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THE PATTERN OF DISTRIBUTION OF LANTHANIDE ELEMENTS IN SOILS AND PLANTS

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Key Word Index—*Vaccinium vitis-idaea*; Ericaceae; red whortleberry; multi element analysis; lanthanides; soils.

Abstract—The concentration of lanthanides (rare earth elements) in plant and soil samples were determined by means of atomic emission spectroscopy with inductively coupled plasma (AES-ICP). The abundance of these elements exhibits the typical distribution pattern reported in geological samples. The total content of the lanthanide elements in plant material seems to be largely independent of the soil substrate.

INTRODUCTION

Lanthanides, also called rare earth elements, comprise a total of 15 elements, of which promethium (Pm) does not occur naturally in the earth's crust [1]. The rare earth elements possess nearly identical chemical and physical properties and form a geochemically coherent group. It is well known that the lanthanides show a general peculiarity in their natural distribution. The rare elements of even atomic numbers are more abundant than those of the adjacent odd atomic numbers, this peculiarity is a rule [2]. In addition, the abundances of elements with even atomic numbers (or with odd atomic numbers) decrease approximately linearly with increasing atomic numbers [3].

In the past little attention has been paid to the concentration levels of the lanthanides, to their behaviour and uptake by plants from soil [4], primarily occasioned by insufficient detection limits of the analytical methods applied, since the concentrations of lanthanides, especially in plants, are very low. Extremely high concentrations of the total lanthanides (2300 ppm) were found in hickory leaves (*Carya* spec.) [5, 6] which make an exception in the plant kingdom in the sense that they are excellent lanthanide accumulators. Further analytical results [7] were obtained, for example in mosses and lichens growing on granitic and radioactive rocks [8] and in three species of *Equisetum* [9, 10]. In this context concentration of lanthanide elements in *Vaccinium vitis-idaea* and *Pinus sylvestris* was analysed, together with the soil substrates in which they grow. The following eco-chemical aspects were considered within the scope of this investigation; (i) obtaining concentration ranges of the lanthanide elements in soils and plants, (ii) investigating plant–soil relationships of lanthanides and (iii) describing the distribution patterns of lanthanides, both in soils and in plants.

RESULTS AND DISCUSSION

In Table 1 all analytical results are presented, obtained by AES-ICP analysis. In Fig. 1 mineral soil concentrations of the lanthanides in ppm (log) are plotted as a function of the atomic number. Relationships in the abundance of individual elements typical of the lanthanides (Harkins rule) were obtained. According to the distribution pattern of Fig. 1 it is reasonable to conclude that the original source of the lanthanides occurring in soil should be the earth's crust [3], since the same distribution patterns have been found in geological samples [8]. The total lanthanide content of the Swedish mineral soil is about ten times greater than that of the German mineral soil, which is in good agreement with other element analyses we have carried out previously [9, 11].

Reference to Fig. 2 shows that the peat bog soils possess the typical distribution pattern of the Harkins rule as well. It can clearly be seen in Fig. 3 that the formation of peat bog soils are independent of the parent mineral materials and thus are unaffected by the soil weathering process [12, 13]. It is therefore to be expected that the upward transport of the lanthanides as well as the other elements from the parent mineral materials should be insignificant [12]. Therefore the import of elements into the peat bog soils is mainly possible by atmospheric deposition. The concentration of 14 rare earth elements were determined by spark source mass spectroscopy for atmospheric aerosol samples collected in the area of Osaka (Japan). The concentration fell between those for sandstone and for granite [3]; both the sandstone and the granite were predominant rocks in the vicinity of Osaka. The atmospheric concentrations of rare earth elements were dependent on the area's geology.

Since the peat bog soils are of plant origin, it is to be expected that plants belonging to these ecosystems should exhibit the Harkins distribution. *Vaccinium vitis-idaea* and *Pinus sylvestris* show the typical distribution pattern of lanthanides (Figs 4 and 5). The deviations from the Harkins rule that can be seen in Figs 4 and 5 could possibly be attributed to analytical variations (e.g. the Tb and Ho content in *Vaccinium vitis-idaea* grown on the German mineral soil). Accumulation of lanthanides in plants seems to be independent of the concentration present in the substrate.

Table 1. Concentration data of lanthanides, obtained by AES-ICP analysis (mg/kg)

	S1	S2	S3	S4	L1	L2	L3	N1	N2
La	34	1.4	5.4	1.9	0.34	0.23	0.13	0.26	0.30
Ce	56	2.1	8.4	2.7	0.74	0.33	0.21	0.37	0.37
Pr	14	0.44	1.4	0.71	0.14	0.078	0.07	0.062	0.12
Nd	26	0.99	3.6	1.2	0.10	0.13	0.073	0.15	0.16
Sm	5.9	0.20	0.86	0.25	0.027	0.049	0.024	0.032	0.03
Eu	1.5	0.032	0.17	0.060	0.0056	0.0040	0.00082	0.0049	0.0053
Gd	5.0	0.16	0.70	0.21	0.023	0.027	0.011	0.025	0.023
Tb	1.2	0.044	0.20	0.051	0.014	0.0047	0.012	0.012	0.022
Dy	5.0	0.14	0.80	0.18	0.021	0.021	0.0086	0.022	0.02
Ho	1.1	0.033	0.19	0.041	0.0041	0.00025	0.0042	0.0051	0.0039
Er	1.7	0.050	0.26	0.054	0.0054	0.0077	0.0015	0.0068	0.006
Tm	0.48	0.014	0.058	0.015	0.001	—	—	0.0011	0.0017
Yb	2.8	0.072	0.38	0.077	0.0086	0.01	0.0025	0.0082	0.0085
Lu	0.38	0.014	0.054	0.012	0.0023	0.0019	0.0012	0.002	0.0019

S = soil, L = leaves, N = needles.

Table 2. Place of origin and description of the samples investigated

Sample no.	Location	Remarks
S1	1 km south of Abisco, north Sweden	Sandy loam, podsol, pH = 3.8
S2	10 km south of Abisco, a peat bog called 'Stordalen'	Peat bog, pH = 2.6
S3	Achmer, 15 km north of Osnabrück, Germany	Heavily leached sand dune, pH = 3.9
S4	20 km north east of Osnabrück, a peat bog called 'Venner Moor'	Peat bog, pH = 2.6
L1	Grown on S2	A composite sample from different plants of *Vaccinium vitis-idaea*
L2	Grown on S1	Same as L1
L3	Grown on S3	Same as L1
N1	Grown on S3	A composite sample from several trees of *Pinus sylvestris*
N2	Grown on S4	Same as N1

S = soil, L = leaves, N = needles.

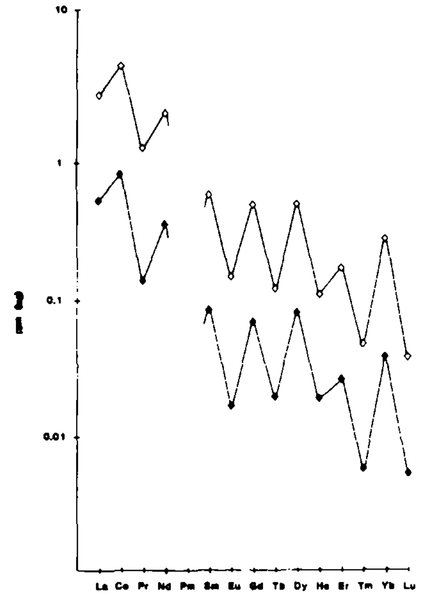

Fig. 1. Mineral soil concentrations of the lanthanides in ppm (log) plotted as a function of the atomic number. ◇ = Abisco, ◆ = Osnabrück.

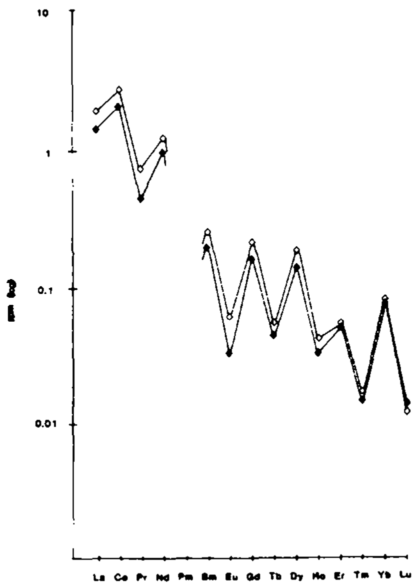

Fig. 2. Peat bog soil concentrations of the lanthanides in ppm (log) plotted as a function of the atomic number. ◆ = Abisco, ◇ = Osnabrück.

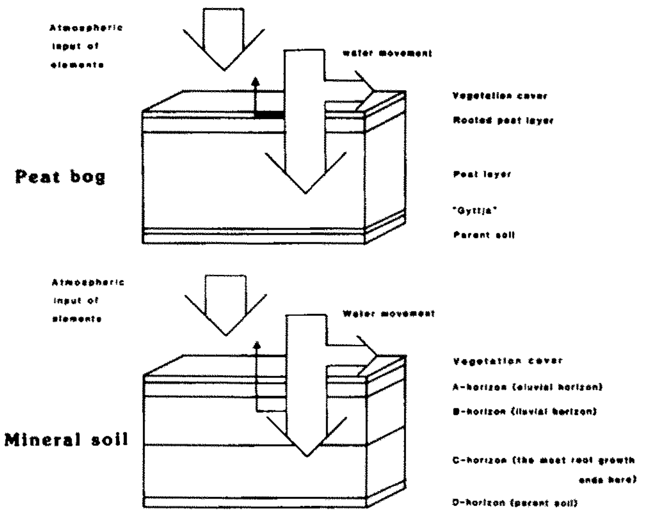

Fig. 3. Schematic comparison of the investigated ecosystems in cool temperate climate.

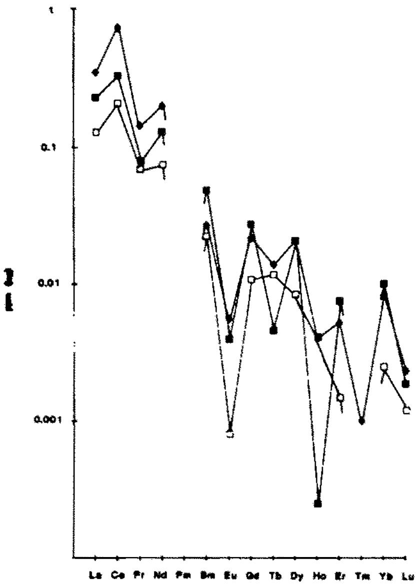

Fig. 4. *Vaccinium vitis-idaea* concentrations of the lanthanides in ppm (log) plotted as a function of the atomic number. ◆ = Grown on the Swedish peat bog soil, ■ = grown on the Swedish mineral soil, □ = grown on the German mineral soil.

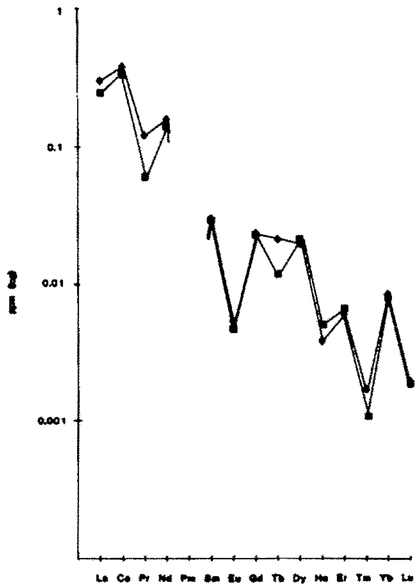

Fig. 5. *Pinus sylvestris* concentrations of the lanthanides in ppm (log) plotted as a function of the atomic number. ■ = Grown on the German mineral soil, ◆ = grown on the German peat bog soil.

Since the concentration of individual lanthanide elements frequently vary according to the Harkins rule it may be possible to calculate the concentration of an unknown lanthanide element once the relationships of elements to each other are known.

EXPERIMENTAL

Peat bog soil, mineral soil, pine needles (*Pinus sylvestris*) and Vaccinium leaves (*Vaccinium vitis-idaea*) were randomly collected from different locations in Europe (see Table 2). Sampling was made as carefully as possible to avoid contamination from the environment. Soil samples were taken as random catches from the upper 60 cm of the soil profile. the samples were dried at 80° for 48 hr, were sieved by a nylon sieve with mesh-size of 2 mm ϕ and were sent to the Environmental Pollution Control Center/Osaka in Japan. They were then analysed by a combination of ion-exchange preconcentration and AES-ICP analysis: The accuracy of the method was checked by analysing parallel biological reference materials (NBS SRM 1571 and 1575) and geological reference material (USGS G-2 and BCR-1), [3].

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