REE enrichment in groundwaters of the polysulphide ore deposit Freiberg

Anreicherung von Selten Erden Elementen in Grubenwässern der Polysulfidlagerstätte Freiberg

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The rare earth elements (REE) are considered to be relatively immobile during weathering and alteration of rocks (e.g., McLennan 1989), though more recent studies have shown, that at least the light REE (LREE) are not that immobile (e.g., Price et al. 1991; Polat et al. 2003). The assumed immobility was in part based on the low concentration of REE in river and ocean waters (typically in the range x – xx µg/l; e.g. Elderfield et al. 1990). Likewise, the high ionic potential suggests that the REE are expected to be rather immobile in aqueous environments, as they should tend to form hydroxides.

The advent of analytical procedures with higher sensitivity, in particular ICP-MS techniques, have stimulated renewed interest in the aqueous geochemistry of the REE (e.g., Elderfield et al. 1990). Möller (2000) and Worral & Person (2001) for example, used REE patterns of groundwaters as fingerprints for the identification of the host rocks of groundwaters.

Preliminary work by Baake et al. (1989) has shown, that acid mine waters and sinter deposits in the polysulfide ore deposit Freiberg are in part highly enriched in REE. This study extends this work in order to adress the following questions:

1. what is the source of the REE concentrated in acid mine waters, the host rocks of the deposit (i.e. the Freiberg Gray Gneiss) or gangue (i.e. calcite, fluorite)?
2. what controls the REE patterns in acid mine waters, the composition of the REE source or interaction of the waters and deposits (sinters)?

The present contribution is largely a status report on ongoing research and is mainly focussed on the chemistry of the mine waters.

1 Procedures

Water samples (100 ml), taken in the underground workings of the Freiberg Mine and the Mulde River, were filtered using 0,45 µm cellulose acetate filters. Unfiltered water samples were collected for comparison. Both sample types were acidified immediately after collection with HNO_3. Acidified solutions (about 5% HNO_3) were analyzed using a Perkin-Elmer ELAN 5000A quadrupole inductively coupled plasma mass spectrometer. For cabonates, 0.5 g samples were dissolved at 50 °C in 2 ml conc. HCl and solutions were diluted 1:10 before measurement. As internal standard 10 µg/l Rh were added. In order to minimize isobaric interferences, the following isotopes were measure: ^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{147}Nd, ^{147}Sm, ^{151}Eu, ^{160}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu. Detection Limits are 0.05µg/l for Y, La, Ce, Pr, Nd, and Er, and 0.005 µg/l for Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb, and Lu.

2 Results

Water samples are subdivided into waters from veins with sulfide mineralization, waters from veins filled with barite and fluorite, waters from barren fractures and mixed waters. Overall, the REE concentrations vary by five orders of magnitude, the highest concentrations being found in waters percolating in mineralized veins. The lowest concentrations, which are in the same range as the river waters of the Mulde River, were found in unmineralized fractures and veins carrying fluorite-barite mineralization.

As already indicated by leaching experiments (e.g. PRICE et al. 1991) and Eh-pH-diagrams (e.g. BROOKINS 1989) and known from data for geothermal (e.g., MÖLLER 2000) and mine waters (e.g., LEYBOURNE et al. 2000; WORRAL & PERSON 2001), the REE concentration in the water increases with decreasing pH. In water with pH = ca. 2.5 total REE contents are 11-13 [mg/l. Even higher REE contents of up to 690 [mg/l total REE contents have been reported for mine waters from the Bathurst Mining Camp, Canada (LEYBOURNE et al. 2000). In a plot pH vs. log[ΣREE] a linear relationship between total dissolved REE's and pH is indicated (Fig. 1).

REE concentrations in filtered water samples and unfiltered water samples are almost identical in waters with high total REE contents and low pH (Fig. 2, 3; see also analyses Sa5f and Sa5u in Table 1), suggesting that the REE may be truly in solution. It should be noted, however, that ELDERFIELD et al. (1990) found that waters passed through filters with pore size 0.2 µm sometimes had lower total REE contents than when passed though 0.4 µm pore size. In samples with higher pH and lower total REE, filtered waters contain in part significantly lower total REE concentrations compared to unfiltered waters (Fig. 3, 4; see for example analyses Sa9f and Sa9u in Table 1). This is perhaps related to the stability of Fe-hydroxides in waters with higher pH, to which the REE are absorbed.

All waters show moderate enrichment in light rare earth elements (LREE) in chondrite normalized plots (Fig. 5). Highly mineralized waters exhibit a significant Eu-anomaly, which is not obvious in the waters with low concentrations of REE. On the other hand, waters with low REE concentrations exhibit positive Y-anomalies.

A potential source of the REE concentrated in the mine waters is the Freiberg Gneiss which forms the host rock of the vein mineralization. Within this study, a sample of this rock was analyzed and used for normalization in Fig. 6. REE-rich waters normalized to the gneiss exhibit negative Eu-anomalies, which, however, might be due to the sample selected for normalization (SACHSE 2002), which does not exhibit an Eu-anomaly. TICHOMIROVA et al. (2001) reported virtually identical REE patterns for Freiberg Gneiss except that their samples do exhibit Eu-anomalies. In addition, we note that with decreasing total REE contents, an increasing Y-anomaly develops.

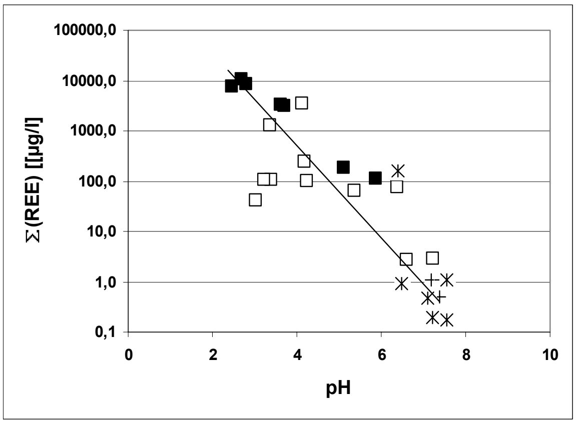

Figure 1: Total REE contents of water samples [µg/l] plotted vs. pH (filled symbols represent samples from veins with sulphide mineralization, open squares are mixed waters, crosses represent samples from veins with fluorite-barite mineralization, and stars samples from non-mineralized fractures).

In contrast, calcite from the veins appears not to be a potential source of the REE in mine waters (work in progress) because most calcite samples studied so far show less LREE enrichment than the groundwaters or are even LREE depleted (Fig. 7), which would require some fractionation process during dissolution. In addition, several samples (not plotted in Fig. 7) exhibit significant *positive* Eu-anomalies.

Several authors (e.g., MÖLLER 2000) have pointed out that Y because of its trivalent oxidation state and of its ionic size, which is similar to that of Ho, should behave in a similar way as the REE during igneous processes, whereas during dissolution and precipitation processes Y may behave differently. Hence Y-anomalies probably do not reflect host rock compositions but rather processes related to dissolution and transport. The increasing Y-anomaly observed in Freiberg Grey Gneiss normalized patterns hence may reflect incomplete dissolution whereas the lack of a notable Y-anomaly in acidic waters with high REE contents indicates unfractionated transfer of REE and Y from the host rock to the waters.

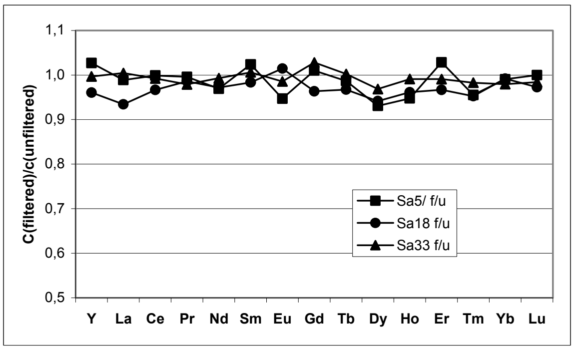

Figure 2: REE concentration in filtered water samples from veins with sulphide mineralization relative to concentrations in unfiltered samples.

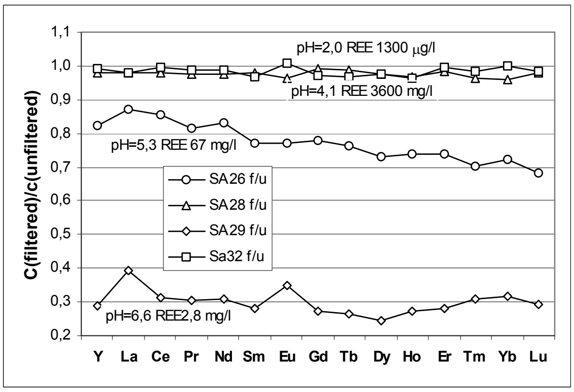

Figure 3: REE concentration in filtered mixed samples relative to concentrations in unfiltered samples, pH values and REE concentrations are provided at the patterns.

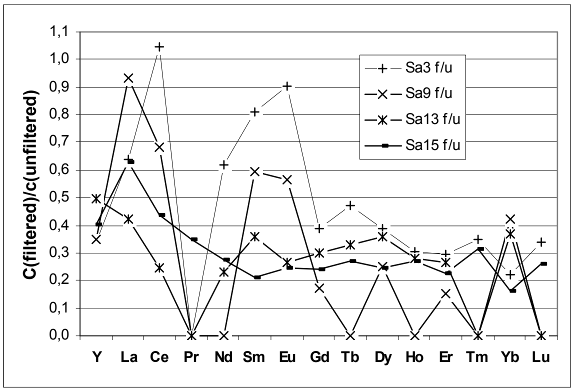

Figure 4: REE concentration in filtered samples relative to concentrations in unfiltered samples for waters from barite-fluorite veins and from unmineralized veins (note that values of 0 indicate that concentrations in the filtered sample were below detection limits).

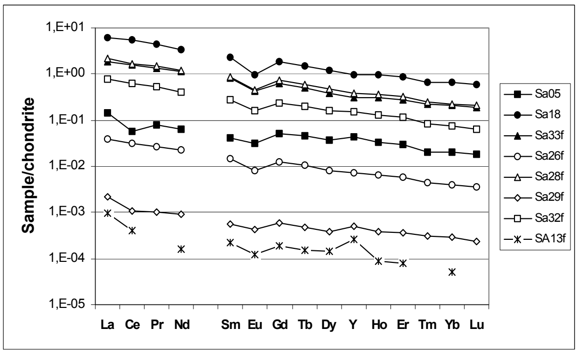

Figure 5: Waters from vein with sulphide mineralization (filled symbols, symbols as in Fig. 1) and mixed waters (open symbols, symbols as in Fig. 2) normalized to chondritic values (BOYNTON 1984).

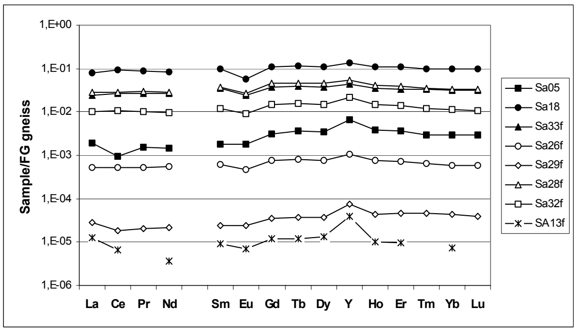

Figure 6: Waters from vein with sulphide mineralization (filled symbols, symbols as in Fig. 1) and mixed waters (open symbols, symbols as in Fig. 2) normalized to the Freiberg Grey Gneiss (SACHSE 2002).

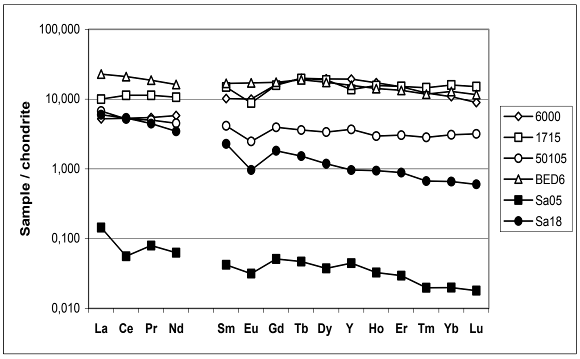

Figure 7: REE patterns of gangue calcite (open symbols) compared to REE patterns of highly mineralized waters (closed symbols). Chondritic values from BOYNTON (1984).

Table 1: REE concentrations in mine waters [µg/l]: Samples Sa5, Sa18, and Sa33 come from veins mineralized with sulphides, whereas samples Sa3 and Sa9 come from fluorite-barite veins (letters 'f' and 'u' indicate filtered and unfiltered samples, respectively). Samples Sa26, Sa28, Sa29and Sa32 are mixed waters, samples Sa13 and Sa15 come from unmineralized fractures (letters 'f' and 'u' indicate filtered and unfiltered samples, respectively).

Sample	**Sa5f**	**Sa5u**	**Sa18f**	**Sa33f**	**Sa3f**	**Sa3u**	**Sa9f**	**Sa9u**
Y	78.57	76.52	1700	544	1.06	3.11	0.25	0.71
La	44.65	45.16	1850	568	0.35	0.55	0.25	0.27
Ce	45.0	45.1	4330	1280	0.27	0.26	0.16	0.23
Pr	9.69	9.73	543	166	bdl	0.08	bdl	bdl
Nd	37.7	38.9	2070	683	0.23	0.37	bdl	0.10
Sm	8.21	8.02	445	161	0.030	0.037	0.021	0.035
Eu	2.32	2.45	70.9	30.5	0.014	0.016	0.006	0.010
Gd	13.3	13.1	471	161	0.043	0.11	0.012	0.068
Tb	2.22	2.25	72.2	23.8	0.010	0.020	bdl	0.008
Dy	12.06	12.96	382	126	0.052	0.13	0.019	0.074
Ho	2.35	2.48	67.6	22.4	0.013	0.043	bdl	0.015
Er	6.19	6.02	185	58.9	0.040	0.14	0.008	0.054
Tm	0.64	0.67	21.6	7.08	0.006	0.018	bdl	0.008
Yb	4.15	4.19	137	44.4	0.025	0.11	0.023	0.054
Lu	0.58	0.58	19.3	6.10	0.006	0.018	bdl	0.009
pH	5.10	5.10	2.68	3.61	7.40	7.40	7.34	7.37

bdl = below detection limit

	Sa26f	**Sa26u**	**Sa28f**	**Sa29f**	**Sa29u**	**Sa32f**	**SA13f**	**SA13u**	**SA15f**	**SA15u**
Y	12.7	15.5	677	0.90	3.11	262	0.47	0.94	67.0	167
La	12.4	14.2	678	0.68	1.72	242	0.30	0.71	51.1	81.3
Ce	24.9	29.0	1330	0.86	2.74	499	0.32	1.30	64.9	149
Pr	3.27	4.02	183	0.13	0.42	63.5	nn	0.12	5.72	16.4
Nd	13.8	16.7	735	0.55	1.77	249	0.09	0.41	17.6	63.5
Sm	2.89	3.75	169	0.11	0.39	54.7	0.043	0.12	2.73	13.1
Eu	0.60	0.77	33.2	0.031	0.090	11.5	0.009	0.034	0.83	3.33
Gd	3.23	4.15	194	0.15	0.55	62.2	0.050	0.17	5.58	23.4
Tb	0.49	0.64	28.5	0.023	0.085	9.54	0.007	0.023	0.97	3.60
Dy	2.59	3.55	154	0.12	0.51	52.2	0.045	0.13	5.11	21.0
Ho	0.46	0.63	26.4	0.027	0.10	9.14	0.006	0.023	1.12	4.13
Er	1.23	1.66	68.5	0.078	0.28	23.7	0.017	0.062	2.30	10.3
Tm	0.14	0.20	7.85	0.010	0.033	2.64	nn	0.007	0.34	1.09
Yb	0.83	1.16	47.1	0.060	0.19	15.6	0.010	0.028	0.96	5.89
Lu	0.12	0.17	6.61	0.008	0.026	2.03	nn	0.006	0.20	0.75
pH	5.34	5.34	4.10	6.58	6.58	3.34	6.48	6.48	6.40	6.40

bdl = below detection limit

Table 2: REE concentrations [µg/g] in calcites (samples 6000, 1715, 50105, BED6) and Freiberg Gray Gneiss (samples FGGn01-1, FGGn01-2).

Sample	6000	1715	50105	BED6	FGGn01-1	FGGn01-2
Y	34.1	24.3	6.5	27.8	10.5	13.9
La	1.62	3.09	2.08	7.06	20.7	26.2
Ce	4.28	9.15	4.19	17.0	40.3	54.2
Pr	0.66	1.38	0.61	2.28	5.30	7.07
Nd	3.48	6.37	2.70	9.69	21.7	28.9
Sm	1.99	2.90	0.81	3.27	3.97	5.27
Eu	0.73	0.65	0.18	1.25	1.22	1.31
Gd	4.18	4.09	1.02	4.51	3.65	4.78
Tb	0.94	0.93	0.17	0.90	0.531	0.698
Dy	6.25	6.04	1.08	5.59	2.99	3.86
Ho	1.23	1.12	0.21	1.02	0.5	0.7
Er	3.15	3.19	0.64	2.80	1.49	1.95
Tm	0.40	0.47	0.092	0.38	0.2	0.2
Yb	2.26	3.33	0.64	2.69	1.23	1.57
Yb	2.26	3.33	0.64	2.69	1.23	1.57

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