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Rare Earth Elements (REEs) as Natural Tracers in Mine Waters

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Abstract. Rare earth elements (REE) in mine waters from two European mines are analysed and discussed: Straßberg/Harz (Germany) and Georgi-Unterbau/Tyrol (Austria). From the REE patterns differences in the mine and surface waters can be seen, which are attributed to the mineralogy. Furthermore, the REEs' qualities as natural tracers are described and the results interpreted in conjunction with the findings of artificial tracer tests conducted at the two sites. Accordingly, REEs can be used as natural tracers in mines to study stratification and hydrodynamic conditions.

Introduction

Trace elements are widely used to characterize the geochemical evolution or petrologic composition of rocks, sediments or archaeological artefacts (Petrascheck 1956; Taylor and McLennan 1988; Seim and Tischendorf 1990; Knacke-Loy et al. 1992). Though, trace elements and in some cases REEs (Rare Earth Elements) are regularly analysed during hydrogeochemical investigations of mine waters (e.g. Wolkersdorfer 1996; Sanden 1997; Davis et al. 1998), systematic investigations of trace elements or REEs in mine waters of different mining sites have rarely been conducted. Important case studies of REE pattern distributions and their behaviour in mine waters were given recently by Worrall and Pearson (2001) in Great Britain and Protano and Riccobono (2002) in Italy. Contrary to a lack of REE studies for mine waters, the use of REEs as tracers in ground and surface waters has been reported and their complexes studied more frequently (e.g. Davis et al. 1998; Johannesson et al. 1994, 1996a, 1996b, 2000; Johannesson and Lyons 1995)

In this article, the results of REE investigations in a German fluorspar mine and an Austrian silver-barite mine will be reported. Both cases were supplemented by mine water tracer tests to examine the hydrodynamic conditions in the flooded mine (Wolkersdorfer et al. 2002; Wolkersdorfer and Hasche 2001).

Case Studies

Straßberg/Harz Fluorspar Mine (Germany)

In 1991 the Straßberg fluorspar mine was closed due to economic and environmental reasons (Kuyumcu and Hartwig 1998). Situated in the Mid Harz Fault Zone of the eastern Harz Mountains approximately 30 km south of Quedlinburg and 6 km west of Harzgerode, the Straßberg mine was the most important producer of fluorite in the former GDR (Mohr 1978). Besides fluorite, the hydrothermal polymetallic mineralisation of the vein structures comprises approximately eight ore and less than a dozen secondary minerals (Kuschka and Franzke 1974; Junker et al. 1991).

At the beginning of mining silver, copper, and lead were the targets of the miners. From the 18th century until 1990, mining focused on fluorspar, which was mainly found in the deeper parts of the mine (Bartels and Lorenz 1993). Between 1950 and 1970, the VEB Harzer Spatgrube joined the three most important deposits of the Straßberg mining district by driving two deep adits on the 5th and 7th level (from north to south: Brachmannsberg pit: No 539 Shaft, Straßberg pit: Fluor Shaft and Glasebach pit: Glasebach Shaft).

After installing a 3-adit-system in 1998 to control the mine drainage, the mine's owner suggested to conduct a tracer test within the flooded part of the mine. The aim of the tracer test was to investigate the hydrodynamic conditions within the mine, the pathways of the water between the three pits and the potential of a mine water stratification in the three pits. Therefore, a multi-tracer test with 15 µm diameter microspheres and club moss spores (*Lycopodium clavatum*) was carried out. Accompanying, field parameters, major ions and trace elements were analysed.

From the results of the tracer test it became clear that all parts of the mine are hydraulically well connected. Generally, the flow direction during the tracer test was from north to south, thus explaining the similar chemical composition of the mine water in the Fluor and Glasebach shafts. Finally, it could be shown that under the current flow regime, with the 3-adit-system working, no stratification will be achieved.

Georgi-Unterbau Silver-Barite mine (Austria)

Some kilometres south of Brixlegg in Tyrol/Austria, the historical silver-barite mines of the famous Kogel mining area can be found. One of these underground pits is the Georgi-Unterbau with its flooded underground works. Since medieval times silver-bearing fahlore was mined and between 1947 and 1968 barite was mined.

In 1887 the miners started to drive the Georgi-Unterbau, which opened up rich fahlore and barite resources. Starting in 1900, a 100 m deep two compartment blind shaft was sunk, connecting the 20, 40, 70 and 100 m main levels and the 10, 75 and 80 m sublevels (Pirkl 1961; Mutschlechner 1984; Krischker 1990; Hanneberg and Schuster 1994) as well as the 14-Nothelfer pit and the Barbara pit with each other. It was partially to fully flooded since the 1950's (Hießleitner 1951; Schmidegg 1953) and pumped out again in 1984 and 1988 for ore prospecting (Krischker 1990). Since 1990 the blind shaft has been flooded and therefore, stationary hydraulic conditions exist.

All parts of the mine are within the Devonian Schwaz Dolostone (*Schwazer Dolomit*) of the Northern Tyrol Greywacke area (*Nordtiroler Grauwackenzone*). Typically, the Schwaz Dolostone is a very hard, light white to light grey dolostone, being highly brecciated and fissured in the area investigated. The dolostone hosts silver and mercury bearing fahlores (there under Schwazite) as well as barite, the mineralisation being bound, but not restricted, to the breccia zones (Pirkl 1961, Wöbking 1982). Grundmann and Martinek (1994) and Schnorrer (1994, 1996) described 20 ore minerals being characteristic for the Schwaz Dolostone and a total of over 132 minerals for the Schwaz-Brixlegg area, there under REE minerals. According to Arlt and Diamond (1998), who investigated fahlores of the Schwaz-Brixlegg mining area, the fahlores of the Georgi-Unterbau comprise of 41 % Cu; 0.5 % Ag; 2 % Fe; 5 % Zn; 0.7 % Hg; 0.02 % Mn; 16 % Sb; 9 % As; and 26 % S. Unfortunately, no data on REE concentrations in the rocks of the Greywacke and their interpretation can be found in the literature.

A first physico-chemical investigation of the flooded blind shaft was conducted in December 2000. It became clear that the mine water is stratified, clearly showing two water bodies separated from each other at the 40 m level. In addition to the temperature and salinity measurements water samples were taken to be analysed on site and in the laboratory. Further investigations, including two tracer tests with 15 µm microspheres and uranine, were conducted in August 2001 and February 2002.

Sampling Procedures

Samples in the Straßberg mine were collected between May and July 2000 on a weekly basis in the three shafts at depths of 1—2 meters below the surface and the Uhlenbach brook. Only one sample was taken at the Siptenfelde brook. The Georgi-Unterbau was sampled in December 2000, May 2001, August 2001, and February 2002 with a down whole sampler in 10, 30, 55 and 90 m depths of the blind shaft.

In all samples, the temperature, salinity, redox potential, and pH value were measured directly after sampling with a multi parameter instrument Ultrameter 6P (Myron, Carlsbad CA). Fe^{2+} and total iron were measured with a Hach DR/890 and Hach DR/2500 (Hach, Loveland CO) and acidity as well as alkalinity with a Hach Digital Titrator. All samples were filtered through 0.45 µm cellulose acetate filters (Sartorius, Göttingen) using a 1000 mL Nalgene Bottle Top Filter (Nalge Nunc, Rochester NY). Two aliquots were used for analyses, one without acidification (500 mL), the other one with acidification (50 mL) and were stored in a cool place between sampling and analysing.

Main ions were analysed at TU Bergakademie Freiberg with ion chromatography and trace elements with an ICP-MS at TU Dresden/Tharandt. Fluoride concentrations were measured electrochemically with a WTW F500 (Wissenschaftlich-Technische Werkstätten, Weilheim) and SE20/EB reference electrode (Sensortechnik Meinsberg, Meinsberg).

Results and discussion

Depending on the pH of the water, the samples contained REE means between 0.2 and 17 µg L^{-1}, with the higher concentrations at low pH values (Table 1). From the 51 samples reported here, the Straßberg/Harz Flour Shaft contained the highest REE concentrations, whereas the Georgi-Unterbau only contained between 0.2 and 1 µg L^{-1} of rare earth elements. All REE concentrations are normalized against the Post-Archean Australian Shales PAAS Standard (Taylor and McLennan 1988), as no standard has been defined for mine waters yet.

Water samples of the Georgi-Unterbau, because of their higher pH values, regularly have Tm, Yb, and Lu concentrations below the detection limit. Taylor and McLennan (1988) also have shown that waters with high pH values, such as sea waters, have Tm and Lu concentrations below the detection limits.

Figs. 1 and 2 illustrate the REE patterns of the Straßberg/Harz mine and the Georgi-Unterbau, respectively. For comparison reasons, in Fig. 1 also the normalized mean of REEs in the Georgi-Unterbau is reported. Fig. 2 gives details of the three sampling campaigns in different depths of the flooded blind shaft at the Georgi-Unterbau mine. All samples show characteristic enrichments in REEs with intermediate masses (MREEs) compared to REEs with low (LREEs) or high (HREEs) masses; an effect observed by many authors before, but still not understood in detail (see Protano and Riccobono 2002 and Johannesson et al. 1996a, b). Only the samples from Georgi-Unterbau, the Glasebach Shaft and the Uhlenbach brook show significant Eu anomalies. These are missing in the No 539 and Flour Shaft patterns. As seen in Fig. 1, based on the relative abundances, three groups of water types can be distinguished at the Straßberg mining site: mine water in the

Table 1. Number of samples taken and sum of rare earth elements as well as pH at each location.

Sampling point	number of samples	Σ REE, µg L^{-1}	pH, 1
Fluor Shaft	7	16.96	6.45
Glasebach Shaft	5	3.22	6.84
No 539 Shaft	11	2.64	6.62
Siptenfelde brook	1	1.87	–
Uhlenbach brook	5	0.93	7.18
Georgi-Unterbau 10 m	3	0.99	7.75
Georgi-Unterbau 30 m	3	0.17	7.65
Georgi-Unterbau 55 m	3	0.15	7.69
Georgi-Unterbau 90 m	3	0.25	7.77

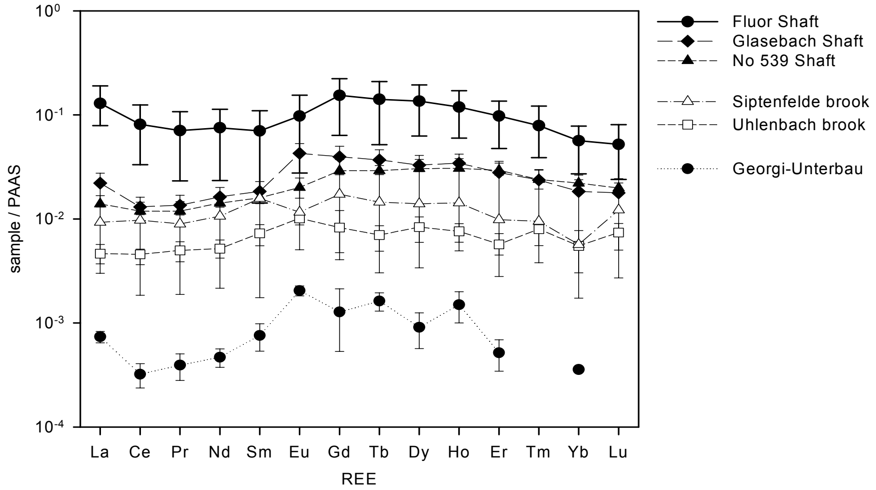

Fig. 1. Rare earth element (REE) patterns for the Straßberg/Harz and Georgi-Unterbau mine and surface waters normalized to Post Archean Australian Shales (PAAS). Filled symbols: mine waters; open symbols: surface waters. Error bars for 25 % and 75 % percentiles.

Flour Shaft; mine water in the Glasebach and No 539 shaft; and surface waters in the Siptenfelde and Uhlenbach brook. Between the surface waters and the mine waters there are 1.5 magnitudes of difference, which might be attributed to the different contact times with the different rock types. As the Siptenfelde brook is the sewage water discharge of the settlement Siptenfelde with a population existing mainly of elder people, the small Gd anomaly might be deduced from anthropogenetic effects as observed elsewhere (Bau and Dulski 1996). Such an effect can't be observed in the mine waters and the Uhlenbach brook, which dewaters a forest only. Furthermore, the mine water of the Glasebach Shaft is more closely related to the water samples of the No 539 than to the Flour Shaft. This is interesting in so far, as from the relative arrangement of the shafts, the No 539 and Flour Shaft waters should have been more similar. Nevertheless, the tracer test with microspheres and *lycopodium* spores proved this chemical result to be correct.

In the case of the Georgi-Unterbau, the REE patterns show a higher spatial and temporal variability than the Straßberg ones. This seems to be unusual, as the geological situation for the Georgi-Unterbau mine is less complicated than for the Straßberg mine. On the other hand, the mineralisation – even if most of the ore has been mined – in the Northern Tyrol Greywacke is exceptionally varied as described in the chapter "Case Studies".

First of all, the difference of 0.5 magnitudes in the relative abundances between the winter and spring/summer sampling campaigns is remarkable. It is assumed, that this difference is due to seasonal variations and therefore is currently investigated in more detail. All MREEs are enriched, and the HREEs are mostly under the detection limits. Moreover, a strong positive Eu anomaly and a negative Nd anomaly can be observed. However, the three elements with the biggest variability (Pr, Nd, and Eu) don't have systematic, depth dependent REE patterns. Yet, it is not clear if the differences are due to the analytic precision or temporal variations and changing stratification in the flooded shaft.

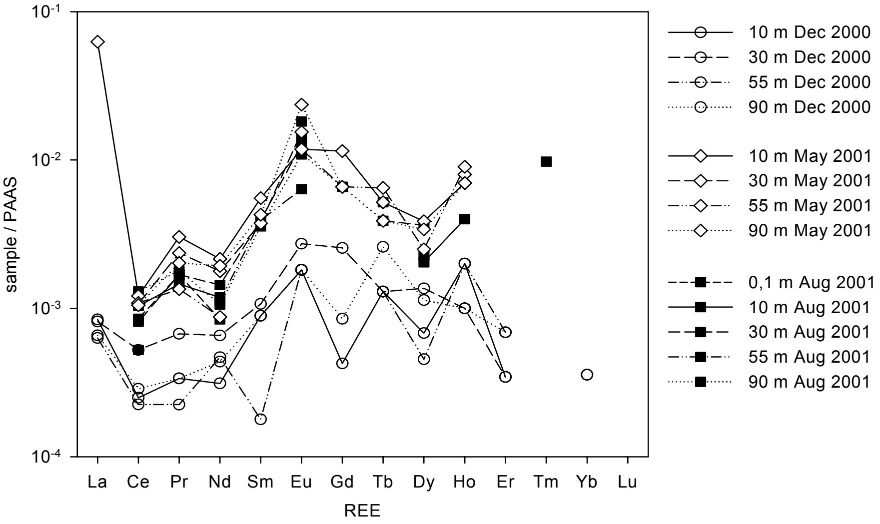

Fig. 2. Depths depended rare earth element (REE) patterns for the Georgi-Unterbau mine waters normalized to Post Archean Australian Shales (PAAS). Data of three sampling periods in December 2000, May, and August 2001, respectively.

Conclusions

Mine and surface waters from the Straßberg/Harz and Georgi-Unterbau/Tyrol mines with distinct mineralisations show significant differences in REE concentrations and PAAS normalized REE patterns. As a general rule, mine waters with low pH values tend to be enriched in REEs, whereas higher pH values result in lower REE concentrations. Contrary to the Straßberg mine waters, the Brixlegg ones show a distinct relative enrichment in MREEs, which might again be due to the mineral assemblage of the deposits. Consequently, the REE concentrations seem to be controlled by both, physico-chemical parameters of the water and the local geology.

In the Straßberg case, the mine water of the No 539 Shaft and the Glasebach Shaft have similar PAAS normalized REE patterns. Thereby, a good connection between the Glasebach pit and the Brachmannsberg pit must be assumed and has been approved by an artificial tracer test. As the Flour Shaft is between the two other shafts, and also hydraulically connected to them, it can be concluded, that the hydraulic connection of different shafts in a single mine does not necessarily result in an overall mixing of the water pool even if no stratification can be observed in the shafts.

On the other hand, the PAAS normalized REE patterns in the Georgi-Unterbau blind shaft clearly prove, that REEs can be used to study stratification in flooded underground workings. Especially Pr, Nd, Eu, and Dy seem to be good tracers in well buffered carbonated waters, as their variation exceeds those of the other REEs. However, the temporal and depth dependent variations show, that not all factors controlling REE mobilization seem to be understood yet.

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