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Rare Earth Element mobility in a weathering profile – a case study from the Karkonosze Massif (SW Poland)

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ABSTRACT:

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The rare earth element (REE) contents of soils were determined to study the behaviour of REE in the weathering profile. The bedrock for the soils was the Karkonosze granite. A five-step extraction scheme was conducted on six soil profiles in order to determine the ability of REE to be released to the environment. Sequential extraction indicated that the REE are mostly concentrated in the organic and Fe–Mn oxyhydroxide soil fraction. Heavy REE appear to be more leachable than light REE. The change in concentration has been determined using the Nesbitt and Markovics formula. The soils from the soil profiles are enriched in REE in comparison to the parent rock.

Key words: Sequential extraction; Rare earth elements; Weathering; Soil.

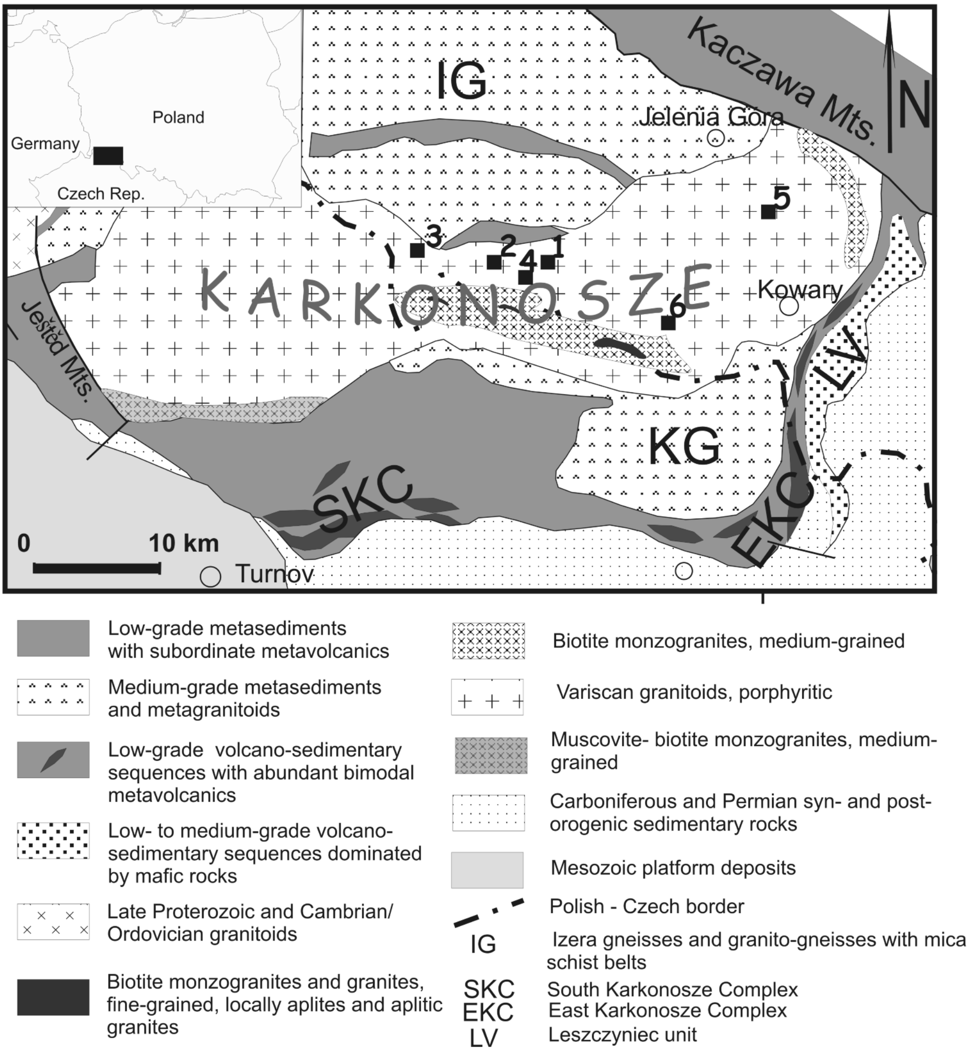
INTRODUCTION

The mobility of Rare Earth Elements (REE) in deuteric processes of acidic (felsic) rocks has been studied by many authors. However, so far there are no unequivocal results on the fractionation of elements between hydrothermally altered or weathered rocks and the soils developed from these rocks.

Earlier reports (e.g. Martin *et al.* 1978; Gromet and Silver 1983) showed that REE do not undergo fractionation during subareal weathering. The lack of fractionation and low solubility of REE species provided the opportunity to apply REE as a tool for the identification of the source material of sediments and rocks changed by weathering. Later studies showed, however, that REE undergo mobilization and fractionation during weathering processes (Nesbitt 1979, 1996; Nesbitt *et al.* 1980; Middelburg *et al.* 1988; Nesbitt and Markovics 1997; Aubert *et al.* 2001; Aubert *et al.* 2004). The distribution of REE in the soils developed on granites was analyzed by Gouveia *et al.* (1993). They observed a decrease in the REE content in the middle and upper part of the saprolite horizon and showed that selected elements from the light REE [LREE] group concentrated in the A_h horizon. However, that report did not provide any data on the pH of the soil profile or the composition of the soil solutions percolating the profile. Van der Weijden and van der Weijden (1995) suggested a lack of a consistent trend in the REE behaviour in the soils developed on felsic rocks. Although these authors suggested that the distribution of REE in the soil profile depended on the composition of the solutions penetrating the profile, they did not analyze such a composition. Nesbitt (1979) observed preferential leaching of heavy REE [HREE] in the most weathered soil horizon. Braun *et al.* (1990, 1993) confirmed this observation, i.e. a relative concentration of LREE in comparison to HREE in the weathered residuum. Byrne and Lee (1993) indicated the role of REE complexation by organic and inorganic ligands that can be present in soil solutions (see also Schijf and Byrne 2001). REE can also be adsorbed onto Mn-oxides and hydroxides (Ohta and Kawabe 2001), as well as onto clay minerals and Fe and Mn oxides and hydroxides coating clay minerals (Aide *et al.* 1999; Aide and Smith 2001). REE are rather immobile in post-magmatic (high-temperature) processes (Förster 2000). Hydrothermal carbonates can incorporate REE (Cantrell and Byrne 1987; Johannesson *et al*. 1996). Dissolution of the minerals incorporating REE results in: (a) formation of carbonate and phosphate REE complexes (Lee and Byrne 1993; Johannesson *et al.* 1996); (b) formation of organic complexes with REE (Cantrell and Byrne 1987; Schijf and Byrne 2001); (c) adsorption of REE onto Mn oxides and hydroxides (Ohta and Kawabe 2001); and (d) adsorption of REE onto clay minerals or clay minerals coated with Fe and Mn oxides and hydroxides (Aide *et al.* 1999; Aide and Smith 2001). Transformation of REE-bearing minerals can also result in the recrystallization of phosphates (REE-bearing) into secondary minerals such as rhabdophan and florencite (Taunton *et al.* 2000).

Despite the fact that REE have very similar chemical properties, analysis has shown their variable chemical activity (Cantrell and Byrne 1987; Lee and Byrne 1993; Johannesson *et al.* 1996; Schijf and Byrne 2001) and preferential migration of some REE in the weathering processes of rocks and minerals (Braun *et al.* 1993, 1998; Gouveia *et al.* 1993; Prudencio *et al.* 1993; Braun and Pagel 1994; Ohta and Kawabe 2001; Schijf and Byrne 2001)

This study is focused on magmatic rocks from the Karkonosze Massif in south-west Poland and on the soils developed from them. The Karkonosze granites are accompanied by granodiorites, pegmatites, aplites and



Text-fig. 1. Map of Karkonosze Mountains showing the location of sampled sections; 1 – Michałowice, 2 – Szklarska Poręba Huta, 3 – Kobyli Potok, 4 – Czerwona Jama, 5 – Karpniki, 6 – Krucze Skałki lamprophyres (Borkowska 1966; Klominsky 1969). The formation of the rocks resulted mainly from mixing of mantle- and crust-derived magmas (Słaby *et al.* 2002; Słaby and Götze 2004; Słaby and Martin 2008). Different stages of the differentiation of the magmas in the Karkonosze Massif led to considerable changes in trace element concentrations, including REE enrichment or depletion (Słaby and Martin 2008).

The aim of the present study is to show that REE underwent mobilization during weathering and fractionation between the rock, soil, and solutions percolating the host rock. Phases that could have had a dominating influence on pedogenic processes and REE behaviour include accessory minerals like apatite, xenothyme, zircon and allanite; as well as major rock-forming minerals such as alkali feldspars, plagioclases, and micas. Accessory minerals such as apatite, xenothyme, zircon, and allanite occur in low quantities in the rocks studied. Of the major phases, the rock-forming minerals, biotite and feldspar, have higher REE concentrations.

THE KARKONOSZE PLUTON – GEOLOGICAL SETTING, PETROLOGY AND SOILS

The Karkonosze–Izera Massif comprises the south-central part of the Western Sudetes in the north-eastern margin of the Bohemian Massif. The Western Sudetes with their mosaic composition are considered to be part of the Saxo-Thuringian Zone (Behr *et al.* 1984; Franke *et al*. 1993).

The Hercynian Karkonosze intrusion is composed mainly of peraluminous, in some cases metaluminous, type I granites (Chappel and White 1974; Wilamowski 1998). They are generally represented by biotite granite, rarely two-mica granite. Klominski (1969) recognized four types of biotitic granite, a two-mica granite, and three types of granodiorites in the Karkonosze pluton. Słaby and Martin (2005, 2008) simplified the typology of the rocks,distinguishing porphyritic and equigranular granite as well as hybrids.

Porphyritic granites are present within almost the entire area of the Karkonosze Massif, and are characterized by the presence of numerous phenocrysts, biotite schlieren and spherical or ellipsoidal enclaves of mafic rocks (Słaby 2002). Modal analysis of the enclaves indicates that their composition differs significantly from that of the granites. They are depleted in quartz, enriched in plagioclases, and pass from monzonite granite through granodiorite into monzonites and diorites (Borkowska 1966; Słaby and Martin 2008).

The porphyritic granite is composed of K-feldspar (megacrysts and groundmass crystals), plagioclases (partly sericitized with occasional epidote), quartz, and biotite that forms concentrations of several individuals (mafic clots), or appears as single and randomly distributed crystals. Porphyritic granite occasionally contains small quantities of hornblende, muscovite, fluorite and accessory minerals (Borkowska 1966).

Numerous aplites and accompanying pegmatites occur in the Karkonosze granite. The main minerals present in the pegmatites include: quartz, K-feldspar, plagioclase, biotite and muscovite. Lithium-rich micas, aegirine, hornblende, garnets, magnetite, ilmenite, hematite, titanite, wolframite, cassiterite, tourmaline, beryl, topaz, numerous sulphide mineralization minerals (arsenopyrite, pyrite, bismuthinite and marcasite), bismuth and native silver, as well as many other rarer minerals such as gadolinite, Y-hingganite, and hydoxylbastnaesite are also present (Pieczka and Gołębiewska 2002).

Studies of the origin of the melts that crystallized into the Karkonosze Massif (Słaby *et al.* 2003; Słaby and Galbarczyk-Gąsiorowska 2002; Słaby *et al.* 2002; Słaby and Götze 2004: Słaby and Martin 2008) indicated that the main process influencing the composition of the massif was mixing of mafic and felsic magmas and fractional crystallization. Both the mafic and felsic melts display distinct differences with regard to the concentration of their major as well as trace elements, particularly REE.

REE are incorporated in many minerals of the Karkonosze granites: apatite, zircon, allanite, calcite, biotite and feldspar. In some cases, they form their own mineralization, such as gadolinite $(Y,REE)_2Fe[BeSiO_4|O]_2$ or hingganite – $Y(Y,REE)_2[BeSiO_4|OH]_2$ (Pieczka and Gołębiewska 2002).

Rock weathering and soil formation depend on many factors, *inter alia* climate, morphology, composition of the solutions percolating the bedrock, vegetation and, particularly, the bedrock composition. The soil types in the Sudetes, including those derived from the Karkonosze granite, are strictly connected with the nature of the bedrock and with the geomorphology (Borkowski 1966, 1998).

The soils in the Sudetes are generally acidic or poorly acidic. According to the “Geochemical Atlas of Poland” (Lis and Pasieczna 1995), the pH in the study area ranges from 4 to 5. Groundwater pH in the area varies from very low (3.2) to almost neutral (6.5). The ground- and surface water is poorly mineralized (100 mg/dm^3) and presents the following composition: HCO_3–SO_4–Ca–Mg or SO_4–Ca–Mg (Kryza *et al.* 1995; Bocheńska *et al.* 1997; Dobrzyński 1997, 2005, 2006,). The acidic reaction of the environment is the result of weathering of ore minerals, particularly sulphides, natural sources(e.g. fulvic organic acid) and acid rains (Sienkiewicz *et al.* 2006). All sources supply considerable amounts of SO_4 and NO_3, heavy metals and aluminium to the soil (Kryza *et al.* 1993, 1995, 1997; Kmieć *et al.*1994; Kryza *et al.* 1994; Bocheńska *et al.* 1997a, b).

Total organic carbon (TOC) content in soils in the A_0 horizon (classification of soils according to the Polish Soil Society) in the area of the Karkonosze granite varies between 2 and 30% (Kuźnicki 1973; Borkowski *et al.* 1993; Borkowski 1998) and decreases with depth. In acidic brown soils developed from granite, distinct mobilization of humus compounds in the humified part of the organic matter of the A_0 horizon takes place at very low pH and shows very high exchangeable acidity (Mazurski 1978).

In the Karkonosze Massif, brown acidic soils are characterized by a high content of free iron, whereas the free aluminium and silica contents are much lower. The concentration of iron in the soils of this area reaches 1–4wt% according to the "Geochemical Atlas of Poland" (Lis and Pasieczna 1995).

The soils of the Western Sudetes typically show a low content of exchangeable alkaline cations, the sum (S) of which varies between 0.80–2.99 mval/100 g (Borkowski *et al.* 1993).

SAMPLING AND METHODS

Rock samples were collected from five different outcrops: Michałowice, Szklarska Poręba Huta, Kobyli Potok, Czerwona Jama, Karpniki, Krucze Skałki (Text-fig. 1). The description of the samples is shown in Table 1. All samples were ground. Their decomposition was performed in a Multiwave Perkin Elmer/PAAR Physica closed microwave system (Laboratory of Water, Soils and Rock Chemistry, Faculty of Geology, University of Warsaw). The reagent used for demineralization was aqua regia in the ratio 3:1 (6 ml HCl + 2 ml HNO_3 per 0.5 g of sample). The solutions obtained were diluted to 50 ml with deionized water and stored in tightly sealed polyethylene vessels at temperatures from –2°C to –4°C to prevent precipitation of hydroxides. Their precipitation could act as a matrix for capturing elements from solutions and binding them in insoluble complexes, which would influence the results of analysis. The proposed dissolution procedure was chosen in order to dissolve all phases susceptible to weathering and able to provide bio-available elements to the soil.

In all samples (rock and soils), major elements such as Ca, Mg, K, Na, and Al, as well as Ti, Zr, Hf (ICP-EAS Varian VISTA PRO/Laboratory of Water, Soils and Rock Chemistry, Faculty of Geology, University of Warsaw) and REE (ICP-MS Elan 6100 DRC Perkin Elmer/Laboratory of Applied Analytical Chemistry, Faculty of Chemistry, University of Warsaw) were determined.

Soil samples were collected from pits located above each quarry or exposure from which rock samples were collected. In all of the soil profiles, three soil horizons were distinguished (humus-ferric horizon *A/Bfe*, illuvial horizon *Bfe*, debris horizon *Bfe/C*). The only exception was the Michałowice profile, where four horizons were present: humus-ferric horizon *A/Bfe*, ferro-humic horizon *Bbr*, illuvial horizon *Bfe*, debris horizon *Bfe/C* (Table 2). The characteristics of particular soil horizons and their thicknesses indicate poorly developed mountain soils with low contents of humus and clay minerals.

The carbon content in each soil and humus fractions was determined using the volumetric method with potassium dichromate in a TOC 5000 A apparatus (Department of Soil Environment Sciences, Warsaw University of Life Sciences – WULS/SGGW). Decalcification of soil was carried out with 0.02 M H_2SO_4, the humic acids were next separated by reaction with 0.1 M NaOH. Subdivision into humic and fulvic acids was made by acidifying alkaline extracts to pH 1.

The degree of humification was calculated according to the following algorithm: degree of humification = C fraction (D + KH + HF)100%/TOC (C – fraction concentration; D – decalcitation; KH – humic acids; KF – fulvic acids; TOC – total organic carbon) (Department of Soil Environment Sciences, Warsaw University of Life Sciences –WULS/SGGW).

Sample location	**GRANITE***	**WEATHERED GRANITE ***	**PEGMATITE***
Michałowice	Mgr 8	--	Mpeg 10, Mpeg14
Szklarska Poręba Huta	SPHgr 7	SPHgzw 15	SPH peg 5
Kobyli Potok	KPgr 3	--	KPpeg 1, KPpeg 4, KPpeg 12, KPpeg 16
Czerwona Jama	--	--	CJpeg 9
Karpniki	--	Kgzw 6	Kpeg 11, Kpeg 13
Krucze Skałki	--	--	KSpeg 2

*M, SPH...KS – symbol of location, gr – granite, gzw – weathered granite, peg – pegmatite, 1...16 – number of samples

Table 1. Symbol and number of rock samples

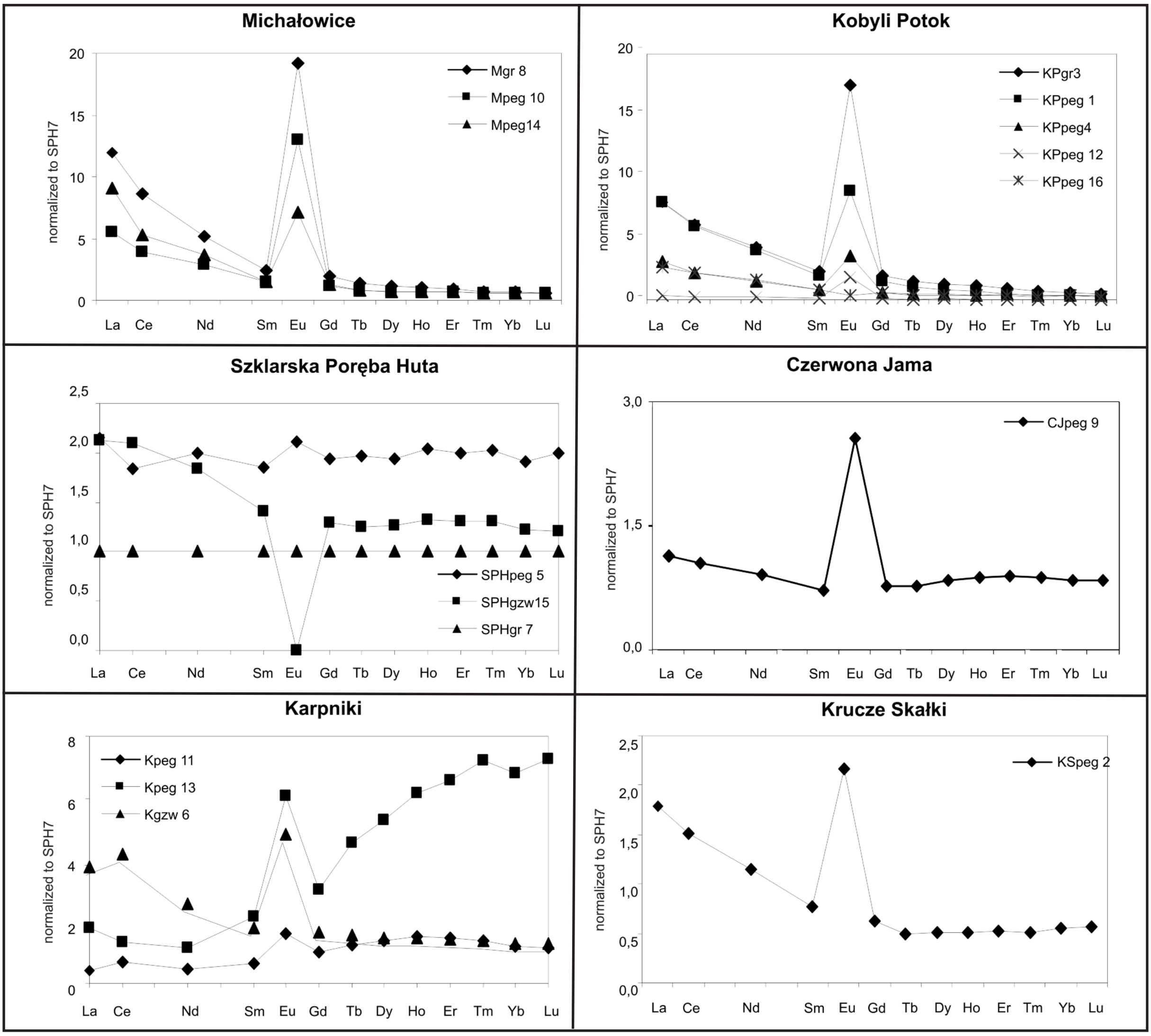
The soil pH (pH $_{H_2O}$ and pH$_{KCl}$) was determined using a laboratory pH meter.

Soil samples were subdivided on sieves into two fractions: <1 mm and >1 mm. Extraction was carried out for all soil horizons in all soil profiles for the first fraction <1 mm. Sequential extraction was conducted according to the five-stage procedure of Kersten and Förstner (1987). Many procedures have been proposed for sequential extraction, e.g. Tessier *et al.* (1979), Chester *et al.* (1988); however the procedure of Kersten and Förstner (1987) seems to be the most suitable in the present investigation.

The five-step procedure (Kersten and Förstner, 1987) uses the following reagents:

Sample rocks	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Mgr 8	45.67	88.89	10.00	34.78	6.52	0.60	5.90	0.85	5.27	0.93	2.92	0.40	2.81	0.38
Mpeg 10	20.99	39.74	5.06	19.12	3.95	0.41	3.58	0.52	3.50	0.65	2.16	0.30	2.33	0.33
Mpeg 14	34.95	54.26	7.09	24.76	4.17	0.22	3.74	0.51	3.42	0.63	2.19	0.31	2.48	0.34
SPHgr 7	3.83	10.29	1.51	6.77	2.71	0.03	3.09	0.63	4.80	0.92	3.29	0.54	4.34	0.64
SPHpeg 5	8.23	18.97	3.07	13.53	5.05	0.07	5.96	1.24	9.28	1.88	6.58	1.09	8.31	1.26
SPHgzw 15	8.16	21.62	2.98	12.49	3.82	0.00	3.98	0.79	6.05	1.21	4.31	0.70	5.32	0.77
KPpeg 1	30.19	62.89	7.66	29.01	6.23	0.55	6.03	0.94	5.94	1.06	3.17	0.39	2.56	0.32
KPgr 3	30.16	61.15	7.34	27.13	5.42	0.28	4.75	0.65	3.73	0.59	1.70	0.19	1.35	0.15
KPpeg 4	11.95	22.84	2.73	9.93	2.09	0.11	1.94	0.28	2.03	0.36	1.34	0.19	1.73	0.25
KPpeg 12	1.51	2.50	0.29	1.19	0.29	0.06	0.30	0.01	0.38	0.02	0.19	0.00	0.21	0.00
KPpeg 16	10.11	22.96	2.93	10.56	2.32	0.01	1.89	0.25	1.74	0.29	1.06	0.14	1.28	0.16
CJpeg 9	4.32	10.80	1.47	6.09	1.93	0.08	2.38	0.48	4.00	0.80	2.92	0.47	3.64	0.53
Kgzw 6	14.46	43.06	4.43	17.32	4.86	0.15	5.14	0.98	7.00	1.37	4.64	0.73	5.53	0.83
Kpeg 11	1.56	6.98	0.60	3.07	1.76	0.05	3.12	0.78	6.61	1.42	4.87	0.73	5.16	0.74
Kpeg 13	6.86	13.93	1.68	7.76	5.80	0.19	9.42	2.88	25.32	5.69	21.53	3.88	29.46	4.60
KSpeg 2	6.83	15.53	1.99	7.78	2.11	0.07	1.93	0.32	2.46	0.47	1.74	0.27	2.40	0.36
Soils sample	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
M1	20.60	45.40	3.00	11.89	2.66	0.31	3.01	0.43	2.56	0.49	1.44	0.22	1.50	0.23
M2	3.92	14.66	1.42	6.72	2.09	0.19	2.44	0.40	2.48	0.49	1.46	0.22	1.47	0.21
M3	31.66	63.32	3.72	13.15	2.65	0.42	3.06	0.40	2.21	0.40	1.11	0.16	1.12	0.18
M4	55.02	107.30	8.20	29.21	5.08	0.51	6.36	0.78	4.21	0.78	2.20	0.33	2.14	0.32
SPH1	17.92	37.06	2.44	8.94	2.11	0.17	1.66	0.20	1.07	0.20	0.62	0.10	0.74	0.13
SPH2	3.48	7.42	0.86	3.42	0.68	0.07	0.66	0.09	0.44	0.07	0.16	0.02	0.12	0.02
SPH3a	18.48	40.98	2.49	9.25	1.70	0.15	1.80	0.21	1.02	0.17	0.44	0.07	0.47	0.07
KP2	19.38	37.90	4.53	16.95	2.94	0.44	3.10	0.37	2.10	0.39	1.16	0.17	1.08	0.17
KP3	6.62	15.88	1.61	7.07	2.57	0.07	3.16	0.64	4.41	0.98	3.20	0.56	4.13	0.64
KP4	4.00	11.52	1.10	4.87	1.74	0.04	2.01	0.40	2.71	0.58	1.92	0.35	2.59	0.39
CJ2	14.46	35.78	1.92	7.12	1.57	0.16	1.34	0.21	1.18	0.22	0.66	0.10	0.72	0.12
CJ3a	34.54	106.61	9.14	34.06	6.68	0.44	7.47	1.05	6.33	1.21	3.54	0.52	3.45	0.53
CJ3	27.60	66.18	3.22	11.71	2.51	0.17	2.86	0.41	2.36	0.46	1.34	0.21	1.47	0.22
K1	4.40	16.88	0.57	2.21	0.68	0.08	0.97	0.21	1.55	0.36	1.15	0.20	1.46	0.23
K1a	8.84	17.90	1.15	4.41	1.29	0.13	1.67	0.33	2.36	0.52	1.68	0.28	2.08	0.33
K2	14.11	30.34	3.85	15.15	3.69	0.28	4.49	0.83	5.47	1.13	3.60	0.57	3.85	0.61
KS1	14.64	31.52	1.99	7.78	1.70	0.17	1.98	0.32	2.07	0.44	1.37	0.21	1.47	0.23
KS2	19.32	41.48	2.51	9.62	2.18	0.23	2.57	0.45	3.05	0.66	2.06	0.32	2.26	0.34
KS3	14.68	31.18	2.01	7.57	1.52	0.16	1.53	0.19	0.93	0.14	0.35	0.04	0.28	0.04

Table 2. REE concentration in rocks and solis [ppm]

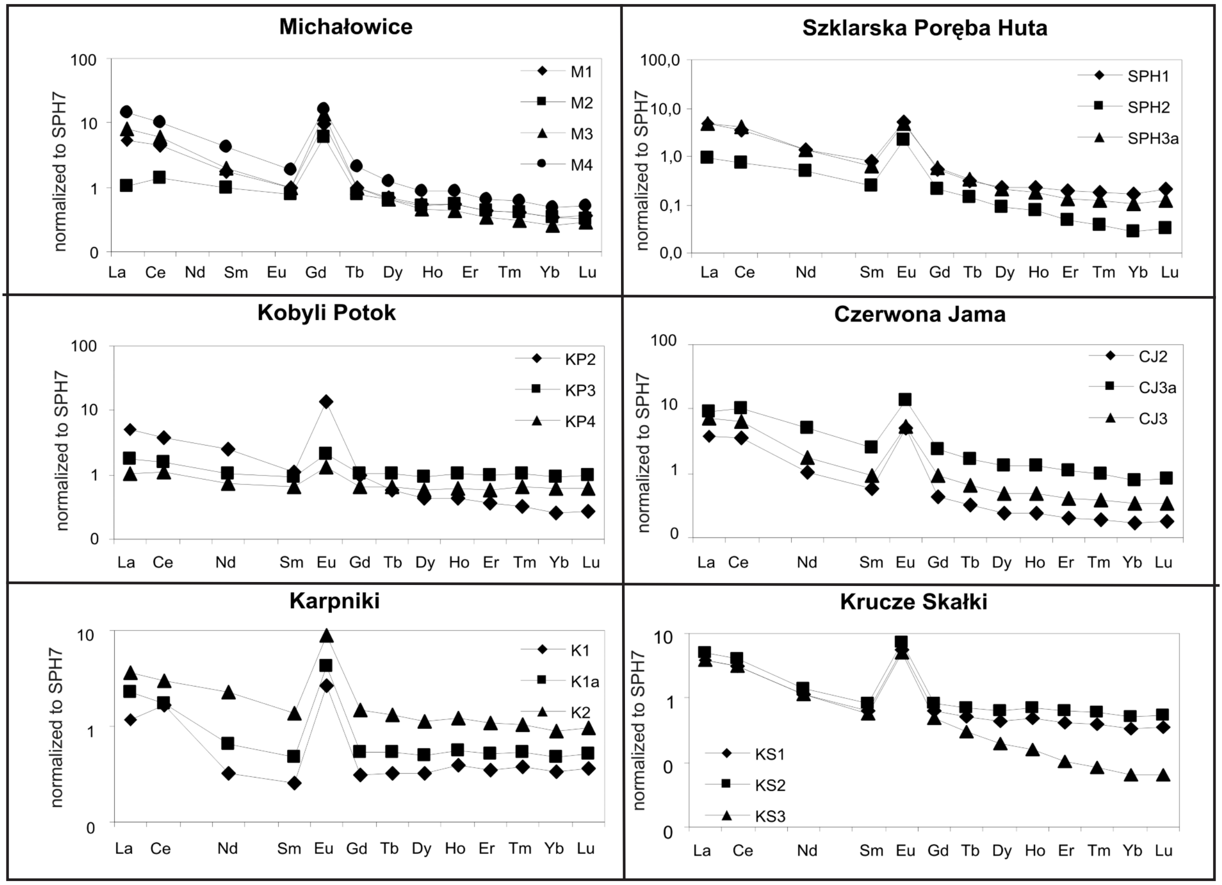


Text-fig. 2. Concentration of REE in the rock samples

Localization	Soil horizons*	Thickness [cm]	Samples
Michałowice	humus - ferric (A/Bfe)	25	M1
Michałowice	ferro - humic (Bbr)	45	M2
Michałowice	illuvial horizon (Bfe)	40	M3
Michałowice	debris (Bfe/C)	> 90	M4
Szklarska Poręba Huta	humus - ferric (A/Bfe	15	SPH 1
Szklarska Poręba Huta	illuvial horizon (Bfe)	25	SPH2
Szklarska Poręba Huta	debris (Bfe/C)	> 40	SPH3a
Kobyli Potok	humus - ferric (A/Bfe	10	KP2
Kobyli Potok	illuvial horizon (Bfe)	5	KP3

* Systematyka Gleb Polski – IV – Roczniki Gleboznawcze T.XL, no.¾. PWN, Warszawa 1989.

Table 3. Horizons of soils



Text-fig. 3. Concentration of REE in the soils samples normalized to SPH7

- stage I: extractant –ammonium acetate - 1mol/dm^3 (ion exchangeable fraction);
- stage II: extractant – dilute acetic acid - 0.1mol/dm^3 (carbonate fraction);
- stage III: extractant – hydroxylamine – 0.01 mol/dm^3/acetic acid (25%) (reducible fraction);
- stage IV: extractant – hydrogen peroxide (30%) acidified by concentrated (68%) nitric acid (organic/sulphidic fraction);
- stage V: extractant – hot concentrated (68%) nitric acid (residual fraction).

200-mg samples were mixed with one of the extractants (in 1:50 ratio), shaken in a horizontal position for 2 h in a shaker (Unimax 1010, Heidolph), and then

symbol of samples	TOC[%]	decalcitation	humin acid [%]	fulvic acid [%]	humine [%]	cha/cfa*	degree of humification [%]
M1	4.50	0.52	1.10	1.17	1.71	0.94	62.00
M2	5.83	0.50	1.30	2.11	1.92	0.62	67.07
SPH1	8.05	0.89	3.05	2.01	2.10	1.52	73.91
SPH2	7.28	1.09	1.75	2.74	1.70	0.64	77.29
KP2	14.91	0.90	3.80	3.81	6.40	1.00	57.08
KP3	4.35	0.99	0.91	0.64	0.64	0.50	85.29
CJ2	3.59	0.34	0.63	0.84	1.78	0.75	50.47
CJ3a	0.45	0.09	0.02	0.14	0.20	0.14	55.56
K1a	0.70	0.08	0.10	0.15	0.39	0.73	48.57
K1	0.65	0.09	0.08	0.19	0.29	0.42	55.38
KS1	12.28	0.62	3.05	1.35	7.26	2.26	40.88
KS3	7.31	0.82	2.05	2.81	1.63	0.73	77.70

* cha – concentration of humin acid; cfa – concentration of fulvic acid

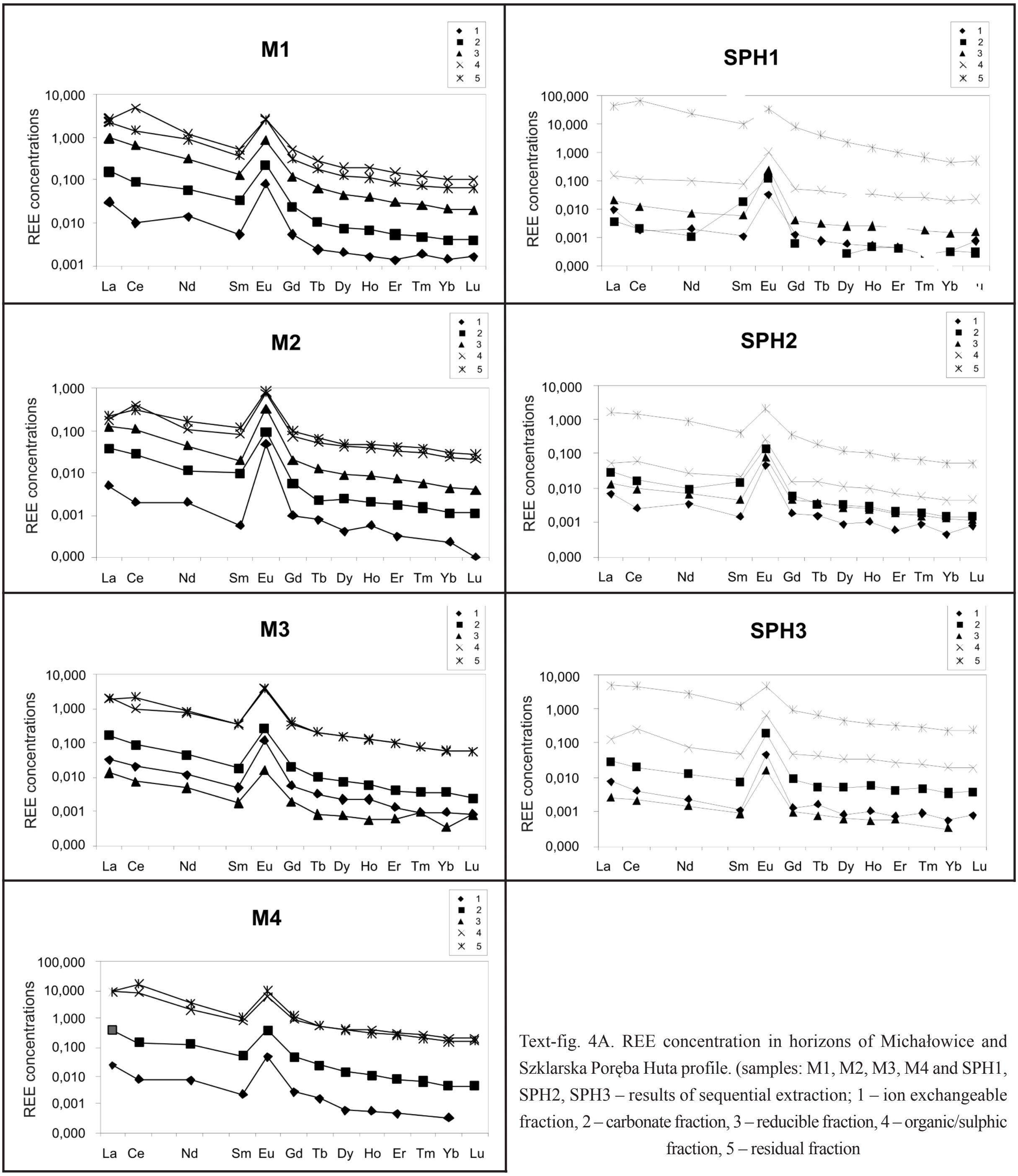
Table 4. Organic matter [%]

centrifuged (Hettich Zentrigugen EBA 21) for 15 min at 14 000 rev./min. After decanting into polypropylene vessels, each extractant was acidified in order to prevent precipitation of hydroxides and frozen. The composition of the solution after extraction (after defrosting) was analysed using an inductively coupled plasma mass spectrometer (ICP-MS Elan 6100 DRC Perkin Elmer/Laboratory of Applied Analytical Chemistry, Faculty of Chemistry, University of Warsaw).

Model of Nesbitt and Markovics (1997)

The degree of enrichment or leaching of REE during weathering processes in relation to its concentration in fresh rocks in the study area was calculated based on one selected element that showed relatively immobile behaviour in these processes.

The percentage change of the ratio between the REE content in the soil and the bedrock was calculated



Text-fig. 4A. REE concentration in horizons of Michałowice and Szklarska Poręba Huta profile. (samples: M1, M2, M3, M4 and SPH1, SPH2, SPH3 – results of sequential extraction; 1 – ion exchangeable fraction, 2 – carbonate fraction, 3 – reducible fraction, 4 – organic/sulphic fraction, 5 – residual fraction using the following formula (Nesbitt 1979; Nesbitt et al. 1980; Nesbitt and Markovics 1997):

$\%\ change = 100\ \{(Ti/X)_p - (Ti/X)_s/(Ti/X)_p\}$

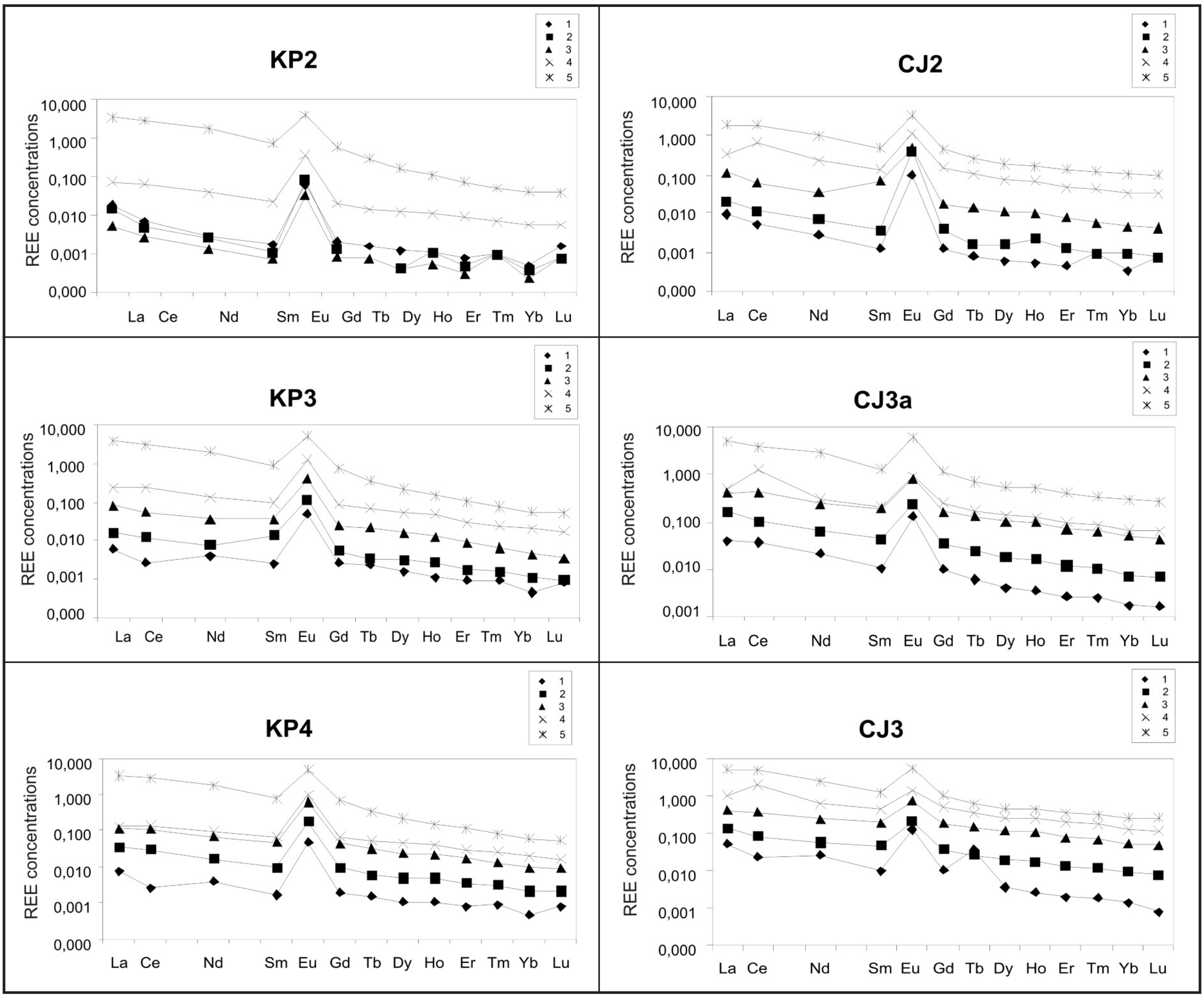
where: Ti – concentration of Ti in rock or soil; X – concentration of selected element in rock or soil; index “s” marks sample of weathered rock or soil; index “p” marks sample of fresh bedrock.

The bedrock herein refers to the rock on top of which soil samples were collected. Titanium was selected as the immobile element because it displayed the lowest change in concentration during rock-soil transformation. An attempt to create the model using Zr and Hf to represent the immobile elements did not give satisfactory results. In both cases, the percentage changes of the ratio between the contents of these elements in the profile were too high. Similarly, the application of Al as the immobile element was excluded because of the easy mobilization of Al in an acidic environment.

RESULTS

Rocks

The granite rocks from Michałowice are the most enriched in REE, whereas the pegmatites are depleted in REE. The enrichment is caused by considerable amounts of mafic components in the hybrid magma that crystallized to form the Michałowice granite (Słaby and Martin 2008). In all rock types studied a predominance of LREE over HREE is observed. The absolute concentrations of REE in sample SPHgr7 from the Szklarska Poręba Huta granite are much lower than in the granite from Michałowice and vary within a range of 10 to 0.6 ppm (Table 3). The Szklarska Poręba Huta granite is a product of crust-related magma crystallization. This magma is extremely REE-poor (Słaby and Martin 2008). Although the total REE concentration is low, the con-



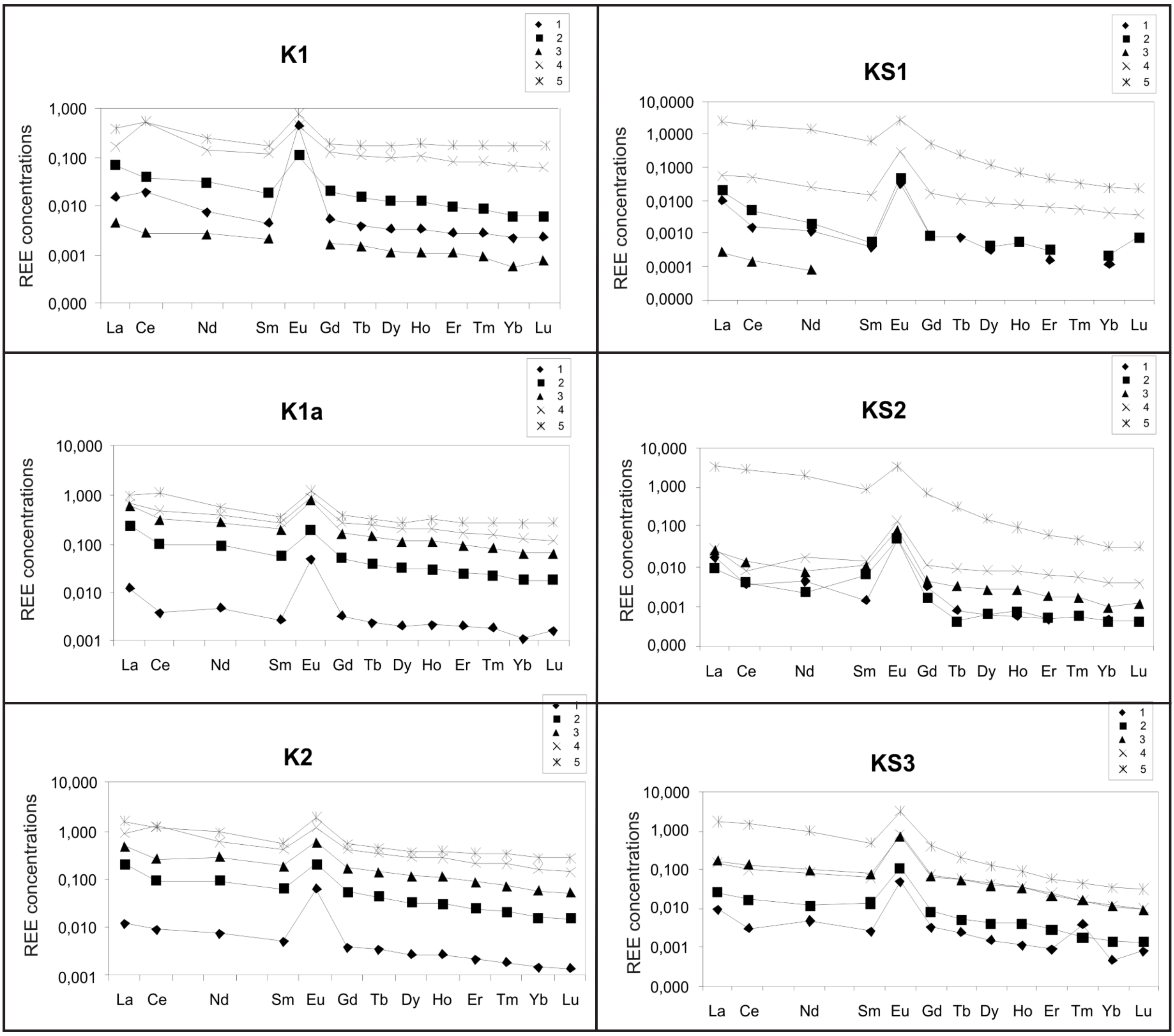
Text-fig. 4B. REE concentration in horizons of Kobyli Potok and Czerwona Jama profile. Samples: KP2, KP3, KP4 and CJ2, CJ3a, CJ3 – results of sequential extraction; 1 – ion exchangeable fraction, 2 – carbonate fraction, 3 – reducible fraction, 4 – organic/sulphic fraction, 5 – residual fraction centration of LREE is higher than that of HREE. The REE diagram for the Kobyli Potok section (Text-fig. 2) is similar to that for Michałowice, albeit the total concentrations of REE are lower (from 63 to 0.2 ppm) (Table 2). The Czerwona Jama (pegmatite) and Krucze Skałki (pegmatite) sections show similar REE diagrams (Text-fig. 2). A predominance of LREE over HREE as well as a distinct positive europium anomaly can be noted. The total concentrations of REE in both samples of pegmatite rocks are also similar (from 15 ppm in Krucze Skałki to 0.1 ppm in Czerwona Skała) (Table 2). The REE plot for the Karpniki section is completely different. The plot for sample Kgzw6 from this section is characterized by LREE-enrichment. Sample Kpeg11 shows HREE oncentrations. A distinct positive europium anomaly also appears (Text-fig. 2). In the case of the pegmatites, a distinct predominance of HREE over LREE (Kpeg13) can be observed. Generally, total REE concentrations vary between 43 ppm (weathered granite) to 0.05 ppm (pegmatite) (Table 3).

Detailed results of chemical analysis for each of the studied sections are presented in the diagrams (Text-fig. 2) and in Table 2.

Soils

Overall analysis of soils

The results are presented in Table 2 and in Text-fig. 3. The normalization for REE was carried out against granite sample (SPHgr7), which represents the crystallization product of the most evolved crustal melt. In all of the soil profiles formed on the previously discussed granitoid-



Text-fig. 4C. REE concentration in horizons of Karpniki and Krucze Skałki profile. Samples: K1, K1a, K2 and KS1, KS2, KS3 – results of sequential extraction; 1 – ion exchangeable fraction, 2 – carbonate fraction, 3 – reducible fraction, 4 – organic/sulphic fraction, 5 – residual fraction pegmatoids, a distinct enrichment in LREE compared to HREE was observed (Table 3). As with the rocks plots, a positive europium anomaly was also observed in the soil profiles. The diagrams show the same HREE content in practically all of the soil profiles (Text-fig. 3). Differences can be observed in the case of concentrations in particular soil horizons. In some profiles the highest content of REE was observed in the debris horizon, whereas in other soil profiles it was in the illuvial horizon. In order to explain these differences, further analyses were performed to determine the concentrations of the fractions (exchangeable, carbonate, sulphide and oxide, organic matter) which could bind REE in soil horizons.

Organic matter

Table 4 presents the results of the determinations of the organic matter, which was made using the volumetric method with potassium bichromate.

In almost all the soil profiles a predominance of fulvic acids over humic acids was observed. The degree of humification varied between 48 and 77%
Sequential extraction of the soils

symbole of soils samples	pH $_{KCl}$	temperature [^{0}C]	pH$_{H2O}$	temperature [^{0}C]
KS1	2.78	20.0	3.15	17.1
KS2	2.82	18.9	2.89	17.1
KS3	2.62	18.9	2.84	17.2
K1	2.73	19.4	3.10	17.9
K1a	3.32	20.0	2.71	17.4
K2	3.26	20.2	3.50	17.3
SPH1	3.21	19.7	3.28	17.0
SPH2	2.8	19.4	3.30	17.0
SPH3a	3.82	19.8	4.25	17.1
KP2	2.84	19.7	3.10	17.6
KP3	3.00	19.7	3.09	17.4
KP4	3.26	19.8	3.43	17.6
CJ2	3.00	19.9	3.14	17.3
CJ3a	3.26	19.7	3.41	17.4
CJ3	3.58	19.5	3.67	17.4
M1	2.23	19.4	2.43	17.3
M2	2.97	19.1	3.22	17.5
M3	2.98	19.3	3.33	17.5
M4	2.81	19.0	2.98	17.7

Table 5. pH of soils samples

The concentrations of all of the elements in the extracted solutions are presented on plots normalized to granite (SPHgr7) (Text-fig. 4A–C).

The distribution of total values of REE in particular fractions can be described as increasing from the exchangeable fraction to the mineral fraction. In almost all the soil profiles and horizons, the lowest content of REE was leached during the first step of the sequential extraction (Text-fig. 4A–C). Only in the case of the horizons in the K1, SPH3a, M3 and KS1 soil profiles were smaller concentrations of REE observed in the extracted solutions from the third step than in solutions from the first step of the sequential extraction (Text-fig. 4A, C). The highest REE content appeared in the extracts obtained during the fourth and fifth steps of the sequential extraction. All the soil profiles are characterized by higher leaching of LREE compared to HREE (Text-fig. 4A–C).

Table 5 presents the results of the pH measurements in each soil level.

FRACTIONATION OF REE DURING WEATHERING PROCESSES – DISCUSSION

Sequential extraction carried out for soils from selected profiles in the Karkonosze area has shown the association of the REE with the organic matter fraction and with the Fe–Mn oxides and hydroxides fraction (Text-fig. 4A–C). The binding of the REE with these fractions indicates the easy formation of REE organic complexes and the possibility of REE adsorption onto organic compounds and Fe–Mn oxides and hydroxides. These studies confirm that REE can be fractionated in weathering processes.

Changes in REE concentrations in the soils studied can also be the result of interaction between plant roots, which absorb phosphates (which can contain REE) and carbonates from the soil solutions.

The activity of microbial organisms (bacteria, fungi) can also influence REE mobility (Taunton *et al.* 2000). Biochemical and biological influence on REE migration is not discussed herein.

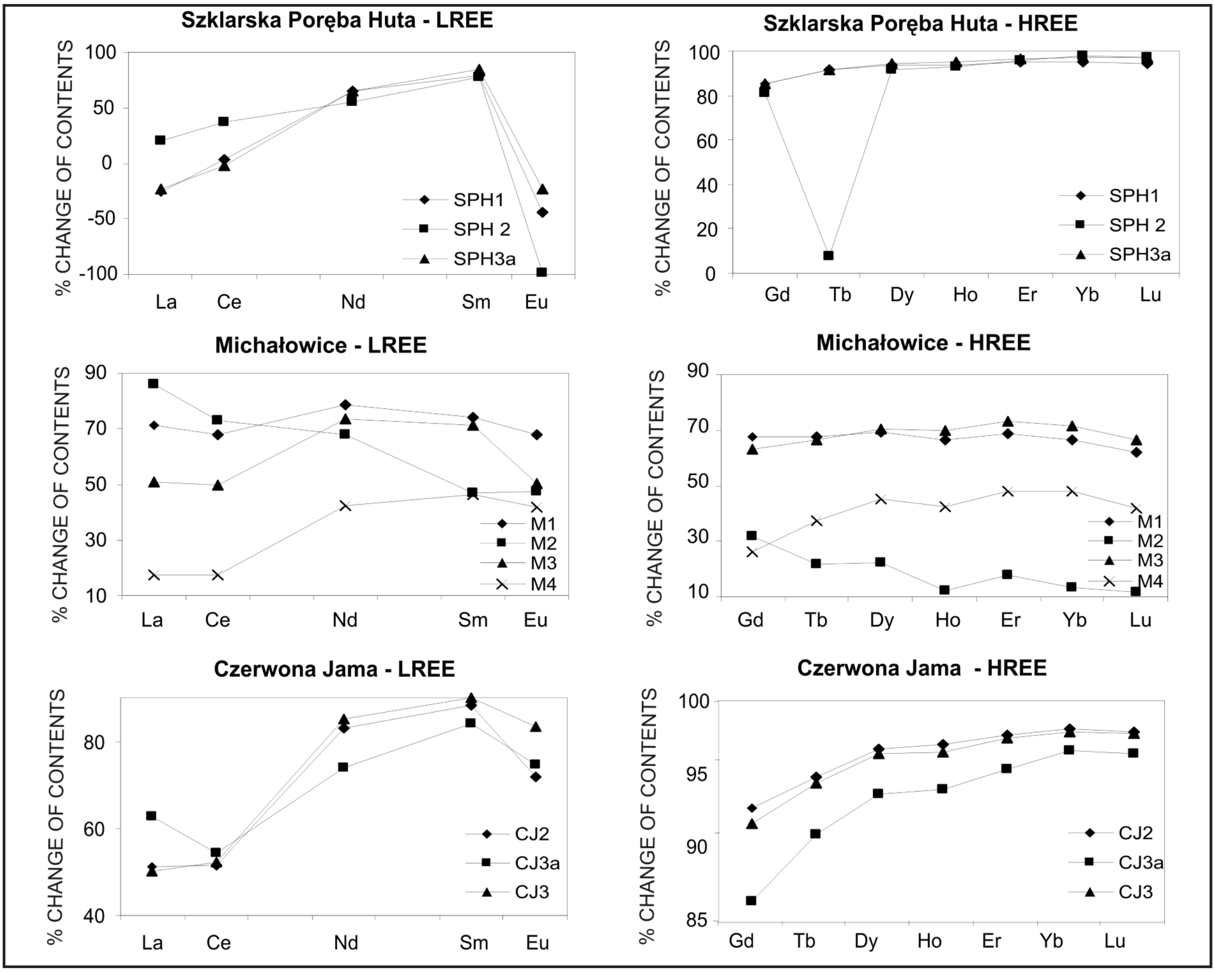
Different concentrations of LREE and HREE were observed in all of the the soil profiles (Text-fig. 5A, B). In some cases, different accumulation of REE could be observed at particular horizons, both in the case of the total REE content as well as in both LREE and HREE. In practically all of the soil profiles a distinct enrichment in REE was observed in the humus-ferric horizon, which may indicate good binding of REE with organic and organic-mineral complexes, as well as the possibility of migration in such forms. In the soil profiles developed on granites, HREE generally predominate over LREE. In the Michałowice soil profile, enrichment in REE (both LREE and HREE) is high in comparison to bedrock (Text-fig. 5A). The Szklarska Poręba Huta soil profile is different, being enriched in HREE and depleted in LREE in relation to the bedrock (Text-fig. 5A). Granites from Szklarska Poręba Huta (SPHgr7) are characterized by a distinct depletion in REE and hence soils derived from these rocks are primarily depleted in REE. LREE migrated with the soil solutions, which resulted in depletion in these elements in soils that already had low REE concentrations. HREE as less mobile are preserved in selected soil horizons.

In all of the soil profiles, lower concentrations of REE were observed in the middle horizon (illuvial or ferric horizon). Good binding of REE with organic matter immobilizes these elements in the first horizon (humus-ferric), whereas from the illuvial horizon they can be transported into the third, debris horizon, resulting in its distinct enrichment in REE.

Influence of TOC content, phosphorus compounds, Fe–Mn oxides and hydroxides, and pH on the mobility of REE

The content of humus compounds largely influences the sorption capability of soils, including the possibility of REE immobilization. A low degree of humification, the predominance of fulvic acids over humic acids and a CKH/CKF ratio below 1 are characteristic of poorly developed brown soils.

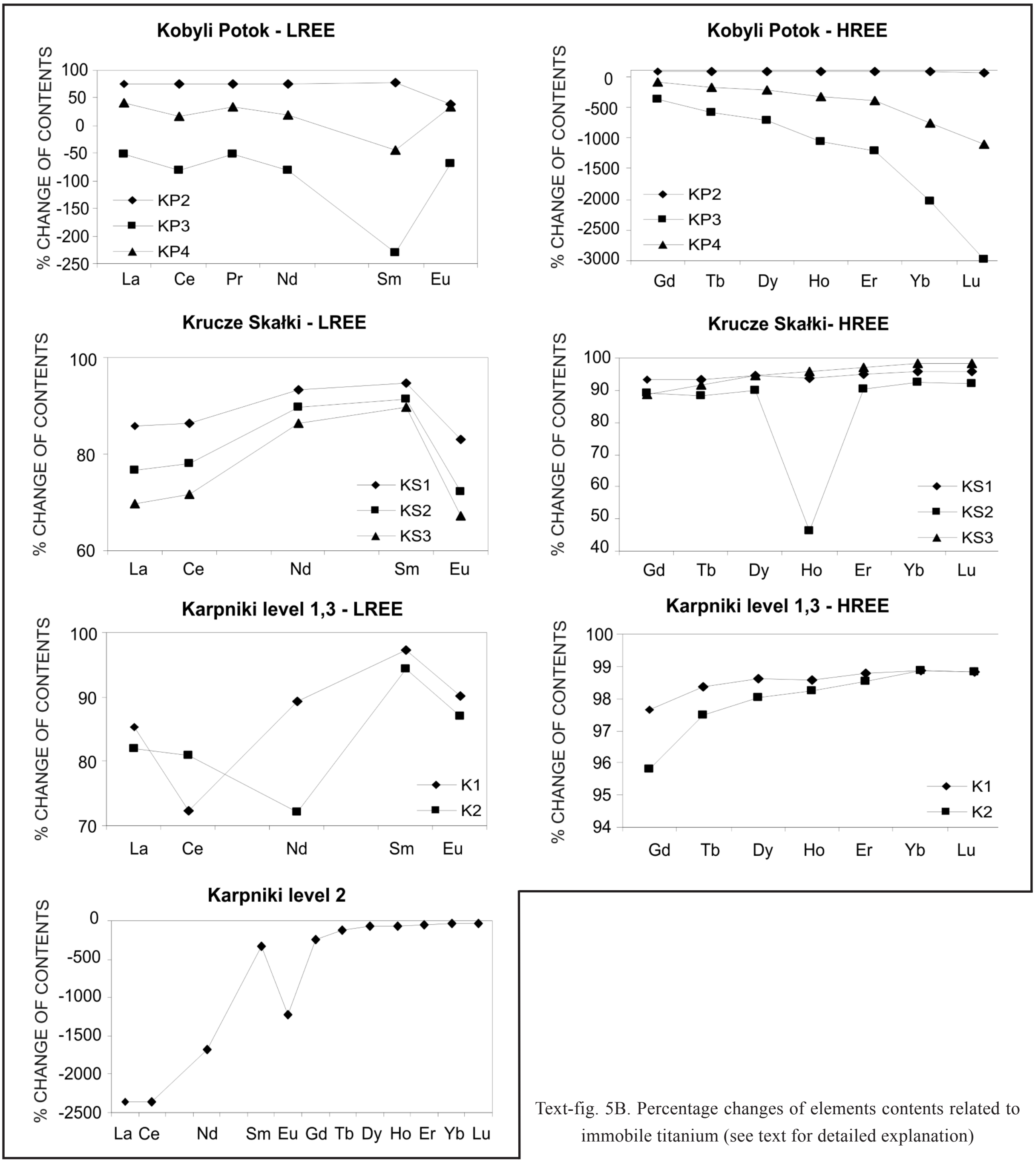
Humus compounds occurring in these soils can be linked with the mineral part of the soil matter in the form of organic-clay compounds. The soils are characterized by a low sorption capacity and a low possibility of REE immobilization. On the other hand, high acidity of the soils increases REE mobility. Similarly, the predominance of fulvic acids over humic acids may influence the mobility of the elements because fulvic acids in free form, as well as salts and organic-clay compounds, are readily soluble in water. Due to this they are very mobile in the soil environ-



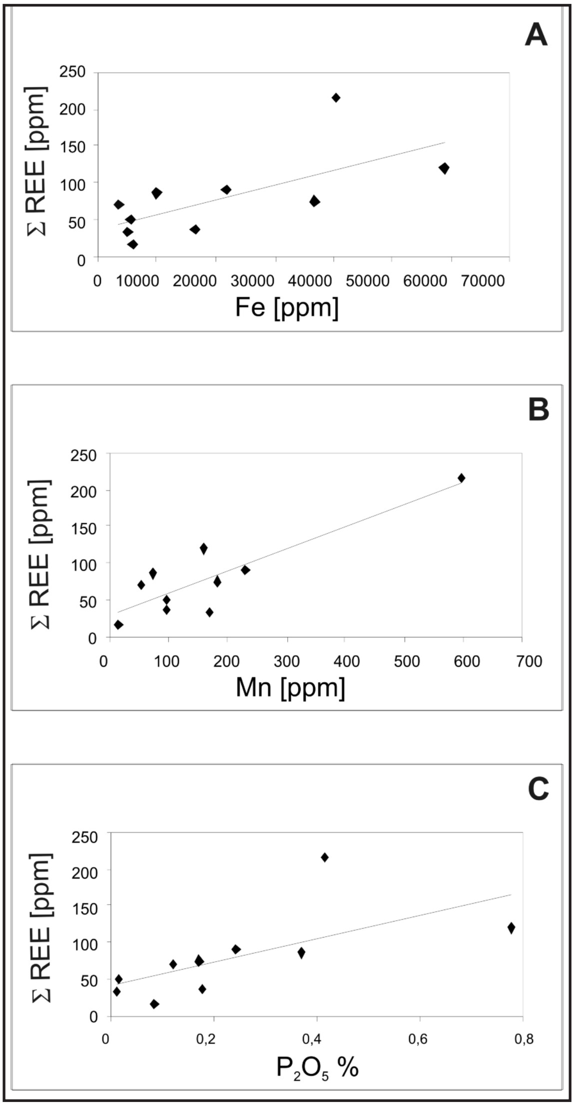
Text-fig. 5A. Percentage changes of elements contents related to immobile titanium (see text for detailed explanation) ment and have a high impact on its formation and evolution.

Comparison between the total REE content and TOC content in particular soil profiles indicates the possibility of some control of migrating REE by organic compounds present in the soils. In the soil samples collected on granites, this relationship was positive, an increase in the content of organic compounds being linked to an increase in total REE content. The relationship observed in soils collected on pegmatites was negative, a decrease in TOC being linked to an increase in total REE content.

Comparison of REE enrichment in soils in relation to REE content in bedrocks (model of Nesbitt and Markovics 1997) shows a good correlation with organic matter content in particular soil horizons. An increase in TOC concentration in the humus-ferric and ferric horizons correlates with REE enrichment in these horizons. This is particularly clearly observable in the Kobyli Potok profile, where high REE enrichment was



Text-fig. 5B. Percentage changes of elements contents related to immobile titanium (see text for detailed explanation)



Text-fig. 6. Correlation between total Fe-, Mn-, P_2O_5% and total REE contents in soil

observed in the first soil horizon where the TOC concentration was also high (14.91%). Likewise, high REE depletion was noted in the second soil horizon, which also displays a lower TOC content. In the Karpniki profile, where the TOC content was very low (0.65%), lower REE concentrations were also observed.

One source of soil acidity is the weathering of ore minerals, mainly sulphides, occurring within the Karkonosze granitoids. A different source is represented by the acid rains that commonly occur in the study area (Sienkiewicz *et al.* 2006). The influence of acid rains is particularly clearly seen in comparison of pH measurements between the humic horizons and weathered parent material. In almost every profile studied, pH was lower in the first horizon, higher in the second one, and again lower in the lowermost soil horizon.

Generally, there is no simple relationship between total REE concentration and the pH of the soil horizons. However, the pH of the soil solutions seems to have a large significance due to the fact that that low values influence the solubility of minerals (apatite, feldspars) that are REE-bearing, providing dissolved species to the soil solution.

The lack of an unequivocal relationship between pH, TOC content and total REE content in single soil horizons can also result from the presence of slightly soluble (crystalline) Fe–Mn oxides and silts in the soils. REE as isomorphic or adsorbed replacements remain immobilized in soils for some time and are not active in the geochemical cycle. A fairly good correlation between Fe and Mn concentration in soils, which was mainly positive in all the soil profiles, may indicate a strong relationship with this fraction (Text-fig. 6A, B).

The results of sequential extraction of the soils indicate a strong relationship between REE, organic compounds and Fe–Mn oxides. In all of the the soil profiles studied, the most intensive leaching was observed in single horizons during the fourth step of the extraction. During this step, REE associated with organic matter and sulphides in a strongly oxidizing environment are extracted. Intensive leaching was then observed in the fifth and the last extraction step. Finally, and not in all soil horizons, considerable leaching was noted in the third extraction step. This step is characterized by elements associated with Fe and Mn oxides. During extraction, hydroxylamine chloride and acetate acid were used. These reagents act on hydrated and amorphous Mn oxides, and to a very small degree or not at all on Fe oxides (including crystalline Fe oxides). Maybe this is the reason why such a low content of REE associated with this fraction was leached during this stage. Good correlation between total Fe content and REE concentration in single soil horizons may indicate that REE could be associated with crystalline Fe oxides, only slightly leachable at this extraction stage (Text-fig. 6A, B).

Low concentration of REE was observed in the exchangeable fraction, which points to low surface adsorption.

Low concentrations of REE associated with the carbonate fraction suggest a low content of carbonate minerals and practically no significant mobility of these elements in the soil profiles studied.

Positive relationships between phosphate content and total REE content in single soil horizons may indicate possible control of REE migration due to the solubility of phosphate minerals (accessory minerals) (Text-fig. 6C).

The published data suggest that at different pH values of the soil solution, REE can occur in different forms. Significant inorganic complexing ions are: CO_3^{2-}, OH^-, F^- (the presence of these ligands was noted in the hydrothermal solutions of the Karkonosze area; KBN grant 6P04D02118 report, 2003). In the absence of those ligands, the ability of absorbing REE increases from LREE to HREE. The presence of ligands results in an opposite trend in the REE absorption. In solutions and natural waters, with pH 7–9, the REE occur mainly as phosphatic complexes. REE may occur as carbonate complexes at pH > 6, whereas with a decrease in pH, the content of free REE ions increases (Johannesson *et al.* 1996). Thus, depending on the bedrock-solution system, REE would display different mobility.

CONCLUSIONS

Soils derived from granites and pegmatites display enrichment in REE in comparison to their bedrocks. The fractionation of REE between rock and derived soil is different in the case of the two rock types investigated: granite and pegmatite. The REE content in the derived soils indicates a distinct geochemical affinity to the granites and the absence of such an affinity to the pegmatites.

Sequential extraction of the soils showed that the REE are generally associated with the organic and Fe–Mn oxides and hydroxides fractions. Good correlation exists between REE and phosphorus concentrations. The rate at which minerals are weathered (mainly accessory minerals, micas and feldspars) and immobilization of REE by organic compounds are two of the main processes controlling the mobility of REE at the rock/soil boundary. REE mobilization may begin with alteration of accessory minerals (particularly phosphates), micas and feldspars. In contrast to the major elements, REE in these processes show low mobility, which may cause their relative accumulation in the debris. Accessory minerals supply the entire spectrum of REE, biotite enriches the debris in HREE, whereas the feldspars supply mainly europium. Positive correlation of REE concentration with organic compounds, phosphorus and metal hydroxides allow us to assume that retention of REE in the soils takes place due to formation of some complexes with organic and inorganic ligands. The retention proceeds due to adsorption and absorption, as well as due to the formation of secondary phosphates.

Different behaviour of REE in the weathering processes is confirmed by the model of Nesbitt and Markovics (1997). It rearranges the REE (LREE and HREE) data by the mobility of particular groups, showing their mobility in relation to the least mobile element in the weathering environment. The model confirms the basic regularities obtained experimentally, i.e. that the highest REE enrichment in relation to the bedrock is observed in the highest soil horizon (humus-ferric horizon), and the lowest in the medium horizon (illuvial horizon). Total content of REE for the soil profiles studied indicates the highest enrichment in the LREE. Application of the Nesbitt and Markovics (1997) algorithm supplies precise data, i.e. this model in many cases indicates higher concentration in HREE in relation to the least mobile element in the rock/soil profile.

All of the soil profiles studied were characterized by an acidic rock-soil reaction. There is no clear relationship between soil pH and REE concentration; however, low pH of the infiltrating solutions influences the weathering of REE-bearing minerals. An acidic reaction favours leaching of REE adsorbed onto the surface of minerals and associated it with organic matter. Moreover, soils characterized by an acidic reaction have low REE absorption abilities.

Accumulation of REE in the organic fraction suggests good bioavailability of these elements to flora and fauna; associating of REE with phosphorus compounds may also have an influence on bioavailability. Good correlation between organic matter content, Fe–Mn concentrations, P and REE confirm this observation.

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