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The behaviour of rare-earth elements and Y during the rock weathering and soil formation in the Říčany granite massif, Central Bohemia

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Abstract

The geochemistry of rare-earth elements (REE) and yttrium has been studied in the soil profile derived from a biotite granite in the area of 'Forest Brook Catchment' (FBC) near Říčany (Central Bohemia, the Czech Republic). The comparison of the variation in the REE and Y concentrations in the individual zones of the profile shows that total content of lanthanides depends on the grain size of the soil material. The horizons abundant in clay fraction (Gr₁, Gr₂) contain five times more REEs than those with a predominance of silt and sand (G₀, Gr₃). The chondrite-normalised soil La–Lu pattern is similar in all profile zones and it behaves as an almost smooth function of the REE ionic radii, or their atomic numbers, respectively. The bulk content of lanthanides in soil is higher than that in the local partly weathered boulders of the parent rocks (syeno- and monzogranite). The content of acid soluble forms of REE (the portion of elements soluble in 0.1 M HNO₃) increases from the umbric horizon A towards the bottom of the profile. Our results indicate that the mobile part of REE is leached and transported to the lower part of the profile by acidic atmospheric precipitation. The REE distribution pattern of surface- and subsurface waters draining the terrain of the catchment confirms this consideration. © 1998 Elsevier Science B.V.

Keywords: Rare earth elements; Granite rock weathering; Soil formation; Mobility; Central Bohemian Pluton

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Introduction

Interest in the geochemical behaviour of the rare-earth elements (REE) and yttrium during rock weathering and soil formation has grown steadily in the past several decades. This interest has been stimulated by the recent evidence that the REE may be mobilised under supergenous conditions through a variety of alteration processes including the solid-water interaction (Nesbitt, 1979; Dudy, 1980; Middelburg et al., 1988; Price et al., 1991; Braun et al., 1993). In addition, recent advances in the study of the secondary dispersion of these elements in the weathering environment are particularly important as they may serve as an indicator of the long-term behaviour of their transuranic analogs in the actinide series. The physico-chemical data of REE are therefore useful with respect to the safe disposal of nuclear waste (Rard, 1988).

In the weathering products and soils, REE and Y may be fixed or immobilised by various mechanisms such as (i) retention in primary minerals which are resistant to weathering, (ii) their incorporation in newly formed crystalline or amorphous phases, (iii) adsorption by clays. The mobilisation and redistribution of lanthanides may be intensified by the accelerated dissolution of certain primary REE minerals, such as apatite and feldspar, through reactions with complexing ions which are present in soil- and surface water.

The purpose of this study is to investigate the distribution and mobility of the lanthanides and yttrium in one particular setting, namely in a small forested catchment without any direct anthropogenic contamination. These results represent part of a more detailed study of the element cycling in an experimental landscape, aimed to distinguish the relative importance of main mobilisation factors of elements in the environment (Martínek et al., 1997; Skřivan et al., 1997). A representative soil profile developed on granite rocks of the Říčany massif was chosen for this study. The analytical data on the fresh parent rock and of waters draining this terrain are also discussed in our study.

2. Materials and methods

2.1. Localisation and sampling

Behaviour of REEs and Y during rock weathering and soil formation was studied in a catchment of a small brook draining the northern part of the Nature State Reserve 'Voděradské bučiny', extending ~ 30 km SE of Prague, capital of the Czech Republic. The forest catchment covers an area of 0.765 km². Its south boundary reaches maximum height of 500 m a.s.l., while the water discharge from the catchment is measured on the site 406 m a.s.l. The mean annual precipitation is 635 mm and the mean annual temperature is 7.3°C. More data about the FBC, as well as on the composition of the forest cover are given in Minařík et al. (1983), Hons et al. (1990), and Skřivan et al. (1995), where the distribution and cycling of some heavy metals is described. Samples of partly weathered parent material were collected from boulders, as no fresh rock exposures in the area of the catchment were available (solid undisturbed crystalline rock appears in depth at least 10 m). The soil profile was sampled from a pit near the closing weir of the catchment, into a depth of 1 m.

2.2. Laboratory procedures

Primary minerals were identified in the thin sections of the rocks by optical microscopy; secondary minerals in the weathering products and the soil were identified by means of X-ray diffraction. The scanning electron microscopy was also used in the study of rock forming- and accessory minerals.

The rock- and soil samples were crushed and pulverised in a mechanical agate mill and after homogenisation they were decomposed in a mixture of HF + HNO₃, and HCl acids. The content of REEs and Y was determined by ICP-MS spectrometry using a Varian UltraMass instrument, in the laboratories of Analytika Ltd. Prague. Indium was used as an internal standard. The accuracy and precision of our data was verified by measur-

ing of the certified reference materials: Granite GM (ZGI), Syenite NIM-S (MINTEK), Granodiorite GSP-1 (USGS). Measured values of the reference materials were compared with published values from the Geostandards Newsletter (Govindaraju, 1989). Differences were within the range 3–9%. The Ba interference with Eu was corrected by running a Ba interference standard. The <0.45 μm water samples were analyzed without preconcentration. The fraction of loosely bound REEs in samples from the soil profile was determined through the extraction of <1 mm soil particles in diluted nitric acid (0.1 M HNO_3 , $V/m = 200$, $t_{\text{ext}} = 24$ h at room temperature, with occasional stirring).

Samples of water were collected from a Thomson weir in 1-month periods. The samples were immediately filtered through a 0.45 μm pore size Sartorius nitrocellulose membrane filter and the filtrate was stabilized with diluted (1:3) nitric acid (Merck, Suprapur: 1 ml of diluted HNO_3 per 100 ml of sample).

Values of the detection limit of determination of the individual elements in surface water, ex-

pressed as $3 \times \text{S.D.}$ (three times the value of their standard deviation in demineralised water), are as follows (in $\mu\text{g l}^{-1}$): La 0.0315; Ce 0.0162; Pr 0.0024; Nd 0.0171; Sm 0.0150; Eu 0.0024; Gd 0.0015; Tb 0.0003; Dy 0.0009; Ho 0.0006; Er 0.0006; Tm 0.0006; Yb 0.0009; Lu 0.0015.

3. Results and discussion

3.1. Parent rock

3.1.1. Mineralogy and bulk chemistry

Granitoids of the Říčany massif form the crystalline bedrock of the area and extend ~ 20 km E of Prague, forming part of the Hercynian Central Bohemian Pluton, being one of its most recent members. It is a typical small intrusion which penetrates near to the Earth's surface and occupies an area of about 80 km^2 . Its mineralogy is monotonous, but the body is structurally variable. It is concentrically zoned: the grain size of equigranular medium-grained rock forming the core increases continuously toward the periphery, so that the rock gradually transforms into a por-

Table 1
Chemical composition of the unaltered parent rocks

Rock type	Monzogranite	Syenogranite	Dyke aplite ^c	Marginal aplite ^d
Oxide (wt. %)	Říčany type ^a	Jevany type ^b		
SiO_2	69.64	70.62	70.43	74.69
TiO_2	0.35	0.29	0.27	0.06
Al_2O_3	15.24	14.80	15.40	14.52
Fe_2O_3	0.72	0.57	1.42	
FeO	1.48	1.28	0.83	0.59 ^e
MnO	0.05	0.04	0.04	0.01
MgO	1.42	1.08	0.70	0.23
CaO	1.43	1.36	1.72	0.85
Na_2O	3.50	3.92	3.80	3.77
K_2O	5.40	5.09	4.48	3.52
P_2O_5	0.35	0.24	0.13	0.11
$\text{H}_2\text{O} +$	0.43	0.41	0.52	0.65
$\text{H}_2\text{O} -$	0.27	0.23	0.27	0.12
Σ	100.28	99.93	100.01	99.12

^a Mean values of 16 analyses (Holečková and Šmejkalová, 1958; Vejnar, 1973).

^b Mean values of 11 analyses by Šmejkalová (1960).

^c Mean values of two analyses by Palivcová et al. (1992).

^d Mean values of eight analyses by Němec (1978) and two according to Vejnar (1973).

^e Total Fe as FeO.

phyric variety carrying large K-feldspar phenocrystals of more than 1 cm in diameter. The average modal composition of the core- and peripheral rock type are almost identical (vol.%): quartz 26 and 29, K-feldspar 31 and 27, plagioclase (16% An) 36 and 35, biotite 6 and 7, respectively (Němec, 1978), muscovite being the minor component. Monzogranite is the predominant rock type of the Říčany body. In the area between Jevany and Černé Vodčřady, the massif is transected by numerous aplite dykes whose average modal composition is as follows (vol.%): quartz 37, K-feldspar 27, plagioclase (9% An) 31. Other constituents are muscovite, biotite and tourmaline in variable amounts. In the SE part of the massif a rock of syenogranitic composition is developed, the Jevany granite. Compared with the Říčany granite its grain is finer, poorer in mafic minerals and its plagioclase is acidic (An 10–12 vol.%). In contrast to the dyke aplites it is tourmaline free. The marginal aplite in the southern part of the massif is genetically related to the aplitic dykes in the centre of the body. The numerous mafic biotite-rich dark enclaves are enclosed in the main granitic rock (Palivcová et al., 1992 for review).

The bulk chemical composition of the rock

types which are supposed to be the parent material from which the soils are derived is given in Table 1. The majority of granitic rocks of the massif belong to the meta-aluminous type with mol.% $Al_2O_3 \leq alk + CaO$ and with $Al_2O_3 > alk$, and some to the peraluminous type (Table 1).

3.1.2. REE distribution

The REE and Y distribution classifies the parent granites as rocks belonging to the group with relatively high content of REE. This is clearly shown in Table 2, where a range of values of older partial analyses by INAA is shown (Bouška et al., 1984; Minařík and Kvidová, 1986).

The chondrite-normalised pattern of REE in rocks is presented in Fig. 1. A relatively wide range of normalised concentrations corresponds to the structural variations and petrological differences between the fresh granite samples (15 samples from quarries were analyzed in the area of the whole massif). Recently Bea (1996) demonstrated that the geochemistry of REE (except Eu) in granitoids is essentially controlled by the behaviour of accessory minerals, whose nature, associations and composition change with the aluminosity of the rock. Generally, the unaltered parent rocks reveal a small to moderate negative

Table 2
REE and Y abundances in parent rock ($\mu\text{g/g}$)

Element	Unaltered parent rock (Říčany massif) ^a	Partly weathered rock in the catchment	
		Syenogranite	Monzogranite
La	17.5–45.0	4.39	19.18
Ce	49.5–107.0	9.13	33.86
Pr	—	0.96	2.66
Nd	14.7–57.0	3.49	8.55
Sm	3.0–6.9	0.87	1.72
Eu	0.36–1.15	0.08	0.49
Gd	—	0.78	1.22
Tb	0.13–1.00	0.15	0.14
Dy	—	1.04	0.74
Ho	—	0.22	0.14
Er	—	0.64	0.43
Tm	—	0.10	0.06
Yb	0.63–2.75	0.67	0.40
Lu	0.03–0.50	0.10	0.07
Y	34.0–54.5	8.56	4.67

^aRange of 15 rock samples by Minařík and Kvidová (1986) and Bouška et al. (1984).

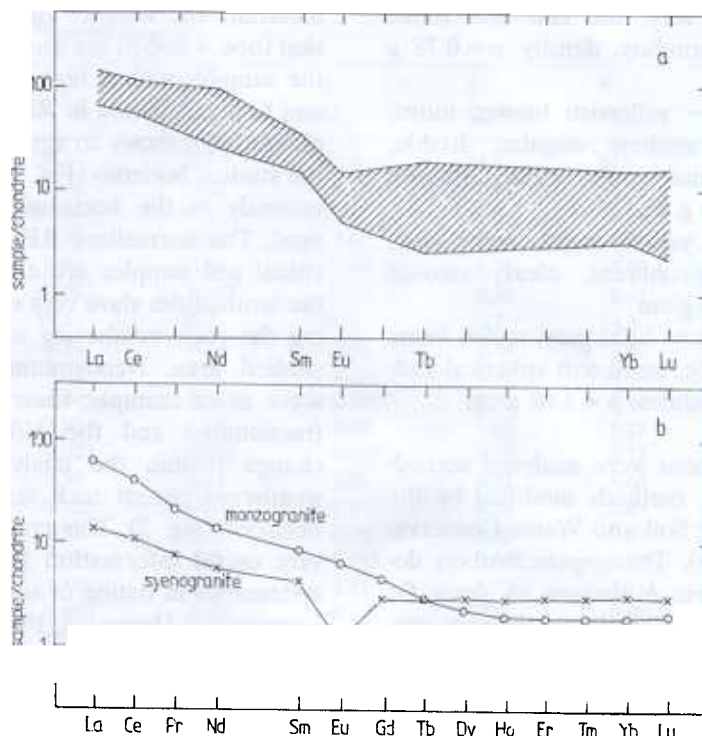


Fig. 1. (a) Range of the REE content normalized to chondrites in fresh parent rocks of the Říčany massif plotted against atomic numbers. Based on 15 analyses (Bouška et al., 1984; Minařík and Kvídová, 1986). (b) Normalized REE distribution plotted against atomic numbers for the partly weathered syeno- and monzogranite in the Forest Brook Catchment near the studied soil profile.

Eu anomaly and the predominance of light REE over the heavy REE. This characteristic is common for most of the continental monzo- and syenogranites (Henderson, 1984).

Partly weathered parent rock was sampled near the soil profile. These surface rock samples designated as monzogranite and syenogranite contain 6.6 and 6.2 vol.% of kaolinite, respectively. In both samples chlorite is the minor component. In comparison to the fresh rock samples, the distribution of REE and Y is very different in the kaolinised granites. These samples are relatively low in lanthanides and especially the weathered syenogranite is extremely depleted in REE (see Table 2). This can be explained by the leaching of surface rock layers with acid atmospheric precipitation in the open environment. The chondrite-normalised pattern of REE (see the Fig. 1b) shows moderate negative (syenogranite) and no (monzogranite) Eu anomaly and the predomi-

nance of LREE over the HREE. This is in accordance with the views of Elderfield et al. (1990), who state that the HREEs are preferentially released to solution during weathering of rocks, as they form stronger complexes with ligands in solution than do the LREEs.

3.2. Soil developed from the granite bedrock

3.2.1. Characteristics of the soil profile

The acid soil (pH/KCl 3.00 in umbric A horizon, 3.46 in the B_w horizon, 3.79 in the G₀ horizon, and 3.43 in the G_r horizon) is classified in the World Reference Base for Soil Resources (Spaargaren, 1994) as a Gleyic Cambisol. The main morphological characteristics of the soil are presented in the profile description:

- A (depth 0–15 cm) — very dark brown moist, loamy sand, moderate coarse granular, very

friable, abundant very fine and fine roots, abrupt, smooth boundary, density $\rho = 0.78 \text{ g cm}^{-3}$.

- B_w (15–30 cm) — yellowish brown, moist, loam, moderate medium angular, friable, abundant very fine roots, clear, smooth boundary, $\rho = 1.23 \text{ g cm}^{-3}$.
- G_o (33–48 cm) — yellow, moist, loamy sand, structureless, non-coherent, clear, smooth boundary, $\rho = 1.80 \text{ g cm}^{-3}$.
- Gr_{1-4} (48–101 cm) — light grey, moist, loam, structureless, plastic, small soft spherical reddish brown iron nodules, $\rho = 1.62 \text{ g cm}^{-3}$.

Seven distinct horizons were analyzed according to Hraško (1962), methods modified by the Research Institute for Soil and Water Conservation, Prague (Table 3). The organic carbon decrease from the umbric A horizon to gleyic Gr horizon mirrors the irregularities in the clay content, reflected in the sorption capacity. The mineralogy of soil is identical in all the horizons.

3.2.2. Distribution of REE and Y

The concentrations of REE and Y in the individual horizons of the profile (down to the depth 1 m) are reported in Table 4. The total content of lanthanides and yttrium is in the range slightly lower than that of the fresh parent rocks (see Table 2). The sum of REE and Y varies between 60 and 250 ppm with small negative or nil Eu anomalies, and with a predominance of LREEs ($La/Lu = 128\text{--}190$). The distribution of REE strongly correlates with the grain-size of the soil

material. The samples abundant in the clay fraction (nos. 4 and 5) are enriched in REEs, whereas the samples with a high portion of sand (nos. 3 and 6) are depleted in REEs. The chondrite-normalised plot shows an almost smooth course in all the studied horizons (Fig. 2a) and it reveals no Eu anomaly in the horizons with high content of sand. The normalised REE patterns of the individual soil samples are almost parallel and that the lanthanides show very small fractionation during the rock weathering and pedogenesis in the studied area. Neodymium and samarium may serve as an example; these two elements are not fractionated and the Nd/Sm ratio does not change (within the analytical error) in partly weathered parent rock samples and in the soil horizons (Fig. 3). This constancy of Nd/Sm is a very useful information for the Nd-Sm isotopic systematics in dating of soils and sediments (McLennan and Hemming, 1992).

Yttrium, with atomic number 39, lies outside of the above mentioned group of elements, but its behaviour during the rock weathering and the pedogenesis is not different from that of the lanthanides, especially of the HREEs with which it is invariably associated in minerals and rocks. The relationship between Y and REE contents in the soil profile is shown in Fig. 4. The correlation is very strong in case of the loosely bound contents.

3.2.3. Mobile forms of REE and Y in soil

The fractions of the loosely bound REE and Y throughout the soil profile are defined as their

Table 3

Main chemical and physical characteristics of the soil profile in the Forest Brook Catchment

Depth (cm)	pH_{H_2O}	pH_{KCl}	T_M (mmol/100 g)	H^+ (mmol/100 g)	Cox (%)	Grain size (mm) expressed in %					
						< 0.01	< 0.001	0.001–0.01	0.01–0.05	0.05–0.25	0.25–2.00
0–15	3.80	3.00	24.00	26.50	4.75	19.00	6.80	12.20	33.70	12.50	34.80
15–33	4.04	3.46	13.70	15.50	0.45	35.60	20.50	15.10	32.90	13.60	17.90
33–48	4.14	3.79	5.10	6.50	0.24	14.80	10.40	4.40	10.10	12.50	62.60
48–67	4.00	3.41	15.20	17.00	0.28	44.60	32.20	12.40	35.80	11.80	7.90
67–74	4.05	3.38	14.60	15.00	0.12	43.60	32.00	11.50	34.10	9.20	13.20
84–87	4.26	3.54	3.80	5.00	0.04	14.60	9.00	5.60	10.80	7.60	67.00
90–100	4.33	3.43	5.70	6.50	0.08	23.30	18.10	5.30	20.30	14.60	41.80

Table 4
REE and Y contents in the soil profile ($\mu\text{g/g}$)

Sample no		A	2 B_w	3 G_r	4 G_{r1}	5 G_r	6 G_{r2}	7 G_{r4}
La	a	30.6	30.8	19.0	46.5	41.6		41.3
	b	0.44	0.42	0.74	2.91	4.32		8.51
Ce	a	59.2	60.3	35.4	88.6	74.9		76.9
	b	0.73	0.81	1.63	4.61	7.39		16.0
Pr	a	6.04	5.98	3.36	8.71	7.90		8.27
	b	0.052	0.052	0.10	0.33	0.61		1.41
Nd	a	19.1	20.2	11.2	26.7	24.3		26.9
	b	0.17	0.21	0.39	1.10	1.82		5.16
Sm	a	4.22	4.27	2.15	6.14	4.78		6.19
	b	0.045	0.047	0.10	0.31	0.44		1.25
Eu	a	1.02	1.08	0.68	1.17	1.12		1.37
	b	0.027	0.045	0.057	0.15	0.17		0.32
Gd	a	3.58	3.61	2.01	4.91	4.66		5.15
	b	0.053	0.041	0.095	0.26	0.45		1.16
Tb	a	0.51	0.51	0.26	0.69	0.63		0.70
	b	0.011	0.010	0.015	0.042	0.091		0.19
Dy	a	2.40	2.57	1.15	3.72	3.11		3.07
	b	0.049	0.051	0.11	0.26	0.47		1.12
Er	a	0.50	0.47	0.21	0.65	0.60		0.62
	b	0.012	0.008	0.014	0.046	0.083		0.18
Tm	a	1.48	1.39	0.75	1.95	1.77		1.80
	b	0.033	0.024	0.040	0.13	0.23		0.55
Yb	a	0.19	0.20	0.09	0.24	0.23		0.20
	b	0.004	0.002	0.004	0.011	0.028		0.061
Lu	a	1.34	1.29	0.62	1.81	1.57		1.50
	b	0.034	0.015	0.035	0.075	0.12		0.36
Y	a	0.20	0.21	0.10	0.29	0.23		0.22
	b	0.005	0.003	0.003	0.011	0.013		0.045
Y	a	11.9	12.9	4.24	18.1	15.8		16.7
	b	0.33	0.23	0.46	1.36	2.23		6.03

a, Total content; b, mobile form of element.

portion soluble in dilute nitric acid (0.1 M HNO_3 , $V/m = 200$, $t = 24$ h). Samples with grain size < 1 mm were extracted at room temperature with occasional stirring. Mobile forms of lanthanides defined in this way express the distribution in soil profile which are significantly different from those of REE total content. The relative amount of the mobile forms of individual lanthanides and Y increases with depth of the sampled horizons (Table 4). While the soluble REE content is negligible in the umbric A horizon, the corresponding value is one order of magnitude higher in the bottom of the profile. This difference is generally higher in the case of HREEs and Y. Shapes of the normalised plots are similar in all the studied

horizons (Fig. 3b), but the initial positive Eu anomaly gradually decreases from the uppermost horizons to the deeper part of the profile. The deepest gleyic horizon (sample no. 7 with the most abundant soluble species of REE) is characterised by a slight negative Eu anomaly ($\text{Eu}/\text{Eu}^x = 0.81$). The observed distinctions in Eu concentration throughout the profile can be explained by the occasional decrease of the redox potential in the deeper soil horizons throughout their waterlogging in periods with heavy rains. The decrease in Eh could be sufficient to reduce the Eu^{3+} species to more mobile Eu^{2+} (at Eh nearing -0.43 V, which is the standard potential of the half-reaction $\text{Eu}^{3+} + e^- = \text{Eu}^{2+}$).

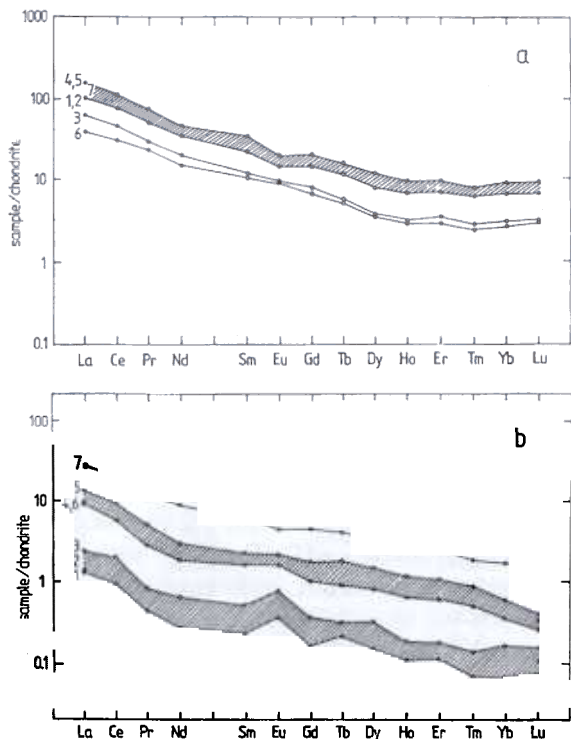


Fig. 2. Normalised REE distribution in individual horizons of the studied soil profile in the Forest Brook Catchment. (a) Total content; (b) acid soluble (mobile) forms of REEs.

It is necessary to explain the considerable differences in the mobile contents of REE and Y between the upper and lower parts of the soil profile. The contribution of the metabolic activity of forest vegetation to the REE distribution is improbable, as the plant uptake of REEs is very low. The levels of REEs in plants are in general 10^{-2} to $10^{-4} \mu\text{g g}^{-1}$ and the depletion factors for lanthanides by plants relative to their bulk soil content are 10^{-4} (Laul et al., 1979). The acid soluble portion of REEs is then more probably leached away by the excess input of protons of the acid atmospheric precipitation and they are relocated in dissolved forms via deeper soil horizons to the ground water and into the surface stream of the catchment.

3.3. Surface stream

3.3.1. Content of dissolved REE in surface water

The content of the soluble forms of REE in

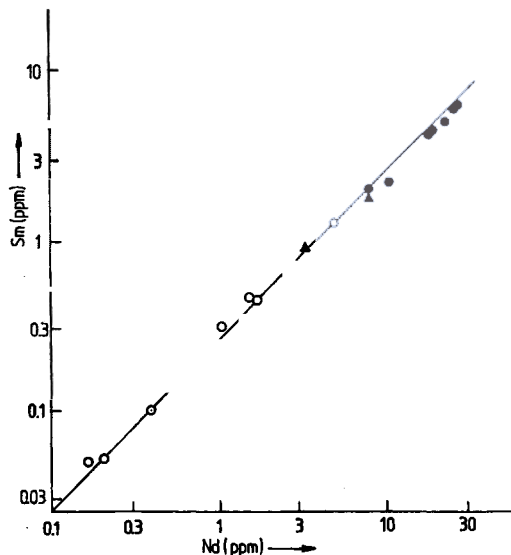


Fig. 3. Correlation between Sm and Nd in partly weathered parent rock and soil in the area of Lesní potok catchment. Triangles, partly weathered monzo- and syenogranite; filled circles, soil samples (total content); empty circles, acid soluble soil forms of REE.

moderately acidic surface water (pH between 4.5 and 5.0) of the FBC, sampled near the soil profile, reaches $5\text{--}7 \mu\text{g REE l}^{-1}$ (see Table 5). The fractionation pattern of the dissolved REE in the surface stream, normalised to average chondrite composition, is shown in Fig. 5.

Calculated speciation of trivalent REE, according to Wood (1990), involves free ions and sulfate complexes as the predominant species in acidic waters low in F^- ($\text{F}^- = 10^{-6} \text{ M}$). Waters of the 'Forest Brook' surface stream, however, contain $\text{F}^- \sim 30$ times higher, which may attain importance in the speciation of REEs.

3.3.2. Mobilisation factors of REE

Mobilisation factors F_M of the individual REE in FBC surface water (REE concentrations in surface water/REE conc. in the deepest horizon, normalised to the respective concentrations of Al — see Table 5) indicates a significantly higher mobility of all the REE in comparison to Al. The growing trend of F_M s in the sequence La–Lu (see Fig. 6) again demonstrates the increasing com-

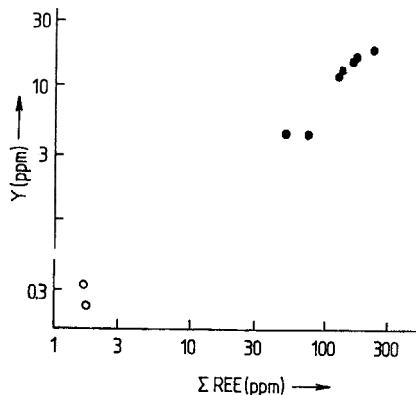


Fig. 4. Yttrium vs. REE contents in soil profile of the Forest Brook Catchment. Dots represent the total content, circles represent the mobile forms (leachable content) of elements.

plexing capacity towards the HREE, as has been shown by Elderfield et al. (1990).

3.3.3. Relative abundances of REE in surface water

To compare the relative REE abundances of the FBC surface water with the data presented by

Elderfield et al. (1990) normalised to the average shale content, the concentrations of REE presented in Table 4 were adjusted in the same manner. The resulting REE relative abundance pattern of the FBC surface stream (based on average values of three samples collected on 4.6.97, 4.7.97, and 31.7.97) is illustrated in Fig. 6, together with selected figures for the Amazon, Connecticut and Delaware rivers, presented by Elderfield et al. (1990, Table 1 and Fig. 1). The comparison reveals that the overall relative abundance of REE in water of the FBC is by far the highest (all values are considerably higher even than data for the Connecticut River water, which was filtered through a coarser — 1 μm pore size — filter). Higher concentrations of REE in FBC water in comparison with those of large surface streams can be attributed (i) to the low pH of the FBC stream, (ii) the presence of higher concentrations of the complexing substances (mainly F^-), and (iii) a lack of suspended matter which acts as an adsorbent for the dissolved species.

No positive Eu anomaly was found in the rela-

Table 5
REE abundances in surface water of the FBC catchment, and mobilization factors F_M of the individual REE with respect to their content in the deepest soil horizon (values are normalised to the respective concentrations of Al):

$$F_M = \frac{c\text{REE}_W}{c\text{REE}_R} \cdot \frac{c\text{Al}_R}{c\text{Al}_W}$$

where $c\text{REE}_R$ is the content of REE in the deepest Gr_4 soil horizon, in $\mu\text{g/g}$; $c\text{REE}_W$ is the average content of REE in surface water, in $\mu\text{g/l}$; $c\text{Al}_R$ is the content of Al in soil (= 58200 $\mu\text{g/g}$); $c\text{Al}_W$ is the content of Al in surface water (= 735 $\mu\text{g/l}$)

cREE Element	Discharge (l/s)			R	cREE _W	F _M
	0.70	2.64	4.06			
	pH of the surface water					
	4.93	4.88	4.77			
	REE content in surface water, ($\mu\text{g/l}$)					
La	1.27	1.33	1.37	41.3	1.31	2.51
Ce	2.32	3.02	2.77	76.9	2.71	2.79
Pr	0.27	0.34	0.31	8.27	0.30	2.84
Nd	1.08	1.35	1.33	26.9	1.21	3.57
Sm	0.24	0.34	0.36	6.19	0.29	3.76
Eu	0.039	0.050	0.046	1.37	0.044	2.54
Gd	0.18	0.24	0.23	5.15	0.21	3.21
Tb	0.028	0.037	0.038	0.70	0.033	3.73
Dy	0.18	0.25	0.21	3.07	0.21	5.31
Ho	0.037	0.047	0.041	0.62	0.040	5.11
Er	0.085	0.12	0.11	1.80	0.099	4.35
Tm	0.014	0.014	0.013	0.20	0.014	5.54
Yb	0.075	0.11	0.099	1.50	0.088	4.64
Lu	0.013	0.018	0.014	0.22	0.014	5.04

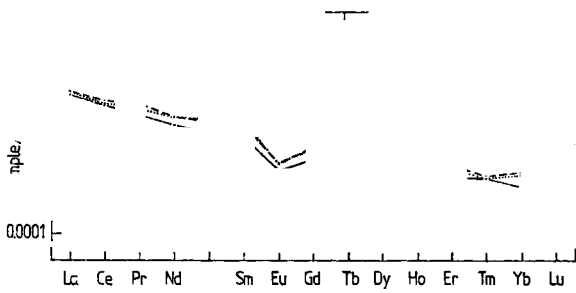


Fig. 5. Chondrite-normalised REE data for selected samples of surface water sampled near the soil profile of the Forest Brook Catchment. Full line, sample no. 34; dashed line, sample no. 43; dotted line, sample no. 52.

tive abundances of dissolved REE in the FBC surface stream. The hypothesis of the preferential mobilisation of the Eu^{2+} in soils thus has no support in the chemistry of the corresponding runoff for this region.

4. Conclusion

Our results demonstrate that the REE in the ‘Forest Brook Catchment’ are mobilised during the rock weathering and soil formation, but their fractionation patterns are not significantly influenced by those processes. The Sm/Nd ratio is almost constant both in the soil samples and in parent rock material of the catchment. The behaviour of Y is not different from that of lanthanides.

A major part of REE and Y is probably incorporated during the rock weathering in the secondary phases such as clays (kaolinite and illite), and their mobile part is transported (predominantly from the exposed umbric A soil horizon) to the deeper parts of the profile and via ground water into the surface streams.

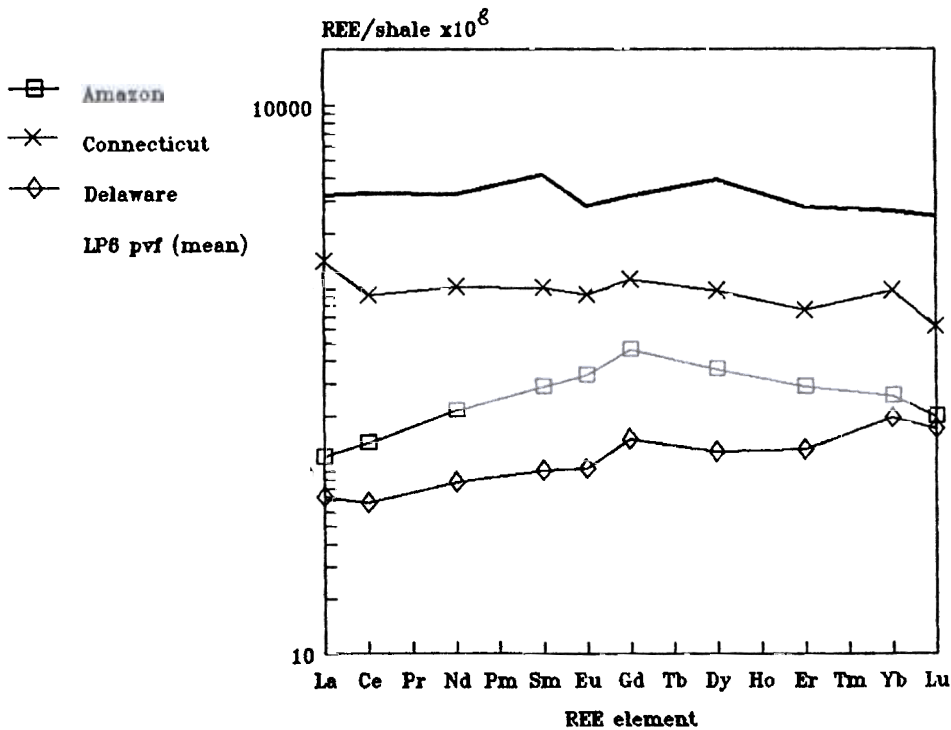


Fig. 6. REE relative abundance pattern of the filtered FBC surface water ($< 0.45 \mu\text{m}$, mean values of three collected samples) normalised to average shale REE content ($\times 10^8$), together with patterns for the Amazon, Connecticut and Delaware rivers adjusted in the same way (presented by Elderfield et al., 1990).

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