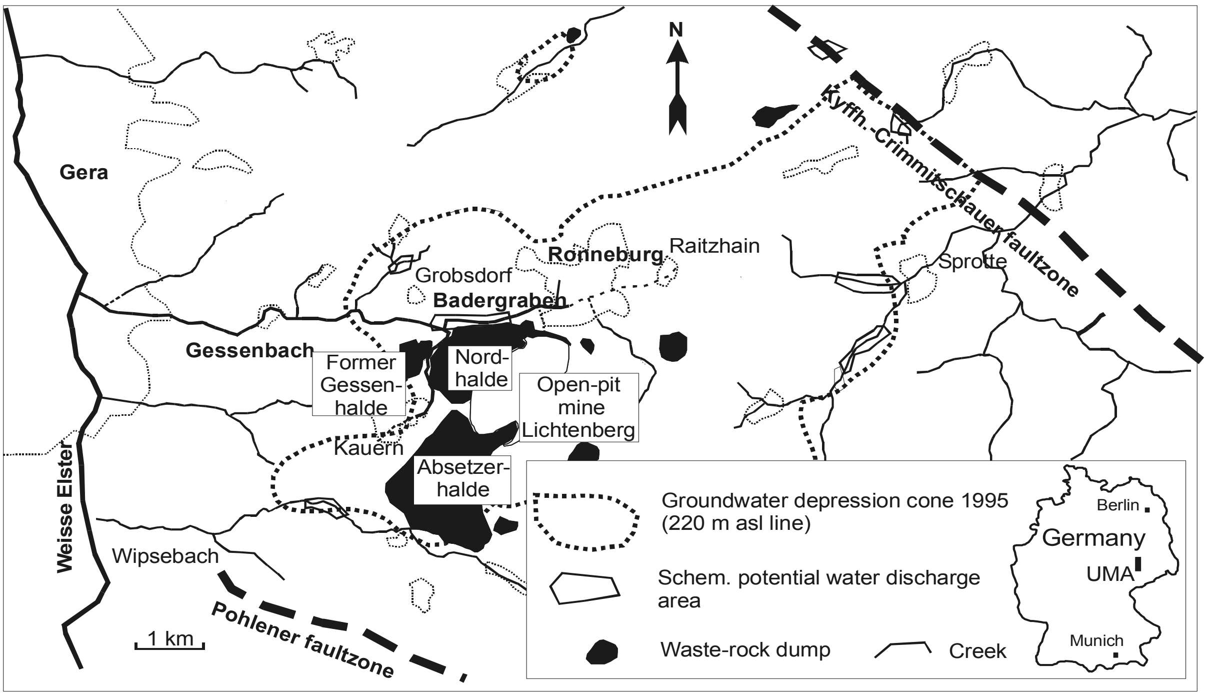

Figure 1: Gessental valley in the Western part of the former Uranium mining area of Ronneburg (GELETNEKY 2002). UMA: Uranium mining area of Ronneburg

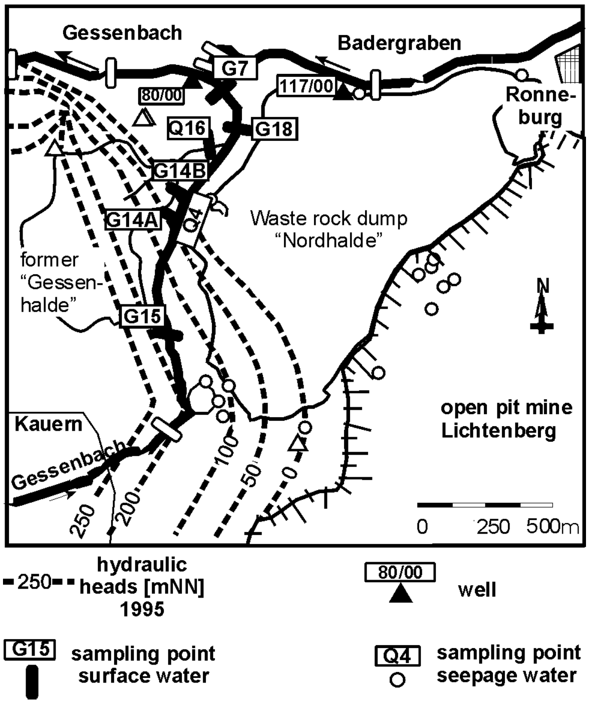

Figure 2: Sampling points of the surface water and groundwater around the waste rock dump "Nordhalde" and hydraulic head of the groundwater depression cone in 1995.

ing into the creek is low (less than 0.5 l/s).

To investigate the impact of the seepage water of the dumps on the Gessenbach creek and the grounddwater sampling was performed regularly at five sampling-locations (G15, G14A, G14B, G18, G7 in Fig. 2, Fig 3).

Before both creeks pass the dump the headwaters are strongly influenced by untreated municipal sewage from Ronneburg and Kauern (G15). The pH of the water is variable but mostly alkaline

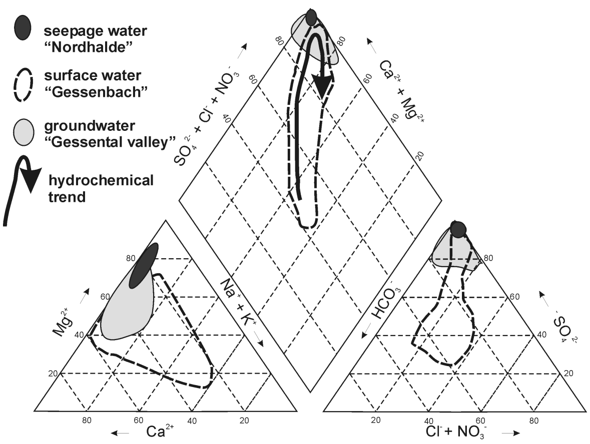

Figure 3: Piper-plot of the main hydrochemistry of the seepage and surface water and the groundwater of the Gessental valley.

(7.5-9). The electric conductivity (1.5-2 mS/cm) is low compared to the seepage water (12 mS/cm). When the Gessenbach creek passes the area of the Nord- and Gessenhalde the water becomes enriched in total dissolved solids (TDS), Fe, Ca, Mg, Al, Mn, SO_4, Si, Cu, Zn, Ni, Cd, Cr, U and REE. In Piper plots hydrochemical trends can be shown (Fig. 3). In the Gessenbach creek the chemical composition of the water changes from an alkaline Ca-Mg-SO_4-HCO_3-type to an acidic Mg-Ca-SO_4-type (Fig. 3).

Some of the components are transported as conservative tracers (Mg, Ca, Na, K, Cl, PO_4), others undergo reactive transport (Fe, Mn, Si, Cu, Ni, REE; GELETNEKY 2002).

The groundwater situation in the valley is strongly influenced by the groundwater depression cone. The alluvial sediments north of the waste rock dumps are only partly saturated with groundwater. However, groundwater in wells 117/00 and 80/00 could be sampled in summer 2000. The water can be classified as Mg–Ca-SO_4-type with a pH varying between 5.3 and 6.4, enriched in Fe, Zn, Ni, Co, Sr and a special REE-pattern (Fig. 3).

1.4 Using REE-patterns as tracers for ARD

Normalizing REE concentrations to Post Archaean Australian Shale (PAAS) 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 in the investigated seepage waters.

For two investigated seepage waters (Q16, Q4, Fig. 2) significantly different REE patterns are obtained. Furthermore, the presence and absence of positive Ce anomalies could be observed. Nevertheless, for the seepage water of the Nordhalde (Q4) – sampled over a period of two years - the shale normalized REE pattern shows only minor variations, although the concentration differs. Thus, REE patterns are independent of REE concentrations and independent of discharge.

At the sampling points in the surface water (G14A, G14B, G18, G7) nearly the same REE pattern were observed (Fig. 4). This represent a diffuse inflow of REE-rich ARD of the dumps into the creek The absolute concentrations of REE in the creek are up to 100 times less than in seepage water due to mixing and (co)precipitation of REE. Lu/La and Sm/La relations show a significant decrease with increasing distance from the dump. This is caused by preferential (co)precipitation of heavy REE with amorphous Fe-hydroxides along the Gessenbach.

The general shape of the REE pattern of the dump Nordhalde can also be found in groundwater wells 117/00 and 80/00. However, the degree of enrichment of heavy REE is less pronounced. Again, the REE patterns of the groundwater samples as a function of time are very similar. The absolute concentrations of REE in groundwater are 1000 times lower than in seepage. A negative Ce anomaly is caused by precipitation of Cerianite due to the Eh-pH conditions in the groundwater (LEYBOURNE 2000).

In order to investigate whether the REE patterns in the seepage water resemble the REE concentrations in the Silurian source rocks LA-ICP-MS measurements were performed using glass beads of the most important lithologies “Ockerkalk” and fine grained alluvial sediments.

In contrast to the patterns of the seepage, the REE patterns of the Silurian rocks are featured by rather flat patterns with enrichment of middle REE (Sm – Dy). The concentrations of REE in the different lithologies differ only by a factor of 2.

Batch experiments using deionised water were performed. Results show that the REE concentrations eluted from the different lithologies differ by a factor of 1000. However, results show a preferentially leaching of heavy REE in all investigated source rocks. The highest absolute concentrations of REE appear in the eluates of the Silurian “Ockerkalk”. This REE pattern closely reflects the pattern found in the seepage water. Therefore, it is assumed to be the most important source for the occurence of this special REE pattern.

5 Conclusions

It is shown that the identification of contaminant sources can be performed using shale normalized REE patterns. It is also possible to follow flow pathes of contamination in surface water and groundwater by using REE patterns.

Both the chemical composition and the REE pattern in the surface water show an influence of acid seepage water, which is originated from the dumps. The hydrochemical patterns of REE in the groundwater are comparable with signatures of the seepage. Both show enrichment in the

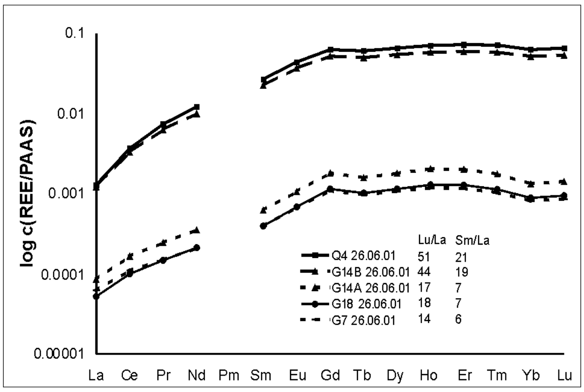

Figure 4: REE concentrations normalized to PAAS in June 2001 with enrichments in middle (expressed as Sm/La) and heavy REE (expressed as Sm/La) along a flowpath in the Gessenbach creek.

middle and in the heavy REE (MERTEN et al. 2002; GELETNEKY et al. 2001).

The REE patterns in the water samples do not reflect the source rock pattern as was demonstrated by laser ablation ICP-MS experiments. Percolation in batch experiments shows that the unique heavy REE enriched patterns are due to preferential leaching especially from Silurian “Ockerkalk”.

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