THE OCCURRENCE OF RARE EARTH ELEMENTS IN SOME FINNISH MIRES

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The content of the more abundant rare earths (RE) (Y, La, Ce, Pr, Nd and Sm) in the ash of 399 peat samples from 26 Finnish mires was determined by X-ray fluorescence spectrometry. The content of all rare earths (La-Lu, Y) in 29 samples was also determined by spark source mass spectrometry. The median RE contents in peat ashes from areas where the bedrock consists of rapakivi granite, granite or archean gneiss are reported. Detailed data concerning the individual mires are also presented. The highest RE contents were found in samples from rapakivi granite areas where a strong negative Eu anomaly was also observed. The RE contents were in general highest at the basal peat layers.

Key words: bogs, peat, rare earths, X-ray fluorescence, mass spectroscopy, granites, gneisses, Finland.

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INTRODUCTION

The rare earth contents in various geochemical and biogeochemical samples have been extensively studied because of their diagnostic importance in geochemistry (Henderson 1984, Taylor & McLennan 1988). The occurrence of rare earth elements in peat, however, has not received such a wide interest. Only some of them are normally included in investigations dealing with trace element contents in peats (Virtanen 1993, Markert & Thornton 1990, Read & Hooker 1989).

During the period of 1974-77 a large number of peat samples were collected from the Finnish mires and their trace element contents were investigated (Minkkinen & Yliruokanen 1978, Yliruokanen 1980a, Yliruokanen 1980b, Yliruokanen 1981). In this paper we present some results of rare earth contents of peat samples which were collected from areas where the bedrock consists of rapakivi granite, granite, or archean gneiss. Fig. 1 shows the locations of the sampled mires on the geological map of Finland. The density of sampling was 1-2 sites/km^2. At each site a vertical profile was sampled, starting from the bottom of the mire. Samples were taken with a Hiller sampler (50 cm x 2.5 cm tube) at one-meter intervals (Minkkinen & Yliruokanen 1978).

X-ray fluorescence (XRF) spectrometry was used for the determination of Y, La, Ce, Pr, Nd and Sm contents in the ash of 399 peat samples from 26 mires. 29 samples were measured by spark source mass spectrometry (SSMS) by which the contents Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were also obtained.

EXPERIMENTAL

The peat samples were ashed in 550 °C. The analytical samples for XRF spectrometry were prepared by pressing 40 mg of peat ash onto a filter-

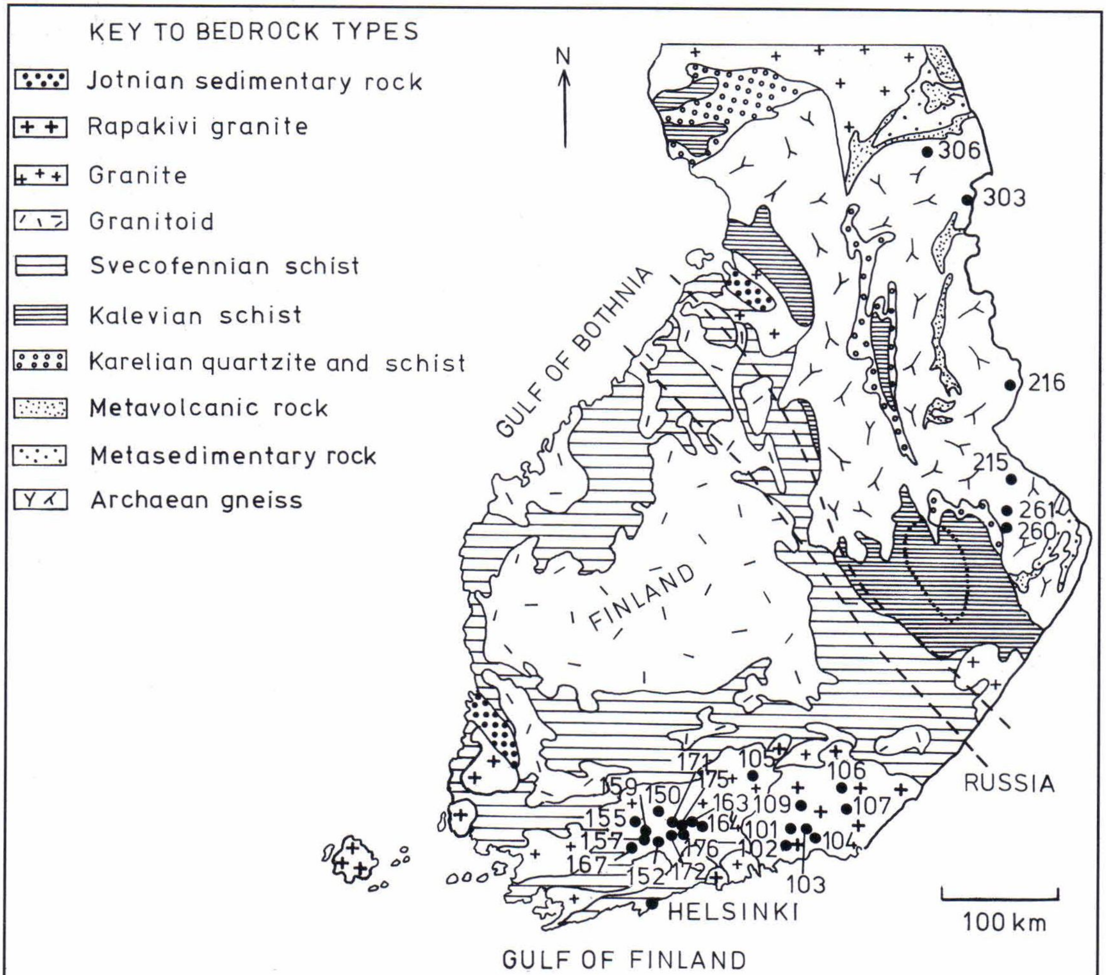


Figure 1. The bedrock map of southern and central Finland and locations of the mires sampled.

paper support. Calibration standards were prepared by mixing 0.5% Rare Earth L Standard (Spex Industries, Inc.) with three different types of synthetic peat ash with compositions that are shown in Table 1.

Table 1. Compositions of the synthetic peat ashes used in the XRF analyses.

reagents	composition (%)		
	1	2	3
SiO_2 [a]	47.55	47.50	69.31
Fe_2O_3 [b]	17.30	8.60	1.98
$CaCO_3$ [b]	30.90	30.90	11.88
Na_2SO_4	1.90	4.30	-
KPO_3 [c]	1.90	3.4	3.27
TiO_2 [a]	0.45	1.7	0.69
Al_2O_3 [a]	-	5.00	5.94
K_2SO_4 [c]	-	-	3.96
NaCl [d]	-	-	2.97

[a] Spex
[b] Merck, p.a.
[c] Sp.K.
[d] Merck, suprapur

XRF intensities were measured by a wavelength dispersive Philips PW1480 spectrometer with an X-ray tube having an Sc-Mo dual anode. For Y K_α fluorescent emission was measured, L_α for La, Nd and Sm and L_β for Ce and Pr. For the excitation of Y K_α radiation the X-ray tube was operated at 80 kV and 30 mA and for the excitation of the *L*-lines 60 kV and 50 mA were used. The analyser crystal was LiF(220) and the measuring time was 60 s. Scintillation detector was used for Y K_α and a flow proportional counter for the *L*-lines. Background signal for Sm was measured on one side only.

Calibration curves for each rare earth element were compiled. Correlation factors for the different elements ranged from 0.973-0.998. Detection limits obtained by the 3σ criterion were 20 ppm for Y and La, 50 ppm for Ce, and 35 ppm for Pr, Nd and Sm. The 3σ values were determined from the signals measured for 8 different synthetic peat ashes without lanthanoid doping. The rather high detection limits are a result of the small sample size which again has been a necessity considering the amount of samples taken.

The SSMS analyses were performed by an A.E.I. double-focusing mass spectrograph MS702 with *rf* spark and electrical detection (Nieminen & Yliruokanen 1974). Samples were mixed with an equal weight of Ringsdorff RW-A graphite powder and compressed to electrodes. Standards containing 50 or 250 ppm of each rare earth element in a synthetic plant ash were applied (Lounamaa 1956). Rhenium was used as an internal standard.

Correlation between results obtained by the two methods mentioned above was good. Correlation coefficients for the different rare earth elements ranged from 0.980 to 0.997.

RESULTS AND DISCUSSION

The bedrock on the sampling sites consists of either rapakivi granite, granite or archean gneiss. The median contents and ranges of Y, La, Ce, Pr, Nd and Sm in peat ashes from these areas are arranged accordingly in Table 2. The data presented were obtained by XRF spectrometry. Also shown are the respective RE contents in post-archean Australian average shale (PAAS) (Taylor & McLennan 1988). The RE contents in PAAS can be considered to represent those of the upper continental crust exposed to weathering and erosion. The median RE contents in the peat ashes from the different bedrock areas were roughly 1-6 times those in PAAS.

The chemical properties of peats depend on the compositions of the peat-forming plants, degree of humification and the mineral substances introduced from outside. The peat types of the now

Table 2. Median RE contents and ranges (ppm) in peat ashes from rapakivi granite, granitic and archean gneiss areas, and in the post-archean Australian average shale (Taylor & McLennan 1988). N is the number of samples.

	PEAT ASHES						SHALE
	rapakivi granite (N=152)		granite (N=190)		archean gneiss (N=57)		RE content in post-archean shale
	median	range	median	range	median	range	
Y	176	<20-3465	50	<20-1303	38	<20-288	27
La	200	<20-1268	46	<20-1482	100	<20-1176	38
Ce	506	<50-2598	110	<50-3075	220	<50-2278	80
Pr	40	<35-294	<35	<35-334	<35	<35-219	8.9
Nd	322	<35-1766	56	<35-1523	82	<35-976	32
Sm	38	<35-401	<35	<35-296	<35	<35-173	5.6

studied samples were mainly *Carex* (C) and *Sphagnum* (S) or their mixtures. In addition, some samples consisted of mixtures of C or S and *Eriophorum, Equisetum* and wood peat. The median ash content in C peats was 3.9%, C,S peats 3.2% and S peats 1.8%. Already Lounamaa (1956) showed that the Y contents in Finnish plants were highest in ferns, followed by lichens and mosses. Later, the RE contents in mosses and lichens gathered from different parts of Finland were determined (Erämetsä & Yliruokanen 1971). Median contents of Y, La, Ce, Pr, Nd and Sm in the ashes of moss samples were 31, 52, 82, 10, 44 and 11 ppm, respectively, and those in lichens were almost the same. As compared with the median RE contents in the peat samples from granite areas, a remarkable similarity can be observed.

The highest median contents were found in the samples from the mires where the bedrock consisted of rapakivi granite. This observation is in accordance with the relatively high RE contents of rapakivi granite in the same area (Koljonen & Rosenberg 1974, Vaasjoki & Rämö 1989). For instance, in Lapinjärvi the La, Ce and Nd contents were reported to be 128, 270 and 100 ppm, respectively (Koljonen & Rosenberg 1974). The average RE contents in granites in Finland are clearly lower compared to those in rapakivi granites. This is also reflected to the RE contents in peat samples from the granite areas.

Recently, Y and La contents in till from different bedrock areas have been reported (Koljonen 1992). The average Y content in till from granite and archean gneiss areas was around 20 ppm. Hence the Y contents would have been expected to be similar in the peat samples from the respective areas. The median Y content in the peat ashes of samples from granite areas, however, was higher than in those from the archean gneiss areas. On the other hand, the La content in till from granite areas was about 30 ppm and in archean gneiss 20 ppm. Therefore the other RE contents would have been expected to be higher in the samples collected from granite areas, but were found to be higher in the samples from archean gneiss areas. The discrepancy between the expected and observed contents is likely due to differences in sampling. The peat samples represent local variations whereas the RE contents in till represent regional averages. The median Pr and Sm contents in the samples from the granite and archean gneiss areas were below the detection limits of XRF spectrometry.

In Tables 3-5 the median contents and ranges of Y, La, Ce, Pr, Nd and Sm in peat ashes from each of the sampled mires are shown. The following observations concerning some individual mires can be made. The Y contents were especially high at Leppisuo and Haisevasuo mires in Luumäki, where the bedrock was of rapakivi granite. At granite areas extremely high RE contents were found at Rajasuo mire in Mäntsälä, where high uranium contents have also been detected (Yliruokanen 1980a). In the samples from Pitkästenjärvi mire nearby a similar phenomenon was discovered. Otherwise the median RE contents were close to those in PAAS. Among the mires sampled at archean gneiss area Vuonissuo mire in Lieksa exhibited the highest RE contents. The medians were comparatively high also at Säynäjäsuo mire in Kuusamo. Nothing definitive can be said about the Säynäjäsuo mire, though, since the number of samples was only 4, and only one profile was analysed. No correlation between the peat type and the RE contents in peat nor the ash content, that would explain the high RE contents found in some of the mires, could be detected.

In general, the rare earth contents were higher in the basal peat layers. The tendency observed in the vertical distributions is in relation with the low mobilities of the rare earth elements. This is illustrated in Fig. 2 where the vertical distribution of four rare earths in three sampling sites from the different bedrock areas are shown. The RE contents both in peat ash and dry peat are presented since the ash contents are often higher in the samples from the basal layers.

The contents of all RE elements in 29 peat ash samples were determined by SSMS and the results were normalised to chondrite (Taylor & McLennan 1988). The abundance patterns for some samples are shown in Figures 3 and 4. In most of the samples analysed in the rapakivi granite area a negative Eu anomaly was discovered. For example in Fig. 3 a strong anomaly can be seen in samples 106/10/550 and 107/2/400. Both of these samples were taken from the lowermost peat layer where the phenomenon is clearly pronounced as a result of reducing conditions. Near the surface the normalised Eu abundance becomes similar to the abundances of the other heavy rare earths. The same changes in Eu content *vs.* depth were detected in all the analysed samples from the rapakivi granite areas.

Normally, the RE abundance patterns in peat samples taken from rapakivi granite and granite areas resembled very much those of rapakivi granite and granite (Koljonen & Rosenberg 1974). In the 8 patterns determined from three different mires situated at granite area the RE abundances were in general quite low. The heavy rare earths could not usually be detected by SSMS except in the samples from the Isosuo mire (105). The increase in RE content towards the basal layers can also be seen in the chondrite normalised abundance patterns. The RE contents were high in the samples from deepest sampling depths at Keihässuo (157) and Isosuo (105) mires, where the heavy RE element contents could also be determined (Fig. 4). In a sample taken near the surface at Keihässuo mire, however, the contents of the RE elements heavier than Nd could not be determined even by SSMS. The abundance patterns for the samples from archean gneiss areas were quite similar to those from granite areas. The patterns were determined for 6 samples from Sarvisuo (216) and Kaitalammensuo (260) mires. The Y, La, Ce, Pr and Nd contents were similar to those in sample 157/7/100 (Fig. 4).

CONCLUSIONS

The median RE contents in the samples from rapakivi granite, granite and archean gneiss areas were 1-6 times the RE contents in PAAS. The

Table 3. Median RE contents and ranges (ppm) in peat ashes from the mires situated at rapakivi granite areas as determined by XRF spectrometry.

code, mire, municipality	Y		La		Ce	
	range	median	range	median	range	median
101 Pöllönsuo, Pyhtää	31-361	148	30-410	128	78-964	333
102 Munasuo, Pyhtää	<20-551	120	<20-853	97	43-1864	246
103 Vehkaojansuo, Sippola	<20-513	87	<20-1108	94	39-2149	232
104 Kajosuo, Vehkalahti	22-368	144	40-1021	237	56-1812	498
106 Leppisuo, Luumäki	<20-1011	261	<20-1268	241	51-2598	452
107 Haisevasuo, Luumäki	<20-3465	255	<20-1031	222	90-2263	493
109 Haukkasuo, Valkeala	40-397	234	44-620	356	129-1324	789

Table 4. Median RE contents and ranges (ppm) in peat ashes from the mires situated at granitic areas as determined by XRF spectrometry.

code, mire, municipality	Y		La		Ce	
	range	median	range	median	range	median
105 Isosuo, Nastola	21-264	50	<20-456	41	56-854	136
150 Piilonsuo, Janakkala	22-142	64	24-181	59	<50-313	85
152 Kurkisuo, Hyvinkää	<20-1303	60	<20-495	41	<50-829	110
155 Luutasuo, Loppi	<20-586	30	<20-873	29	<50-1827	92
157 Keihässuo, Pyhäjärvi	<20-569	33	<20-666	39	<50-1128	91
159 Lenninsuo, Loppi	<20-90	23	<20-60	<20	<50-187	70
163 Junninsuo, Mäntsälä	34-215	64	38-340	59	98-643	146
164 Isosuo, Mäntsälä	37-283	65	34-323	79	98-560	158
167 Toivike, Pyhäjärvi	<20-197	31	<20-142	35	<50-358	67
171 Mustasuo, Hausjärvi	<20-192	35	<20-294	33	<50-521	103
172 Ritassaarensuo, Hyvinkää	<20-92	45	<20-100	32	60-269	78
175 Rajasuo, Mäntsälä	96-856	560	114-1482	843	217-3075	1552
176 Pitkästenjärvi, Mäntsälä	23-309	109	33-368	118	71-679	271

Table 5. Median RE contents and ranges (ppm) in peat ashes from the mires situated at archean gneiss areas as determined by XRF spectrometry.

code, mire, municipality	Y		La		Ce	
	range	median	range	median	range	median
215Rimpisuo, Lieksa	<20-179	55	61-370	127	106-772	292
216 Sarvisuo, Kuhmo	<20-95	<20	<20-349	65	<50-726	108
260 Kaitalammensuo, Eno	<20-35	<20	<20-105	<20	<50-221	65
261 Vuonissuo, Lieksa	<20-288	87	37-1176	215	107-2278	500
303 Säynäjäsuo, Kuusamo	64-137	91	159-544	337	341-1108	735
306 Pötkönsuo, Kuusamo	<20-116	62	26-304	118	89-586	268

Pr		Nd		Sm		number of drilling holes	number of samples
range	median	range	median	range	median		
<35-72	<35	34-444	177	<35-91	<35	4	13
<35-178	<35	<35-851	111	<35-154	<35	4	20
<35-183	<35	<35-916	98	<35-170	<35	7	28
<35-165	50	51-708	242	<35-125	37	6	18
<35-294	53	36-1292	279	<35-272	53	9	41
<35-263	47	<35-1766	168	<35-401	52	7	27
<35-138	62	55-583	404	<35-139	52	1	5

Pr		Nd		Sm		number of drilling holes	number of samples
range	median	range	median	range	median		
<35-91	<35	<35-433	62	<35-80	<35	4	19
<35-37	<35	<35-168	75	<35	<35	4	14
<35-166	<35	<35-865	54	<35-209	<35	4	18
<35-201	<35	<35-912	<35	<35-173	<35	2	13
<35-170	<35	<35-825	47	<35-156	<35	4	19
<35	<35	<35-74	<35	<35	<35	4	14
<35-79	<35	42-350	67	<35-65	<35	5	19
<35-64	<35	37-336	72	<35-60	<35	4	13
<35-47	<35	<35-156	<35	<35-41	<35	3	19
<35-50	<35	<35-311	40	<35-78	<35	3	17
<35	<35	<35-100	<35	<35	<35	2	7
<35-334	146	96-1523	779	40-292	146	3	9
<35-83	<35	<35-398	139	<35-74	<35	3	9

Pr		Nd		Sm		number of drilling holes	number of samples
range	median	range	median	range	median		
<35-96	<35	66-386	143	<35-66	<35	3	10
<35-45	<35	<35-241	58	<35	<35	4	12
<35	<35	<35-82	<35	<35	<35	3	14
<35-219	<35	48-976	201	<35-173	<35	4	9
<35-90	<35	122-426	301	<35-72	<35	1	4
<35	<35	47-219	110	<35-36	<35	3	8

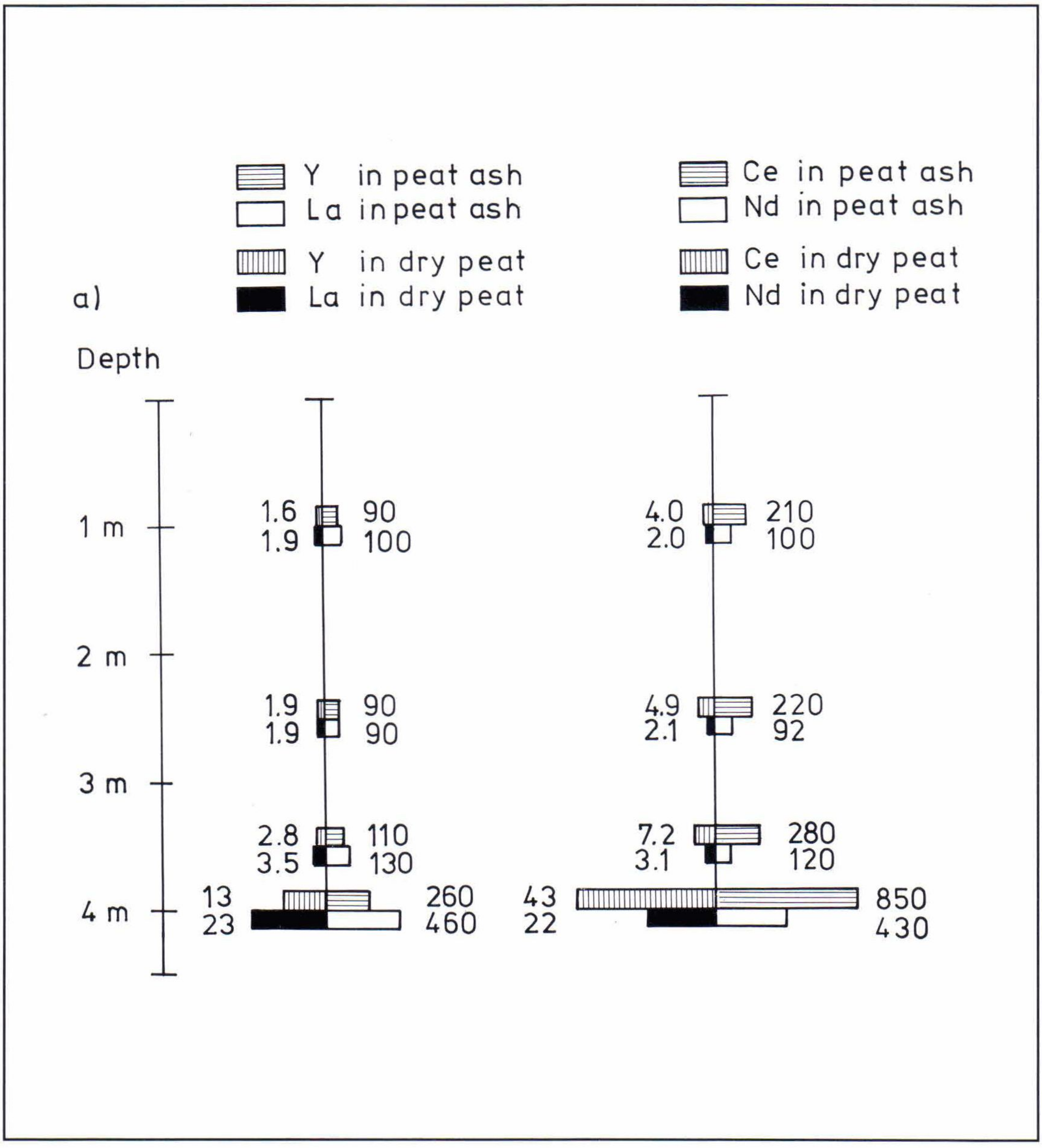
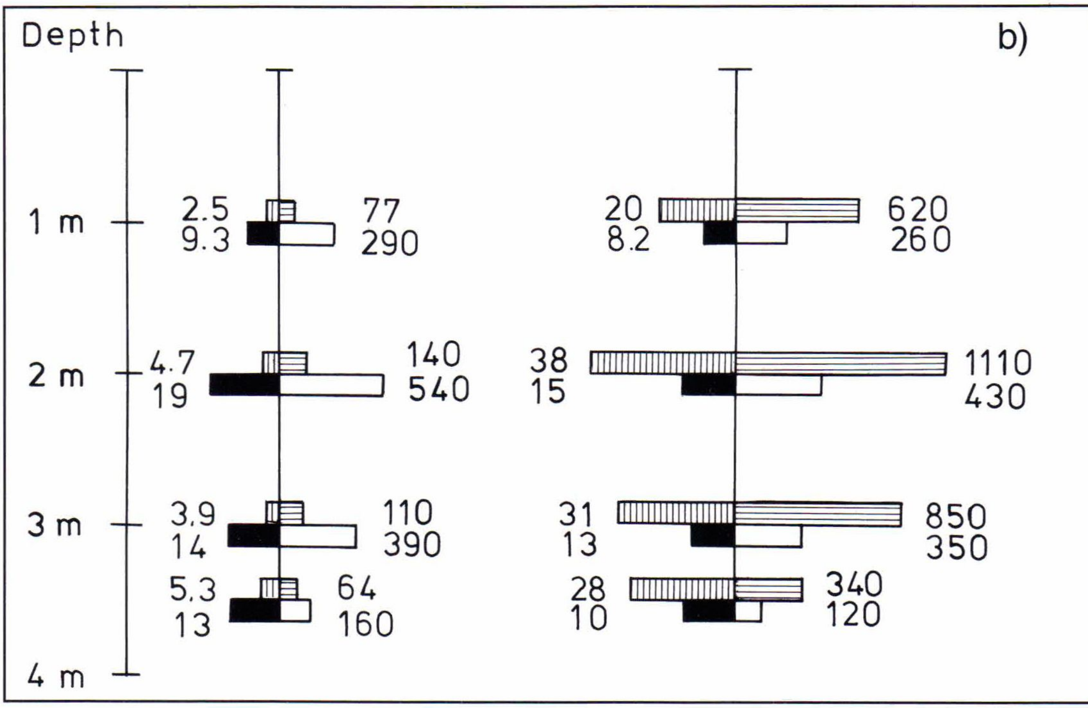


Figure 2. Vertical distribution of Y, La, Ce and Nd contents (ppm) in peat ash and dry peat in three mires.
a) Isosuo in Nastola (105). Bedrock consists of granite; peat in basal layers is Carex *and* Sphagnum *in the two samples from the surface layers.*
b) Säynäjäsuo in Kuusamo (303). Bedrock archean gneiss; peat Carex.
c) Leppisuo in Luumäki (106). Bedrock rapakivi granite; peat Carex.,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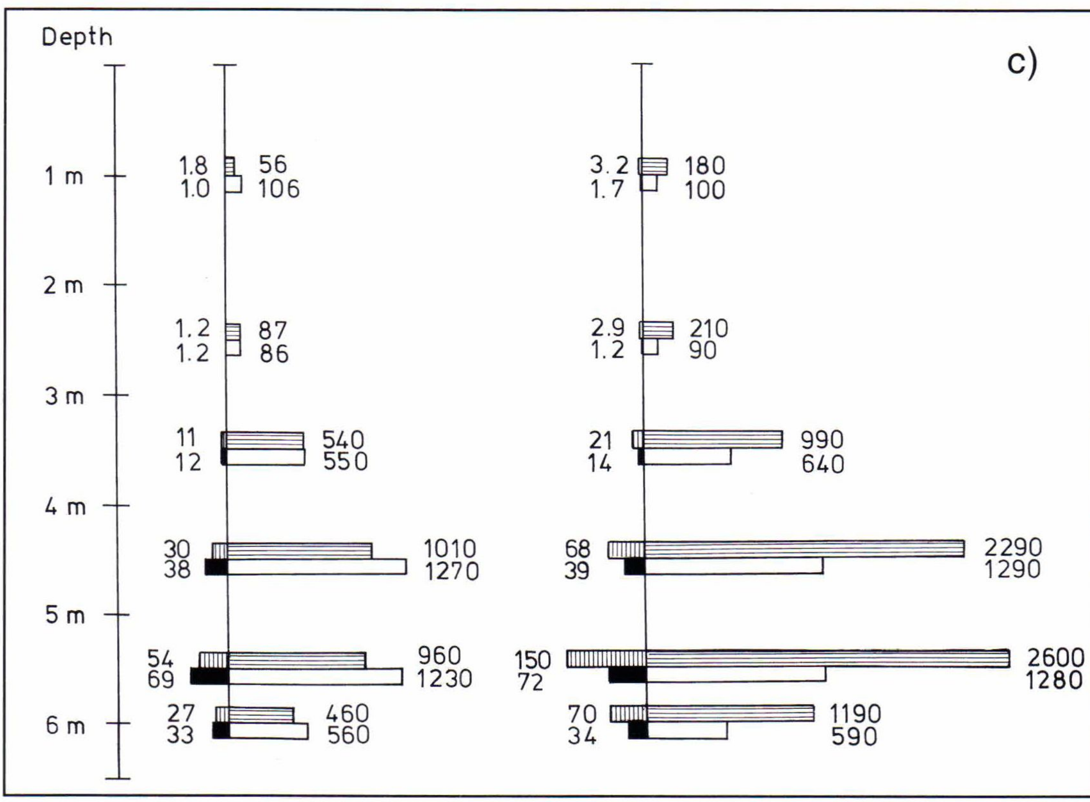
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1.2
87
86
2.9
1.2
210
90
11
12
540
550
21
14
990
640
30
38
1010
1270
68
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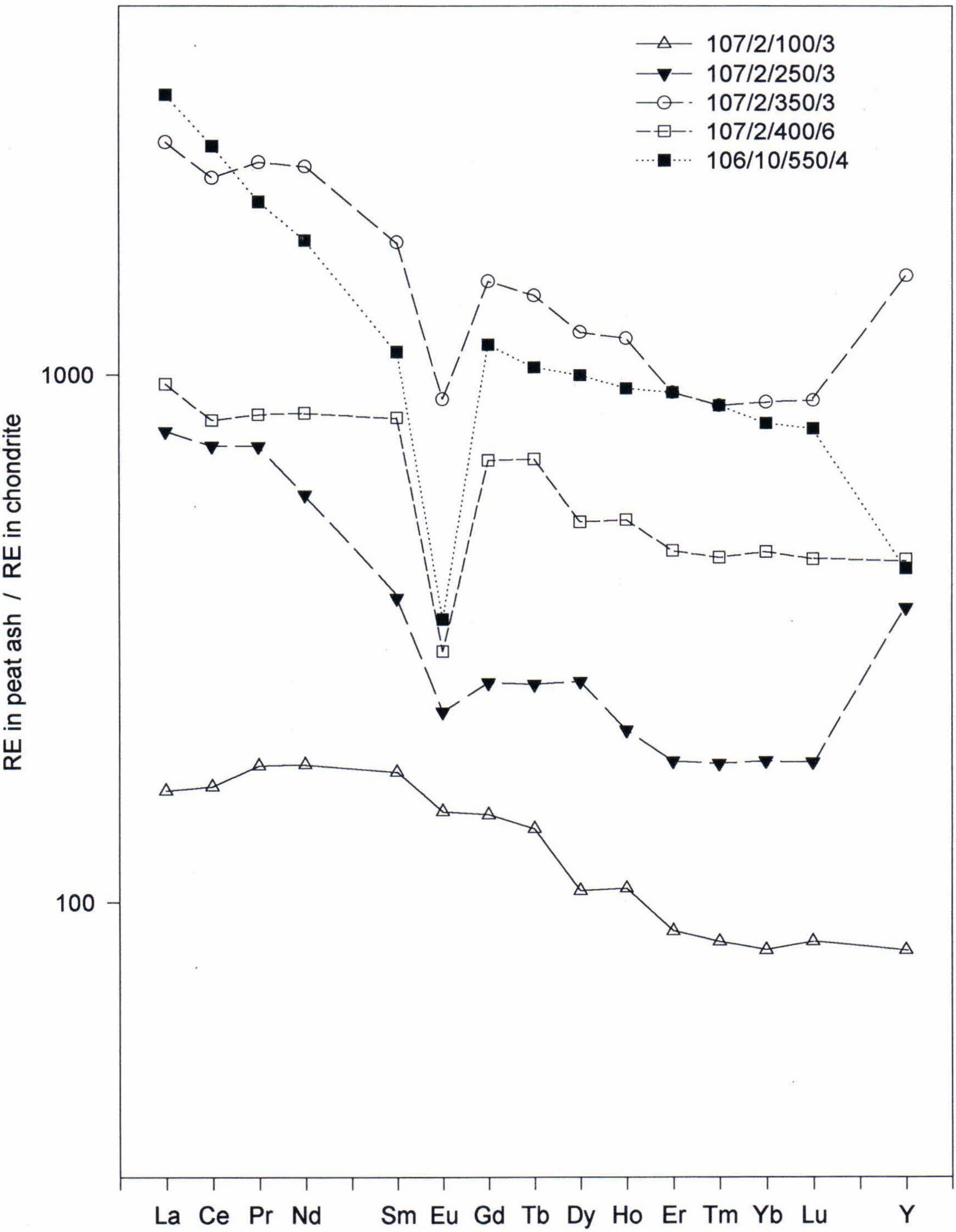

Figure 3. Chondrite normalised RE abundances in some mires where the bedrock consists of rapakivi granite. The code of the mire, the drilling hole number, the sampling depth (cm) and the degree of v. Post humification (1 - 10) are given in the legend.

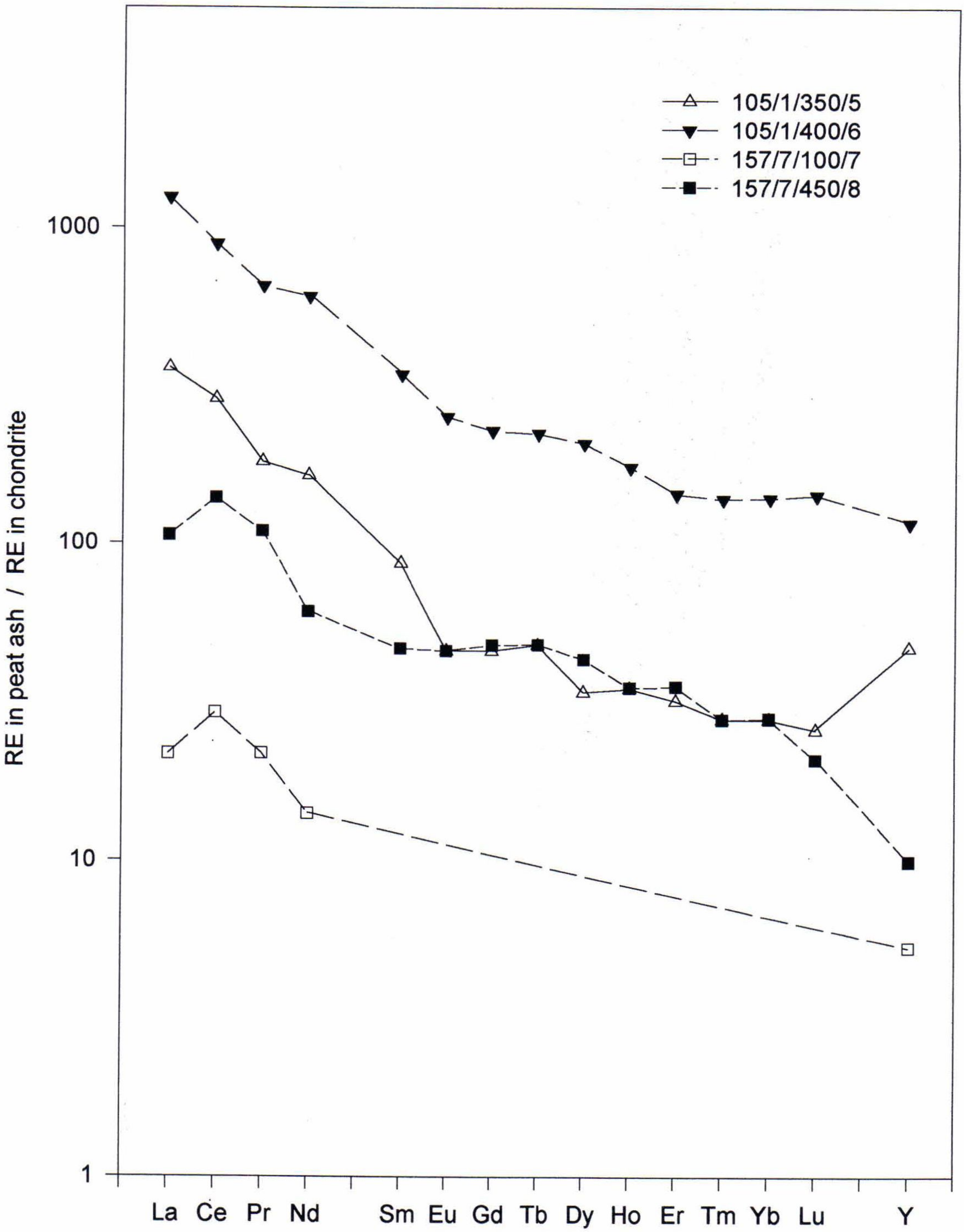

Figure 4. Chondrite normalised RE abundances in some mires where the bedrock consists of granite. Legends as in Fig. 3.

highest RE contents were found in peat samples from rapakivi granite areas whereas in the samples form granite and archean gneiss areas the medians were of the same magnitude. A strong negative Eu anomaly was discovered in the samples from rapakivi granite areas. In general the RE contents were highest at the basal peat layers.

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