



Rare earth elements in soil and in soil-grown plants

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Abstract

Concentrations of the rare earth elements (REEs) La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu were determined in leaves of 6 plant species (Norway spruce, silver fir, maple, ivy, blackberry, and wood fern), and in pertinent soils and soil extracts, also taken from the same site. The distribution of the individual REEs in plants showed little or no agreement with that in the soil or the soil extracts. Ce had a negative anomaly with respect to the soil in all plants. The REE distribution patterns of fir and spruce were almost identical, but differed profoundly from that of the other species. In most cases, concentration ratios between species were a smooth function of the atomic number of the REE. Very similar results were obtained at 2 additional sites.

Introduction

Rare earth elements (REEs, the elements from La to Lu, also termed lanthanides) occur in all plants, but they seem to be neither essential nor toxic and thus have attracted little attention. Laboratory experiments dealt mainly with the potential of the REEs to replace and compete with Ca for binding sites on proteins, and with the effects on membrane stability (Brown et al., 1990). However, little is known of the metabolic consequences of the uptake of REEs by plants; positive effects on crop yields have been claimed, but still lack confirmation (Welch, 1995). There is conflicting evidence whether REEs in plants are deposited at extra- or intracellular locations. In view of the strikingly similar linear accumulation behaviour of the REEs and of Si in conifer needles with time, it has been hypothesized that the REEs are deposited as minor inclusions with the hydrated amorphous silica (Wytenbach et al., 1994), whereas recent work with a hyperaccumulating fern has shown that about 40% of the REEs are bound to high molecular proteins (Guo et al., 1996).

REEs can be taken up through the leaf surface after spraying (Sun et al., 1994), but normally uptake is exclusively by roots. As with most trace elements, REE

concentrations decrease in the order roots > leaves > seeds. Plants growing on soils rich in REE minerals or contaminated with REE containing waste products show very high concentrations (Miekeley et al., 1994). It should also be noted that many mineral P fertilizers, if derived from apatite, contain appreciable amounts of REEs, which may influence the concentration in plants grown on cultivated soils. REE concentrations in plants seem to be extremely variable. A spread of 5 orders of magnitude has been reported for La in leaves of different species from Japan (Koyoma et al., 1987); this can hardly be due to different soil concentrations alone and has been attributed to specific differences between species. Certain ferns contain up to 1 mg/g La and may be considered hyperaccumulators, whereas concentrations in spruce needles can be less than 10 ng/g (Wytenbach et al., 1994). The reason for these very large interspecies concentration differences is completely unknown.

The REEs consist of 15 elements with successive atomic numbers (*Z* from 57 to 71), of which one is unstable (Pm) and does not occur in nature. Under pedological conditions, all REEs form +3 ions; only Ce may also occur as +4. Trivalent REEs behave coherently due to their similar ionic radii which decrease slightly but systematically from the light to the

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heavy REEs. This entails that certain chemical properties, such as the stability of many complexes, show some dependence on the atomic number (Brookins, 1989; Wood, 1993). As a group, however, the REEs are chemically much more homogeneous than other groups of ions with a uniform oxidation state, e.g. the alkali or the earth alkali metals. In view of the similarity of the REEs, the question of a possible fractionation between the individual members of the series in the plant with respect to the soil has attracted some attention. Most investigators concluded that there is no or no significant fractionation (Henke, 1977; Laul and Weimer, 1982; Miekeley et al., 1994). These conclusions are usually based on the comparison of distribution patterns of the REEs in plants and in the soil after normalization to chondritic values; this method, however, is semiquantitative and will only reveal large differences. In addition, much of the analytical work is done by instrumental neutron activation analysis, which at small plant concentrations does not yield sufficiently accurate values for many REEs. More appropriate methods, such as mass spectrometry or activation analysis with a chemical separation, unfortunately are seldom applied to the problem. Whatever analytical method is used, determination of the REEs in plants is complicated by their occurrence in the ubiquitous dust on the plant surface, which must be carefully removed in order to obtain the endogenous plant concentrations (Wytttenbach and Tobler, 1998). It may therefore be assumed that the question of the fractionation of the REEs is not settled, especially with plants having low concentrations.

Literature data (Wang et al., 1997) also suggest that various plant species growing on the same site take up the different REE's – notwithstanding their similar chemical properties – in nonconstant ratios, but this effect has so far not been duly elaborated. Recent work with blackberry and with spruce from the same site, however, has shown not only significant differences between the soil and the plants, but also between the two plant species and even between individual plants of the same species (Wytttenbach et al., 1998).

It was the aim of the present work to investigate several plant species growing on a forest soil with an ordinary, not excessive REE content, to investigate the fractionation of the REEs between the plants and the soil or soil extracts, and to study differences between the various plant species. In order to get reliable plant concentrations, an analytical accuracy of a few percent was aimed for and analysis was restricted rigorously to the endogenous plant concentration.

Materials and methods

Samples were collected on an area of 150×150 m within an experimental forest established in 1901 near Chanéaz in the Swiss midlands at an elevation of 800 m (abbreviated as CHA). The soil of this site developed from a moraine and has an age of about 10 000 yr; it is a gleyic luvisol with characteristics often found for acid forest soils (pH = 3.3, 3.7 and 3.8 at a depth of 5, 15 and 35 cm, LOI = 13.3, 3.6 and 3.2%, CEC = 722, 377 and 329 $\mu\text{eq/g}$). Six soil samples (15 cm) taken within the area showed very uniform total and extractable REE concentrations. The distribution pattern of the REEs in the soil is close to that of the upper continental crust (Wytttenbach et al., 1996) and thus equal to that of many other soils from different parts of the world (Kabata and Pendias, 1992).

Plant samples were collected during the dormant season. Norway spruce trees (*Picea abies*, needles of age class 5) and blackberry plants (*Rubus fruticosus*, leaves) were sampled and processed individually ($n = 6$, but only the mean values are used here). Pooled samples (from about 20 plants) were taken with the other species: Silver fir (*Abies alba*, needles of age class 5), plaintree maple (*Acer pseudoplatanus*, leaves), ivy (*Hedera helix*, leaves) and wood fern (*Dryopteris filix-mas*, leaves and stalks). In addition, 2 plant samples were collected at other sites than CHA: spruce at Auenstein (AUE) and blackberries at Würenlingen (WUR). These sites are also located in the Swiss midlands, at a distance of about 150 km from CHA. No soil analyses were done at these sites, but soils are expected to be similar to CHA, as they also developed from moraines.

Analysis of all plants was done by neutron activation analysis with a chemical separation of the REEs as a group (Wytttenbach et al., 1996); this method is restricted to the determination of La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu, but offers the high sensitivity necessary for small plant concentrations. Precision was evaluated by analysing aliquots of plants, soils and soil extracts with 5 degrees of freedom each and was found to be from 2 to 5% for the various REEs, with the exception of Gd (12%). Accuracy was checked by analysis of the geological standard BCR-1; results deviated by less than 10% from accepted values.

Statistical evaluation was done with SAS (1988). The coefficient of variation is abbreviated as CV, the residual standard deviation in a linear regression analysis as RSD. Graphical representations are in the form of so called distribution patterns; these plot the

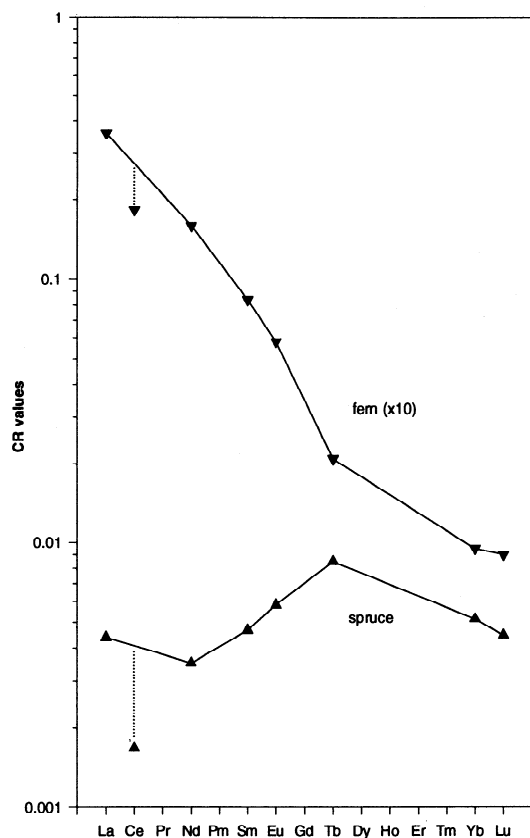


Figure 1. The ratios (CR1) between plant and soil for spruce and wood fern at site CHA. Plant and soil values are from Table 1.

log of a variable (usually a ratio) against the REEs in order of their atomic number, including those where no data are available. In order to facilitate comparison, all log graphs are drawn to the same scale.

Results and discussion

Concentrations of all pooled samples are given in Table 1. Values for the individual subsamples of soils, soil extracts, blackberry leaves and spruce needles are given in Wytttenbach et al. (1996, 1998).

Comparison between the plants and the soils at CHA

Figure 1 gives the concentration ratio plant/soil (CR1) for the two extreme species (spruce and fern); the curves for the other species (not shown) are intermediate. It is evident that these ratios are not constant, but demonstrate a large fractionation of the various REEs between the plant and the soil. This fractionation may be quantified by the variation between the CR1 values

of the individual REEs, or by the ratio of the CR1 values for 2 selected elements (Table 2); in both instances the values should be 1 if there were no fractionation, as is obviously not the case. The same conclusions are reached if the plants are not compared to the soil, but to the soil extracts.

Claims of no fractionation prevail in the literature, but they are most likely due to analytical difficulties or to the uncritical use of the expression 'no fractionation'. Nevertheless it seems that if the soil has a largely anomalous distribution of the REEs, as is the case with heavy mineralized soils, these anomalies are to a certain extent also reflected by the plants (Miekeley et al., 1994; Wang et al., 1997), but the similarity between plant and soil is never so close as to justify the expression 'no fractionation'.

Ce-anomaly

The Ce-anomaly of a plant is conventionally defined relative to the total REE concentration of the soil on which the plant is growing. In the present work the CR1 values of Ce are always much smaller than would be expected from its intermediate position between La and Nd (Figure 1). This anomaly is expressed as $CR1(Ce)/CR1(Ce^*)$, where $CR1(Ce^*)$ is the value expected from the interpolation between La and Nd, and $CR1(Ce)$ the value actually found. The Ce anomaly of the various plant species is given in Table 2. It is always smaller than 1 (or 'negative' in the usual terminology), ranging from 0.28 for ivy with the largest to 0.67 for fern with the smallest anomaly. Individual plants from the same site show a considerable spread in their Ce anomaly: 0.28–0.45 for 5 blackberries and 0.36–0.55 for 6 spruces, but there is no correlation between the anomalies of spruces and blackberries growing on the same spots (Wytttenbach et al., 1998).

As far as can be judged from literature data, a negative anomaly is present in the majority of plants, but there are also cases where it is clearly absent (Henke, 1977). The negative anomaly states that Ce concentrations in plants are less than expected from the concentrations of its neighbour elements. This is due to the fact that in soils Ce, in contrast to all other REEs, can assume a valence of +4, and that this ion has chemical properties differing from the trivalent REEs (Brookins, 1989). The effects of these differences obviously are a reduced availability and/or uptake of Ce into the plant. In seawater, microbially mediated redox processes affect the behaviour of both Ce and Mn (Moffet, 1990), and similar processes may

Table 1. REE concentrations (ng/g d.wt) in the soil, the soil extract and in leaves of various plant species

Species	Site	La	Ce	Nd	Sm	Eu	Gd	Tb	Yb	Lu
Soil (total) ^a	CHA	17800	36100	15000	2820	513	na	381	1470	205
Soil extract ^{a,b}	CHA	1878	3425	1797	459	92.5	na	70.3	152	15.80
Maple	CHA	1078	560	544	103	20.9	106	16.6	22.2	2.80
Wood fern	CHA	637	659	239	24	3.0	8	0.8	1.4	0.18
Blackberry	CHA	336	185	141	27	5.5	27	3.9	5.0	0.62
Ivy	CHA	172	75	67	9	1.8	8	1.1	2.0	0.26
Silver fir	CHA	97	61	65	14	3.2	17	3.5	8.3	1.01
Spruce	CHA	78	60	53	13	3.0	16	3.2	7.6	0.92
Spruce	AUE	110	110	69	14	3.1	16	3.1	6.9	0.83
Blackberry	WUR	76	55	33	6	1.3	6	0.9	1.7	0.21

^aMean of 6 places at CHA.

^bExtraction by 0.5 M acetic acid, 0.5 M NH₄-acetate, 0.02 M EDTA, pH 4.65. Concentrations reported relative to the weight of the extracted soil.

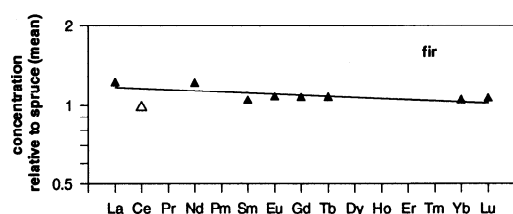


Figure 2. Normalized values (CR2) of silver fir. Normalization is done to Norway spruce from CHA (all values from Table 1). The line is the regression of log CR2 against Z, excepting Ce.

act in the rhizosphere (Laurie and Manthey, 1994). Ce⁺⁴ is metastable in the presence of organic material, but it can be stabilized by complexation and by adsorption onto solids. Mn compounds present as surface coatings on soil particles are suspected to act as sinks for Ce⁺⁴ (Hem, 1978). The conditions leading to the Ce anomaly are not very uniform at the present site, as is shown by the different size of the anomaly in the various species and by its variation between individuals of one species. Small changes of the redox potential of the rhizosphere might have contributed to this variability.

Comparison between plant species at CHA

The various plant species from a common site differ both in the concentration of a given REE (Table 1) and in the relation between the individual REEs. Both aspects can be shown by comparing all species to spruce, i.e. by forming the concentration ratio CR2 (plant/spruce). The resulting curves (Figures 2–4) demonstrate that the CR2 values of the REEs (excepting Ce) do not behave erratically, but change smoothly

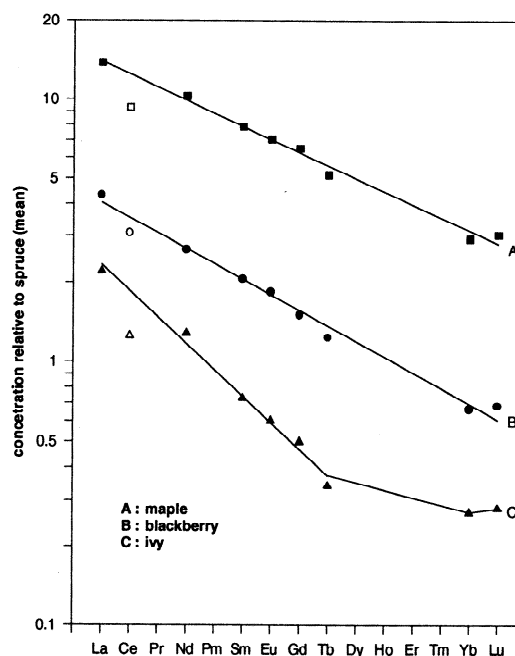


Figure 3. Normalized values (CR2) of maple, blackberry and ivy. Otherwise as in Figure 2.

with their atomic number Z. With most species the log of CR2 is a linear function of Z, decreasing from La to Tb (with ivy) or even to Lu (with the other species). The linearity of these distribution patterns is surprisingly great; the average RSD of the experimental values from the regression line is only a factor of 1.07, what is much less than the scatter present in the comparison of plants with the soil (Figure 1). With fern, log CR2 does not depend linearly on Z, but the values still decrease in a smooth manner from La to Tb

Table 2. Concentration ratio CR1 (plant/soil) and Ce-anomaly for plant species from CHA

Species	CR1 (plant/soil)			Ce-anomaly ^c
	Mean ^a × 10 ³	GSD ^a	La/Lu ^b	
Maple	31.4	1.75	4.5	0.30
Wood fern	4.7	4.10	39.9	0.67
Blackberry	7.9	1.93	6.2	0.34
Ivy	3.1	2.01	7.7	0.28
Silver fir	5.7	1.28	1.1	0.33
Spruce	5.0	1.32	1.0	0.41

^aGeometric mean and geometric standard deviation, GSD, of the CR1 values for 7 REEs (La, Nd, Sm, Eu, Tb, Yb, Lu). Ce is excluded because of its erratic behaviour, Gd because of its missing soil value. With constant values of CR1, GSD should be close to 1.

^bCR1(La)/CR1(Lu) is the ratio between the concentration ratios plant/soil for the first and last member of the REE series. Values different from 1 indicate a fractionation between these 2 elements in the plant with respect to the soil.

^cFor the definition of the Ce anomaly see text. Numerical values are given as CR1(Ce)/CR1(Ce*).

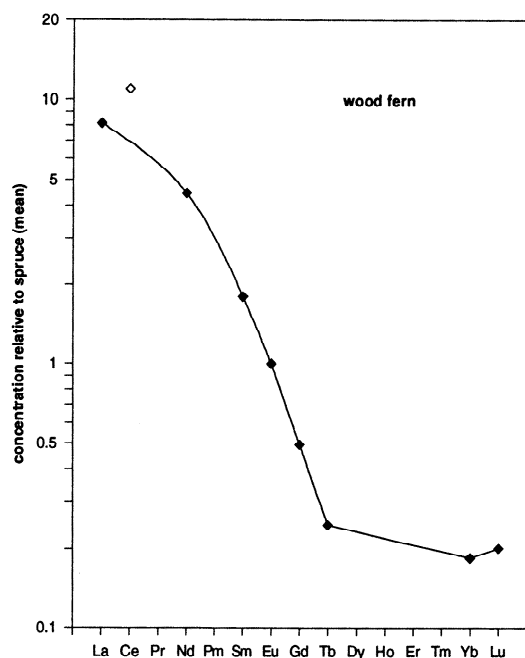


Figure 4. Normalized values (CR2) of wood fern. Otherwise as in Figure 2.

(Figure 4). In all cases Ce does not fit in with the other REEs; it is above the line if the Ce anomaly (Table 2) of the considered species is smaller than the anomaly in spruce (which is the case for fern), and below the line if the reverse applies (all other species).

An almost horizontal line is found in the comparison of fir and spruce (Figure 2). This behaviour may be expected for a series of chemically closely related elements such as the REEs. In all other cases (Figures 3 and 4), however, a very different behaviour is found. The slopes of the lines are negative, indicating a fractionation between 2 REEs in a given species when compared to spruce. As indicated by the different slopes, this fractionation is species specific and can reach very large values, e.g. a factor of 40 for La and Lu between fern and spruce (Figure 4). Investigation of individual plants of spruce and blackberry from CHA has shown that species related fractionations are to a large extent preserved in single plants (Wytenbach et al., 1998).

Different distribution patterns for various species have been observed before (Koyoma et al., 1987; Wang et al., 1997) but this is the first study to show that these differences are so tightly and regularly related to the atomic number. A different rooting depth can be dismissed as the reason for the interspecies differences, because extractions (both with water and Lakanen solution) from different depths have shown only small differences in their distribution patterns (Wytenbach et al., 1998). The strong Z-dependence of the ratios between 2 plant species suggests that the effect is connected to complexing of the REEs. Rhizosphere soil contains siderophores and root exudates, such as phytosiderophores and carboxylic acids, which are involved in the dissolution of the amorphous

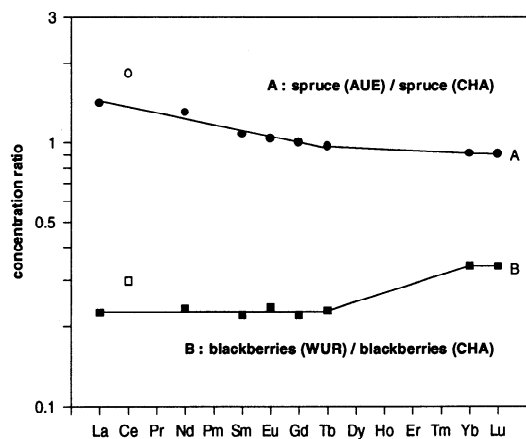


Figure 5. Ratio between identical species from different sites. A: Spruce (AUE)/spruce (CHA). B: Blackberries (WUR)/blackberries (CHA). All values from Table 1.

$\text{Fe}(\text{OH})_3$, and in the uptake of Fe (Jones et al., 1996). These chelates, however, do not only complex Fe^{+3} , but also REE^{+3} , since all these ions bind to carboxylate groups. A certain connection between Fe and the REEs is supported by the observation of a positive correlation between Fe and La plant concentration in the in the 6 species at CHA ($r = 0.94$, $p < 0.01$). The stability of some of the respective REE complexes varies with Z, being greatest for the most heavy REEs (Wood, 1993), and this shift is suspected to contribute to the observed fractionation between plant species. The size of the fractionations, however, suggests that they are not only due to different concentrations, but possibly to a different nature of the involved complexants in the rhizosphere. It is evident from the present results that the distribution patterns of the 2 conifers are about equal and very dissimilar from those of the angiosperms, which in turn differ from the fern from the same site. However, the number of investigated species is too small to draw general conclusions from these observations.

Plant species at other sites

In order to test if results similar to CHA are also present elsewhere, blackberries and spruces were each investigated at an additional site (Table 1). The comparison of identical species from different sites is given in Figure 5. Concentrations in blackberries differ by about a factor of 4, but their ratios are constant from La to Tb (without Ce, $n = 6$, $\text{CV} = 4.5\%$), meaning that the distribution patterns for these elements are exactly equal at the 2 sites. Concentrations in spruces

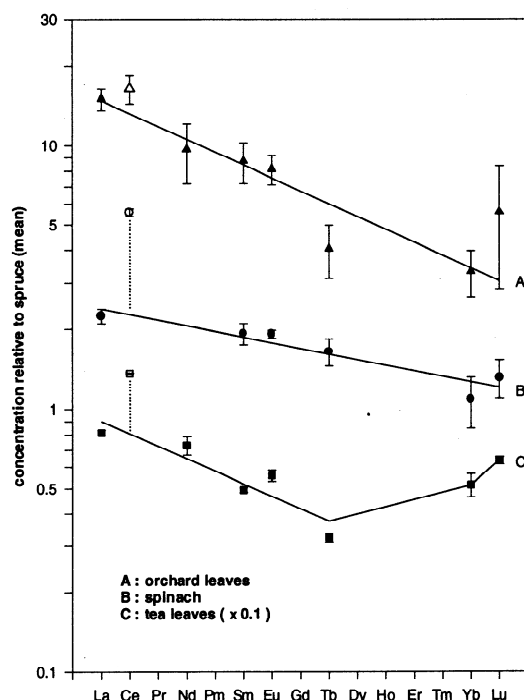


Figure 6. Normalized values (CR2) of botanical reference materials. A: Orchard leaves (NIST-1571, Gladney et al., 1987). B: Spinach (IAEA-331, which was later called NIST-1570A, Bangfa et al., 1995). C: Tea leaves (GSV-4, Sun et al., 1994; values divided by 10 for ease of representation). Error bars refer to values given by authors; they refer to accuracy in case A, but to precision only in case B and C. Normalization is done to spruce from CHA (Table 1).

are similar; as indicated by the slightly sloping curve, their distribution patterns differ somewhat, but again these differences are strongly bound to Z (RSD of the points from the regression line is a factor of 1.04). These results suggest that the species distribution patterns found at CHA are to a large extent also present at the other sites. With both plants, however, Ce, Yb and Lu do not fit in with the other REEs. This shows that the Ce anomaly of a species can be different at different sites. Deviations of Yb and Lu have already been observed in other cases (Figures 3 and 4); it may therefore be that the heaviest REEs do not always follow the strict Z dependence shown by the other REEs.

If the regularities found in this work are of a more general nature, they should also be shown by other plant species. Unfortunately literature values suitable to test this hypothesis are scarce; more often than not the samples come from unusual, mostly highly mineralized sites, or their accuracy is not adequate. Sufficient accuracy may be expected in botanical reference materials; the data of 3 materials, normalized

to spruce from CHA, are shown in Figure 6. Orchard leaves (NIST-1571) were grown in the US, tea leaves (GSV-4) in China, spinach (NIST-1570A) has no defined origin, and in no case is information on the soil available. As with most CR2 data from CHA, the curves are consistent with a linear dependence on Z, which is found from La to Tb with tea leaves and for all REEs in the other cases. Again Ce does not fit in with the other REEs. In spinach, Ce is a factor 2.5 above the line. As the Ce anomaly of spruce, with respect to soil or UCC is 0.41 (Table 2), it can be deduced that the anomaly in spinach with respect to UCC is 2.5×0.41 or 1.0, i.e. this sample seems to be a case with no Ce anomaly. REE values of ferns from Japan have been published by Takada et al. (1996); these concentrations are about 100 times higher than those of the fern from CHA, but have the same exceptionally steep distribution pattern as shown in Figure 4. These examples suggest that the characteristic distribution patterns revealed by the present work may also be found worldwide, and in different species.

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