

Geochemistry and REE pattern of acidic pit lakes in Lower Lusatia (Germany)

Elke Bozau¹, Kurt Friese¹, Hans-Joachim Stärk²

UFZ – Umweltforschungszentrum Leipzig-Halle GmbH

¹ Sektion Gewässerforschung, Magdeburg, Brückstraße 3a, D-39114 Magdeburg

² Sektion Analytik, Leipzig, Permoserstraße 15, D-04318 Leipzig

Three acidic pit lakes of a former lignite mine were investigated for main components and rare earth elements (REE). The highest REE concentration and fractionation (enrichment of light rare earth elements) are correlated to the lowest pH-value and the highest mineralisation of the lake water.

1 Introduction

There are more than 100 acidic pit lakes in Lower Lusatia (Germany) caused by pyrite oxidation in the surrounding dump sediments (GELLER et al. 1998). A sequence of such pit lakes developed in the former lignite mine Plessa-Koyne (Figure 1). These lakes with pH-values of about 3 can not be used as drinking water reservoirs or for recreation activities.

The geochemistry and the rare earth element (REE) contents of three acidic pit lakes ("RL 107", "RL 111", "RL 117") were investigated. Mining periods and morphological data of the investigated lakes are given in Table 1.

2 Methods

Water samples of the lakes "RL 107" and "RL 117" were taken in 1997, water samples of the lake "RL 111" in 1997 and 2001. Temperature,

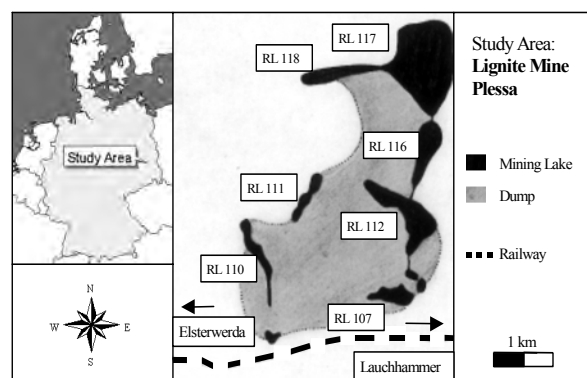


Figure 1: The former lignite mine Plessa-Koyne with the acidic pit lakes (BOZAU & STRAUCH 2002).

pH, redox potential and O₂ in the water column were measured by a multi-parameter probe (Idronaut). Water samples were taken with a water sampler (Limnos). Chemical analyses were performed by ionic chromatography (SO₄, NO₃, Cl), photometry (NH₄), and ICP-OES (Ca, Mg, K, Na, Fe_{tot}, Al) on 0.45 µm filtered samples.

High REE contents in the lake water of all three lakes allowed a fast and relatively simple analysis by ICP-MS without pre-concentration. The chemical method is described in more detail by Bozau et al. (in review). In 1997, not all REE were analysed. The detection limits were improved in 2001.

A detailed geochemical investigation of the mining lake "RL 111" is still going on. Therefore, recent data of this lake are available. Since 1996, remarkable changes of the water chemistry of the mining lake "RL 111" did not occur (KNÖLLER 2000; BOZAU & STRAUCH 2002). In 2002, measurements by the multi-parameter probe indicated that the pH-values of the lakes "RL 107" and "RL 117" are still the same as measured in 1997.

3 Results

The lake water of all investigated lakes has low pH-values, as well as high iron and sulphate concentrations (Table 2, Figure 2). Lake "RL 107" has the lowest pH (2.4) and the highest iron and sulphate concentrations, whereas the lake "RL 117" with a pH-value of 3.0 shows lower iron and sulphate concentrations. K, Na, and Cl do not increase with lower pH-values. The lowest values are measured in pit lake "RL 107". Maybe the precipitation of minerals (e.g.

Table 1: Description of the investigated pit lakes (LENAB 1998).

	RL 107	RL 111	RL 117
Mining period	1897 – 1928	1929 – 1958	1956 -1966
Water level (m a.m.s.l.)	92.3	94.1	92.3
Area (m ²)	122,000	107,000	950,000
Volume (m ³)	230,000	500,000	10,450,000
Max. depth (m)	4.0	10.2	14.0
Average depth (m)	1.9	4.6	11.0

jarosite) from the lake water is responsible for the low K- and Na-values (GÖTTLICHER et al. 2001).

The chemical differences of the three lakes can be explained by the amount of inflowing acidified groundwater correlated to the extent of the bordering dump area. Erosion processes from the dump sediments on the lake shore also contribute to the lake acidification. If there is no thermal stratification in shallow lakes (e.g. lake “RL 107”), neutralisation processes by sulphate and iron reduction in the lake sediments are nearly impossible (PEINE 1998).

The REE concentrations show no significant change within the water profile of each lake and can be correlated with the pH-value and the mineralisation of the water (Figure 3). The North American Shale Composite (NASC, TAYLOR & MCLENNAN 1985) normalised REE pattern are

characterised by an enrichment of the light rare earth elements (LREE). The enrichment of the light REE is also correlated with the pH-value. The lake “RL 107” with the lowest pH shows the highest enrichment of REE (La/Y 3.5), whereas the lake “RL 111” has a La/Y-ratio of 3.0. The REE fractionation probably increases with the acidification process. Speciation calculations indicate that the formation of sulphate complexes do not fractionate REE and can not be responsible for the light REE enriched pattern found in the acidic waters of the investigated mining lakes (BOZAU et al., in review; GIMENO SERRANO et al. 2000).

Compared to other acidic waters (caused by acid rain or pyrite oxidation) the enrichment of LREE seems to be untypical (BOZAU et al., in review). An enrichment of middle rare earth elements (MREE) is mostly found in acidic mine waters (ELBAZ-POULICHET & DUPUY 1999; WORRAL &

Table 2: Chemical characteristics of the investigated lakes (surface water, sampled in April 1997).

	RL 107	RL 111	RL 117
pH	2.4	2.6	3.0
Ca (mg/l)	327	229	102
Mg (mg/l)	45	29	15
K (mg/l)	3.3	3.6	4.3
Na (mg/l)	5.0	5.0	9.1
Fe (mg/l)	585	175	21
Al (mg/l)	47	38	1.7
SO ₄ (mg/l)	2370	1320	429
Cl (mg/l)	4.4	8.5	17
NH ₄ -N (mg/l)	5.0	2.7	1.6
NO ₃ -N (mg/l)	0.9	0.3	0.1
La (µg/l)	182	75	2.6
Ce (µg/l)	390	169	6.7
Pr (µg/l)	34	15	0.6
Nd (µg/l)	118	52	2.3
Sm (µg/l)	18	8	0.42
Eu (µg/l)	4.5	2	<0.1
Dy (µg/l)	15	7	0.4
Ho (µg/l)	2.8	1.3	<0.1
Er (µg/l)	7.7	3.5	0.2
Tm (µg/l)	0.9	0.5	<0.1
Yb (µg/l)	5.0	2.5	<0.1
Lu (µg/l)	0.7	0.3	<0.1

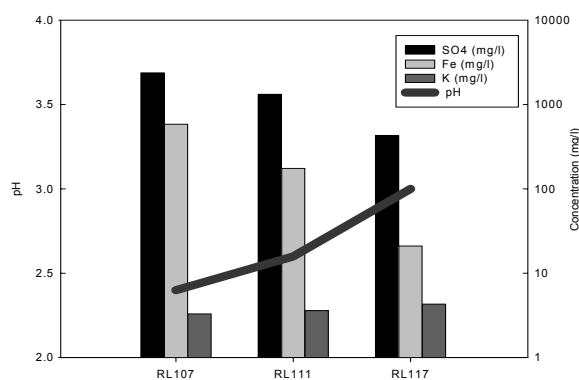


Figure 2: SO₄, Fe, K concentrations (mg/l) and pH-value of the investigated acidic pit lakes (measured in 1997).

PEARSON 2001).

Lignite of the exploited seam has REE contents in the magnitude of the average shale and is also characterised by an enrichment of LREE. First REE investigations of lignite containing dump sediments (data not shown) lead to the conclusion that weathering processes combined with microbiological activity could be responsible for these uncommon REE pattern of the lake water.

4 Conclusions

The investigation of the three acidic lakes showed that the behaviour of REE depends on the acidification processes. The highest REE concentration and fractionation of the lake water are correlated to the lowest pH-value and the highest sulphate and iron concentrations. An enrichment of LREE in the NASC normalised pattern is typical for the investigated pit lakes.

Further investigations including other lakes of the former pit area, groundwater and dump sediments can be useful to understand the fractionation of REE during pyrite oxidation, as well as the geochemical development of the study area.

Acknowledgements

Special thanks are due to our colleagues from the Departments of Freshwater Research and Hydrogeology (UFZ), who assisted sampling and carried out chemical analyses.

References

BOZAU, E., LEBLANC, M., SEIDEL, J.L., STÄRK, H.-J.: Light rare earth elements enrichment in an acidic mining lake (Lusatia, Germany). *Applied Geochemistry* (in review).

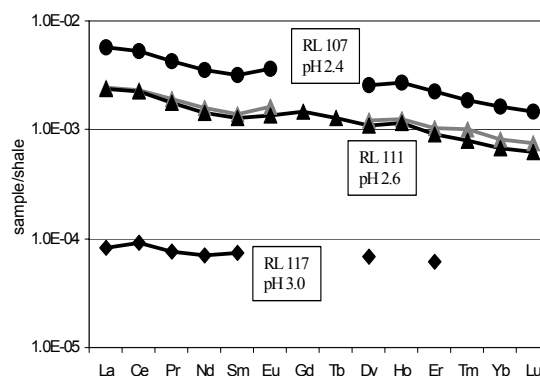


Figure 3: NASC normalised REE pattern of the investigated acidic pit lakes (Lakes "RL 107" and "RL 117" measured in 1997, lake "RL 111" measured in 1997 and 2001).

BOZAU, E., STRAUCH, G. (2002): Hydrogeological aspects on biotechnological remediation of the acidic mining lake 111, Lusatia (Germany). *Water, Air, and Soil Pollution: Focus*, 2, 3, 15 – 25.

ELBAZ-POULICHET, F., DUPUY, C. (1999): Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). *Appl. Geochem.*, 14, 1063 – 1072.

GELLER, W., KLAPPER, H., SALOMONS, W. (1998): *Acidic Mining Lakes*. Springer, Berlin – Heidelberg – New York.

GIMENO SERRANO, M.J., AQUÉ SANZ, L.F., NORDSTROM, D.K. (2000): REE speciation in low-temperature acidic waters and the competitive effects of aluminium. *Chem. Geol.*, 165, 167 – 180.

GÖTTLICHER, J., POHLMANN, M., BOZAU, E., GASHAROVA, B. (2001): Mineralbildungen aus eisen- und sulfathaltigen Wässern. *Beih. z. Eur. J. Mineral.*, 13, 1, 67.

KNÖLLER, K. (2000): Anwendung stabiler Umweltisotope zur Bewertung hydrochemischer Zustände und Prozesse in Folgelandschaften des Braunkohlebergbaus. Ph.D. Thesis, Department of Natural Sciences, University of Leipzig.

LENAB-ABSCHLUSSBERICHT (1998): Niederlausitzer Bergbaufolgelandschaft: Erarbeitung von Leitbildern und Handlungskonzepten für die verantwortliche Gestaltung nachhaltige Entwicklung ihrer naturnahen Bereiche. BMBF-Förderkennzeichen: 0339648.

PEINE, A. (1998): Saure Restseen des Braunkohletagebaus – Charakterisierung und Quantifizierung biogeochemischer Prozesse und Abschätzung ihrer Bedeutung für die seeinterne Neutralisierung. Bayreuther Forum Ökologie, Band 62.

TAYLOR, S.R., MCLENNAN, S.M. (1985): The continental crust: its composition and evolution. Blackwell, Oxford.

WORRAL, F., PEARSON, D.G. (2001): Water-rock interaction in an acidic mine discharge as indicated by rare earth element pattern. Geochim. Cosmochim. Acta, 65, 18, 3027 – 3040.