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REGULAR ARTICLE

Transfer of rare earth elements (REE) from natural soil to plant systems: implications for the environmental availability of anthropogenic REE

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Abstract
Background and aims Rare Earth Elements (REE) are widely used to trace natural geochemical processes. They are also increasingly used by man (electronics industry, medicine, agriculture) and therefore considered as emerging pollutants. The present study documents REE mobility in non-polluted natural soil-plant systems in order to characterize their environmental availability for future anthropogenic pollution.
Methods The study is based on a field approach in non-polluted natural sites with contrasting geological environments (limestone, granite, and carbonatite) and highly variable REE contents.
Results REE concentrations in soils do not directly reflect bedrock concentrations, but depend largely on pedogenetic processes and on the mineralogy of bedrock and soil. The soils of all sites are with respect to bedrock enriched in heavy REE. The REE uptake by plants is not primarily controlled by the plant itself, but depends on the concentration and the speciation in the soil and the adsorbed soil water pool.
Conclusions REE uptake by plant roots are linked with those of Fe. Roots absorb preferentially the light REE. Before translocation, REE are retained by the Casparian strip leading to much lower concentrations in the aerial parts. The transport of the REE within the xylem is associated with the general nutrient flux.

Keywords Emerging pollutant · Environmental availability · Chemical speciation · Root absorption · Translocation

Introduction

Rare Earth Elements (REE) are trace metals including the lanthanide group and yttrium. They have become known to a wide public during the last few years because of supply shortages for the high-tech industry. In fact, a growing number of current or emerging alternative energy technologies (e.g. electric and hybrid vehicles, car catalysts, energy-efficient lighting, wind power) and digital equipment (e.g. flat panel displays, disk drives, digital cameras) contain REE-bearing

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components such as magnets, metal alloys, and phosphors (Haxel et al. 2002; Long et al. 2010). For example, a typical hybrid car comprises approximately 15 kg of REE, in particular neodymium (Nd; www.lynascorp.com; www.molycorp.com). REE are also used in medicine with gadolinium (Gd)-bearing contrast media for magnetic resonance imaging (Azoulay et al. 2007; Kümmerer and Helmers 2000) or lanthanum (La) carbonates for the treatment of renal disease (Bernard et al. 2005; D'Haese et al. 2003; Hutchison et al. 2004). In agriculture REE-doped food is used for pig and poultry fattening (He et al. 2001, 2003, 2010), and in China REE-doped phosphate fertilizers have been applied for several years on a massive scale for growing crops of maize, rice, wheat, potato and cabbage (Liang et al. 2005; Pang et al. 2002; Xiangsheng et al. 2006).

The rapidly growing demand for REE has led to an exponential increase of global REE mining production from about 50 kt/year in 1990 to 70 kt/year in 1995 and 130 kt/year in 2010 (Chen 2011; Haxel et al. 2002; Livergood 2010). This growing use leads to environmental contamination and REE are therefore considered as an emerging pollutant (Kulaksiz and Bau 2011; Yang et al. 2009) . The most frequently detected anthropogenic REE is Gd issued from magnetic resonance imaging and released into the environment through hospital effluents. The presence of anthropogenic Gd leads to a typical positive Gd-anomaly in the REE distribution patterns of surface waters, which has been reported from rivers, lakes and coastal environments in Europe (Bau and Dulski 1996; Elbaz-Poulichet et al. 2002; Hennebrüder et al. 2004; Knappe et al. 2005; Kulaksiz and Bau 2007, 2011; Möller et al. 2000, 2002, 2003; Rabiet et al. 2005), in the USA (Bau et al. 2006; Verplanck et al. 2005), and in Japan (Nozaki et al. 2000; Ogata and Terakado 2006). In China, elevated REE concentrations have been observed in soils adjacent to REE mines and refining plants (Wang et al. 1997; Zhenggui et al. 2001; Zhu et al. 1997) and in agricultural areas with intensive use of REE-enriched fertilizers (França et al. 2002).

REE have previously been considered to be non-toxic and to be readily excreted by animals and man after ingestion (Schwabe et al. 2012). However, recent publications have reported toxic effects of REE in bacteria (Wilde et al. 2002), plants (Babula et al. 2008) and animals (Briner et al. 2000; Che et al. 2010; Feng et al. 2006). In order to contribute to a better understanding of the behavior of the REE within the biosphere, we focus in the present study on the mechanisms controlling the transfer of REE at the soil-plant interface, which is one of the principal routes to introduce anthropogenic trace elements into the biosphere. Earlier studies have shown that solution complexation of the REE with organic and inorganic ligands plays an important role for REE absorption by plant roots (Ding et al. 2005a, b; Liang et al. 2008). However, these studies were based on hydroponic growth experiments and the results can therefore not be directly transposed to natural soil/root interfaces. As a consequence, these mechanisms remain poorly understood for natural systems (Tyler 2004).

In contrast to earlier studies we have therefore not chosen a laboratory (e.g. Ding et al. 2006a, c; Han et al. 2005; Hao et al. 1997; Semhi et al. 2009; Shtangeeva and Ayrault 2007) or field approach in cultivated plots enriched with anthropogenic REE (Ding et al. 2006b; Liang et al. 2005; Xu et al. 2002, 2003), but a field approach under undisturbed natural conditions investigating the REE of the pedo-geochemical background. To take into account environmental variability, 3 field sites with contrasting geo-pedological conditions were selected. All sites were under temperate continental climate conditions. On each site, REE transfer from soil to roots and aerial organs were studied in several tree species (spruce, beech and oak). The objectives of this comparative approach was to assess the roles of geo-pedological and environmental parameters in the transfer rates and transport mechanisms for the REE in soil-plant systems in order to contribute to a better characterization of the environmental availability of anthropogenic REE.

Materials and methods

Chemical properties, normalization, and natural occurrence of the REE

REE include the lanthanide group and yttrium. Within the lanthanide group the ionic radii decrease with increasing atomic number, which leads to a slightly variable behavior during chemical or biological processes (Henderson 1984; Tyler 2004). Under natural surface environments most REE occur as trivalent ions except cerium (Ce), which is transformed to Ce^{4+} under oxidizing conditions (>300 mV at pH 7).

Europium (Eu) is reduced from Eu^{3+} to Eu^{2+} under extremely reducing conditions (<−350 mV at pH 7; Brookins 1989). The REE group can be separated into three sub-groups: the light REE (LREE, La-Sm), the medium REE (MREE, Eu-Td) and the heavy REE (HREE, Dy-Lu). Their particular chemical properties have made of the REE an important tracer for geochemical processes (Henderson 1984; Lipin and McKay 1989). They have also specific magnetic and optical properties, which is the basis for the rapidly growing number of technical applications.

REE data are typically presented as distribution patterns with the individual REE, listed in the order of their atomic number, as categories on the x-axis. The corresponding REE concentrations appear as normalized logarithmic values on the y-axis. Normalization is necessary to smooth the distribution patterns, which would otherwise have a zigzag shape. Typical normalizations for Earth's surface processes are the NASC (North American Shale Composite; Gromet et al. 1984) or PAAS standards (Post Archean Australian Shales; Taylor and McLennan 1985), which both represent average upper continental crust. However, for more detailed studies it may be useful to normalize to a local standard, such as local bedrock, or to present the REE patterns as transfer factors between 2 subsequent reservoirs (e.g. soil/bedrock, root/soil). In the present paper we will use PAAS normalized REE patterns only for the bedrock and present all other data as REE transfer factors. The change of the shape of the REE patterns between 2 successive reservoirs is called "fractionation of the REE", e.g. an enrichment or a depletion in light, medium, or heavy REE.

More specific fractionations are positive or negative peaks in the REE distribution patterns, which are most common for Ce and Eu, and referred to as positive or negative Ce and Eu anomalies. The magnitude of these anomalies is quantified by Ce/Ce* and Eu/Eu* ratios:

$$\mathrm{Ce/Ce}* = \frac{3\ Ce_{norm}}{2\ La_{norm} + Nd_{norm}} \quad \text{and}$$

$$\mathrm{Eu/Eu}* = \frac{Eu_{norm}}{\sqrt{Sm_{norm} * Gd_{norm}}}$$

The subscript "norm" stands for normalized values. Anomalies with Ce/Ce* and Eu/Eu* ratios >1 appear as positive peaks in a REE pattern and are therefore referred to as "positive anomalies". Anomalies with Ce/Ce* and Eu/Eu* ratios <1 yield negative peaks and are called "negative anomalies". The occurrence of positive or negative Ce anomalies is typical for oxidizing conditions where Ce is present as Ce^{4+} and therefore less soluble than the other REE (McLennan 1989). By contrast, on the Earth's surface Eu anomalies are, in most cases, related to the presence of feldspar or feldspar-derived alteration products such as clay minerals (Galan et al. 2007; McLennan 1989).

The average REE concentration of the upper Earth's crust is about 150 mg/kg for the sum of the REE, and 25 mg/kg for neodymium (Nd; McLennan 1989). Typical concentrations in soils are a few tens of mg/kg for Nd and a few hundreds of mg/kg for the sum of the REE (Laveuf and Cornu 2009; Loell et al. 2011; Tyler 2004). The REE concentrations of vegetation are at least one order of magnitude lower than for soils, but vary over several orders of magnitude as a function of plant species and soil concentrations. The highest concentrations are found in roots, where values may achieve a few hundred μg/kg for Nd and a few mg/kg for the sum of the REE (Fu et al. 2001; Liang et al. 2008). In the above-ground biomass of plants, concentrations decrease considerably in the order leaf > stem > grain/fruit and vary in the range of a few μg/kg to a few tens of μg/kg for Nd, and a few tens to a few hundred μg/kg for the sum of the REE (Tyler 2004; Liang et al. 2008). In this study, Nd concentrations were used rather than the sum of the REE to characterize the REE content of a sample, because the Nd concentrations give a more reliable measure for the overall REE content than the sum of the REE, which is strongly influenced by Ce and Eu anomalies.

Field sites

The 3 field sites are located in eastern France and SW Germany all within a distance of less than 200 km (Fig. 1). The climate at the 3 sites is temperate continental with oceanic influence. The geo-pedological conditions of the 3 sites are different: The first site is located on limestone bedrock, the second site on granite and the third site on carbonatite. Carbonatites are carbonates of volcanic origin and strongly enriched in REE. This third site therefore allows the study of soil-plant transfer at elevated REE concentrations. Carbonatites are mined for REE extraction (e.g. in the Mountain Pass area in California; www.molycorp.com) and the carbonatite site

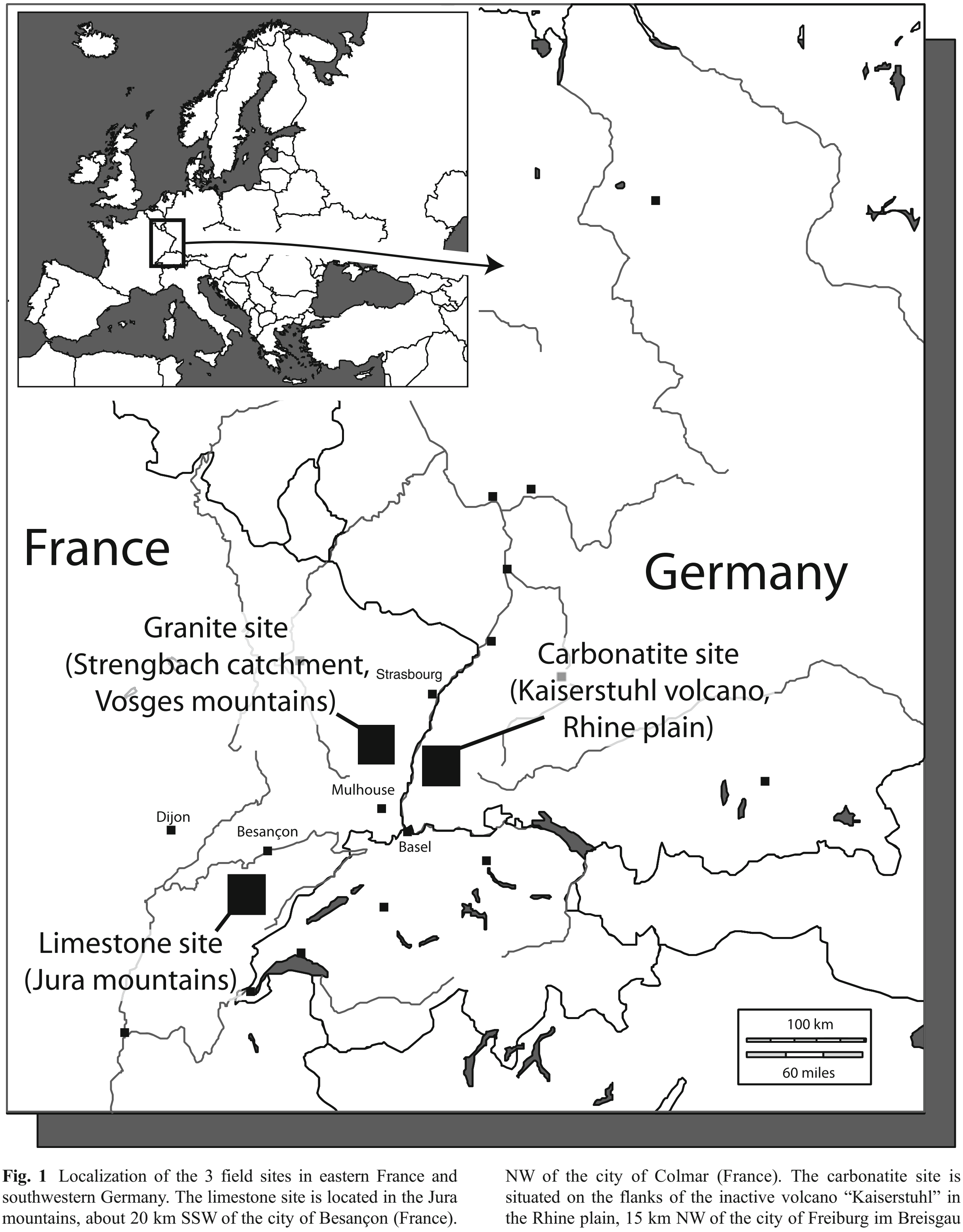

Fig. 1 Localization of the 3 field sites in eastern France and southwestern Germany. The limestone site is located in the Jura mountains, about 20 km SSW of the city of Besançon (France). The granite site lies within the environmental observatory of the Strengbach catchment in the southern Vosges mountains, 20 km NW of the city of Colmar (France). The carbonatite site is situated on the flanks of the inactive volcano "Kaiserstuhl" in the Rhine plain, 15 km NW of the city of Freiburg im Breisgau (Germany)

is therefore also representative for soil-plant transfers in such mining sites.

The general soil parameters of the 3 sites are summarized in Table 1 and their major element composition in Table 2. The limestone site is located on a forested plateau of the Jura mountains close to Cussey-sur-Lison (France) at an elevation of 320 m. The mean annual precipitation is about 1,000 mm/year and the mean annual temperature 10.2°C. The plant cover consists in a natural deciduous forest, punctually interrupted by spruce stands planted for wood production. Three representative field plots were selected on the limestone site. The first plot, with beech, is situated directly on the plateau with eutric cambisol. The second plot is also located in a beech stand, but on a slope at the foot of a limestone cliff. The soil of this stand is as for the plateau an eutric cambisol. The third plot is situated in a spruce stand implanted in a dolina with a luvic cambisol. In the following these 3 plots of the limestone site will be referred to as “beech plot plateau”, “beech plot slope”, and “spruce plot” respectively.

The granite site is located in the Strengbach catchment in the southern Vosges mountains at altitudes ranging from 880 to 1,150 m. The mean annual precipitation is about 1,350 mm/year and the mean annual temperature 6°C (Probst et al. 1992). The Strengbach catchment is a completely equipped environmental observatory with permanent sampling and measuring stations maintained by the laboratory of hydrology and geochemistry of the CNRS/University of Strasbourg (LHyGeS, http://ohge.u-strasbg.fr). The catchment is almost completely covered with forest composed of 80 % spruce and of 20 % beech. The bedrock of the Strengbach catchment is a coarse-grained granite locally affected by hydrothermalism. The soils are coarse-grained and rich in bedrock boulders (Fichter et al. 1998). Two plots were studied, one in a spruce stand with dystric cambisol and the other in a beech stand with entic podzol. The plots are termed “spruce plot” and “beech plot” below and they correspond to the “VP” and “HP” plots, respectively, of earlier publications dealing with the Strengbach catchment (e.g. Stille et al. 2009).

The carbonatite site is located on the inactive volcano “Kaiserstuhl” in the Rhine plane near Freiburg im Breisgau, Germany. The site is located at 360 m altitude with an average annual precipitation of 600 to

Table 1 General soil properties of the plots of the 3 study sites. C org = organic carbon

	Depth [cm]	Texture	Density [g/cm^3]	pH	C org. [wt%]	$CaCO_3$ [wt%]
Limestone site						
Spruce plot plateau	0–12	silt	1.2	5.0	5.2	0.0
	12–30	silt loam		5.1	2.2	0.0
	30–60	silty clay loam		5.1	1.9	0.0
Beech plot plateau	0–8	silty clay loam	0.9	5.7	6.7	0.3
	8–28	silty clay		7.6	5.1	0.4
Beech plot slope	0–21	clay loam	1.1	7.0	9.6	0.4
	21–38	clay		8.0	3.8	0.5
Granite site						
Spruce plot	0–5	silty clay			22.4	0.0
	5–27	silty clay	1.3	4.1	12.7	0.0
	27	silty clay	1.2	4.3	12.4	0.0
Beech plot	0–5	clay		4.1	18.0	0.0
	5–27	silt loam	1.1	4.8	11.0	0.0
	27–70	silt loam	1.0	4.9	5.2	0.0
Carbonatite site						
Oak plot	0–5	silty clay	1.1	5.8	13.1	0.2
	5–26	silty clay	1.1	5.8	11.0	0.2

Table 2 Major element composition and uranium concentrations of bulk soil. Major element concentrations are given in weight percent, uranium in mg/kg. LOI = loss on ignition at 1,000°C in weight percent

	Depth [cm]	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	MnO	Na_2O	K_2O	P_2O_5	LOI	Sum	U
Limestone site													
Spruce plot plateau	0–12	70.5	9.7	0.67	0.38	4.62	0.153	0.54	1.35	0.20	11.3	100.3	3.77
	12–30	70.7	11.5	0.82	0.37	5.58	0.127	0.50	1.38	0.17	7.0	99.1	3.70
	30–60	69.9	12.3	0.89	0.42	6.13	0.118	0.48	1.56	0.17	6.9	99.7	3.74
	average	70.4	11.2	0.79	0.39	5.45	0.133	0.51	1.43	0.18	8.4		3.74
	stdev	0.4	1.3	0.11	0.03	0.76	0.018	0.03	0.11	0.02	2.5		0.04
Beech plot plateau	0–8	54.3	15.1	0.81	0.68	8.46	0.145	0.28	0.59	0.16	17.7	99.1	3.22
	8–28	52.1	15.5	0.85	2.19	8.94	0.217	0.26	0.67	0.19	17.6	99.5	3.19
	average	53.2	15.3	0.83	1.44	8.70	0.181	0.27	0.63	0.17	17.7		3.20
Beech plot slope	0–21	53.8	11.3	0.82	2.67	7.76	0.154	0.23	0.99	0.29	20.0	98.7	2.72
	21–38	55.7	12.4	0.93	7.09	7.88	0.166	0.30	1.32	0.22	12.6	99.3	3.04
	average	54.7	11.8	0.88	4.88	7.82	0.160	0.27	1.16	2.16	16.3		2.88
Granite site													
Spruce plot	0–10	64.0	16.2	0.63	0.07	3.84	0.120	0.57	4.75	0.26	7.2	98.1	4.14
	10–20	65.1	15.1	0.60	0.08	3.51	0.110	0.53	5.11	0.23	7.3	98.2	3.41
	30–40	66.3	15.7	0.62	0.06	3.65	0.106	0.57	4.99	0.26	6.4	99.2	3.54
	50–60	63.4	16.8	0.70	0.07	4.35	0.135	0.58	5.15	0.22	6.3	98.1	3.47
	70–80	65.2	16.7	0.76	0.07	4.52	0.159	0.57	5.26	0.22	5.9	99.9	3.34
	90–100	65.2	17.5	0.75	0.09	4.28	0.180	0.56	5.21	0.21	5.3	99.7	3.43
	average <60 cm	64.7	15.9	0.64	0.07	3.84	0.1	0.56	5.00	0.24	6.8		3.64
	stdev <60 cm	1.3	0.7	0.04	0.01	0.37	0.0	0.02	0.18	0.02	0.5		0.34
[a] beech plot	0–5	56.4	12.8	0.26	0.12	1.30	0.007	1.50	4.02	0.26	22.4	99.4	3.20
	5–20	64.9	16.0	0.33	0.12	1.70	0.011	1.93	4.88	0.26	8.3	98.7	3.60
	20–45	66.9	17.0	0.35	0.13	2.30	0.050	2.21	5.15	0.33	5.5	100.2	4.90
	45–70	66.3	17.1	0.35	0.18	2.40	0.035	2.18	5.33	0.42	5.8	100.3	4.40
	70–100	67.0	17.5	0.56	0.29	2.70	0.071	2.06	5.20	0.36	4.0	100.1	5.80
	100–150	66.5	18.2	0.58	0.26	2.70	0.056	2.32	5.32	0.30	4.0	100.1	7.80
	average <70 cm	63.6	15.7	0.32	0.14	1.93	0.0	1.96	4.85	0.32	10.5		4.03
	stdev <70 cm	4.9	2.0	0.04	0.03	0.52	0.0	0.33	0.58	0.08	8.0		0.77
Carbonatite site													
Oak plot	0–5	61.2	10.5	3.5	4.4	7.7	0.623	0.8	0.9		8.8	98.4	3.9
	5–26	61.4	9.9	2.6	2.0	5.9	0.498	0.7	0.9		14.9	98.7	3.7
	average	61.3	10.2	3.0	3.2	6.8	0.561	0.7	0.9		11.9		3.8

[a] data from Aubert et al. 2001

700 mm/year and a mean annual temperature of 9.9°C. The site is not forested, but mainly occupied by vineyards with a few plots of grassland and trees. The soil is a superficial eutric cambisol about 30 cm deep. Beech and spruce are absent from the site and therefore parts of oaks were sampled.

Field sampling and analytical methods

For the limestone and carbonatite sites the bedrock samples were recovered in close vicinity of the field plots. For the granite site a bedrock outcrop was located at about 300 m from the beech plot. The chemical data of this outcrop were taken from Aubert et al.

(2001). In contrast, no bedrock outcrop was available for the spruce plot. Therefore, 2 granite boulders recovered from a soil profile were analyzed. For all sites, soils were sampled in pits by taking 3–5 subsamples per horizon, which were bulked in the field. All sites were equipped with Teflon (granite site) or polypropylene (limestone and carbonatite sites) lysimeter plates for soil water sampling. The plates were installed at 20 to 30 cm of depth for the limestone and carbonatite sites. For the granite site the soil water data were taken from Stille et al. (2009) who sampled complete soil water profiles from 5 to 70 cm depth in the beech and spruce plots. Tree trunk samples were recovered from slices cut at the heights above ground specified in the supplementary data files. Roots and leaves were sampled on the same tree specimens as the trunk samples. Needle samples were of the current year. Roots were handpicked in pits and sorted by diameter (<2 mm, 2–10 mm, >10 mm). Sap samples of beech (limestone and granite sites) and oak (carbonatite site) were recovered during the rapid growth period at the end of spring (May/June) from small branches by squeezing with a portable nitrogen pressure chamber at about 30 bars.

Bedrock samples were crushed, milled in an agate mill, fused with Li_2BO_4 and dissolved in HNO_3 for analysis by ICP-AES (Jobin Yvon) and ICP-MS (Thermo Xseries 2) at the LHyGeS laboratory at CNRS Strasbourg (France) according to the procedure described by Samuel et al. (1985). Soil samples were sieved (2 mm mesh size), followed by the same digestion and analytical procedure as for the bedrock samples. The detection limit for the REE in soil and bedrock samples was 0.01 mg/kg with a precision better than ±5 %. The $CaCO_3$ and organic carbon content of the soil samples were determined at the laboratory of Chrono-Environnement in Besançon (France) by calcimetry and an Elementar Vario Max carbon analyzer, respectively. Soil pH was determined in distilled water according to ISO 10390.

Roots and leaves were first washed in 50 mL polypropylene tubes for 10 min with acidified ultrapure water from a Millipore Elix–Simplicity chain under continuous agitation in order to remove soil and airborne particles. Afterwards, the samples were rinsed with ultrapure water and dried during 2 weeks at room temperature, followed by 24 h at 40°C in a drying oven. Trunk samples were air-dried, then split into match-sized splints and calcined using a step-wise heating procedure (350, 450, and 500°C during 90, 90, and 120 min respectively).

For chemical analysis about 1–5 g of cleaned roots, leaves or calcined wood were completely digested in closed 120 mL Savillex teflon vessels under clean-lab conditions. Complete digestion was typically achieved after 3 days using a multi-step procedure with a mixture of distilled concentrated HNO_3, ultrapure H_2O_2, and HF on a hot plate at 80°C. After evaporation to dryness the samples were taken up in 15 mL of 1 M HNO_3 for ICP analysis. For sap samples, 1 mL of distilled concentrated HNO_3 was added to about 3 mL of sap, evaporated to dryness and taken up in 15 mL of 1 M HNO_3 for ICP analysis. Soil water was filtered immediately after sampling with 0.45 μm cellulose acetate filters and acidified to pH 2 with HNO_3. The chemical analyses of vegetation and soil waters were as for bedrock and soils realized by ICP-AES (Jobin Yvon) and ICP-MS (Thermo Xseries 2) at the LHyGeS laboratory at CNRS Strasbourg (France) with a precision of <±5 %. The detection limits for the REE was 0.01 μg/kg for vegetation samples and 0.001 μg/L for soil waters. Replicates of selected vegetation samples yielded identical REE patterns with absolute REE concentrations varying in a range of ±10 %.

Results

REE contents in bedrock, soil, and soil water

The bedrocks of the 3 sites were characterized by distinct REE patterns and concentrations (Fig. 2). The raw data of Fig. 2 are available as supplementary data file. For limestone and granite the REE concentrations were in the same range. In contrast, much higher values and a strong LREE enrichment were observed for carbonatite, which is to be expected for this type of rock (Hornig-Kjarsgaard 1998).

The REE concentrations in soils are presented in Fig. 3 as soil/bedrock transfer factors to visualize REE fractionation during soil formation. Only average data are presented because significant depth-trends were absent. The raw data are as for the bedrock available as supplementary data file. The absolute REE concentrations were 3 to 7 times higher for the soils of the carbonatite site than for the other sites. However, the soil/bedrock transfer factors were about 0.5 for the

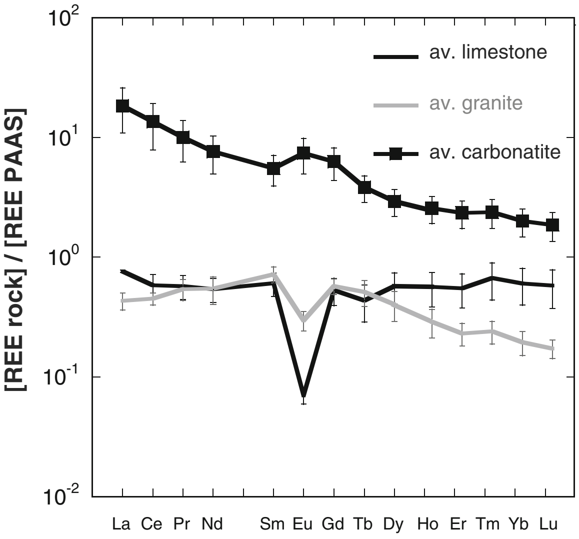

Fig. 2 Average REE distribution patterns in bedrock of the 3 study sites (limestone, granite, carbonatite). The patterns are normalized to PAAS (Post Archean Australian Shales), which represents average upper continental crust. The error bars correspond to the standard deviations of the means, which are based on the values given in the supplementary data files

carbonatite site, and thus markedly lower than for the limestone and granite sites with transfer factors of 2 and 1, respectively (Fig. 3). For all sites the soils were enriched in HREE with respect to bedrock. Furthermore, the soils of the limestone site showed strong positive Eu anomalies. A slight positive Eu anomaly occurred for the soils of the granite site, whereas no significant anomalies were found for the carbonatite site. REE concentrations were correlated with Fe and Al contents in the soils of the limestone site, and with Fe and Mn in the soils of the granite site (Table 3).

Soil water REE are presented in Fig. 4 as soil water/soil transfer factors in order to visualize REE fractionation during soil water/soil interaction. The raw data are available as supplementary data file. The soil data used for normalization are average values of the complete soil profiles for the limestone and carbonatite sites, which are less than 60 cm deep. For the granite site, average values over the uppermost 60 cm of the soil profiles were used for the spruce plot and over the uppermost 70 cm for the beech plot. The soil water/soil transfer factors of the limestone site showed slightly HREE-enriched distribution patterns with negative Ce anomalies. The patterns from the granite site showed similarly a HREE enrichment, completed by a positive Eu anomaly for the beech plot. Only one incomplete REE pattern was available for the carbonatite site. It was enriched in HREE and displayed a negative Ce anomaly as the soil waters of the limestone site.

REE contents in vegetation

REE concentration data of vegetation are presented in Fig. 5. The raw data can be downloaded as supplementary data files. The average Nd concentrations of vegetation varied between 3,700 μg/kg for root and 4 μg/kg for trunk samples. They were lowest for the trunk, intermediate for needles, leaves, medium and large roots, and highest for small roots, which is in agreement with literature data (Fu et al. 2001; Hu et al. 2002; Liang et al. 2005, 2008; Tyler 2004; Wang et al.

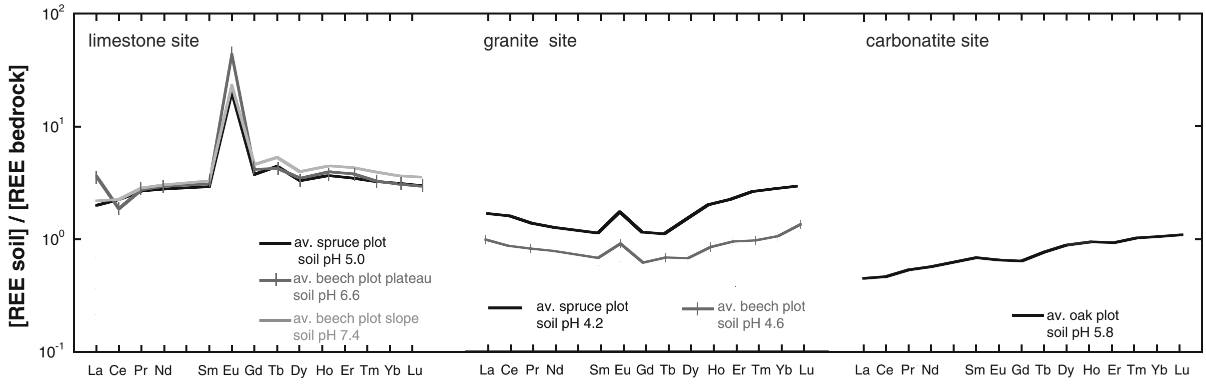

Fig. 3 Average REE distribution patterns of soils of the 3 field sites. The patterns are normalized to local bedrock and represent soil/bedrock transfer factors. The averages and the corresponding standard deviations are those given in the supplementary data files. The average soil pH values are those given in Table 1

Table 3 Pearson correlation matrix for Nd with major and trace elements, organic carbon (C org), and soil pH in soil, soil water, and vegetation. "n" = number of samples, "–" = no data. Values >0.8 in bold

	n	Si	Al	Mg	Ca	Fe	Mn	K	Na	P	U	C org.	Soil pH
Soils													
Limestone site	7	−0.727	**0.933**	0.142	−0.014	**0.813**	0.638	−0.927	−0.661	0.073	−0.393	0.350	0.390
Granite site	12	0.151	0.087	0.755	−0.494	0.799	0.780	−0.789	0.125	−0.513	−0.244	−0.590	−0.600
All sites	15	–	–	–	–	–	–	–	–	–	–	–	0.740
Soil water													
Limestone site	12	−0.186	−0.197	−0.173	−0.171	−0.159	**0.814**	−0.230	−0.173	–	–	–	–
Granite site	6	0.770	0.340	0.440	0.700	0.700	0.370	0.790	−0.760	–	–	–	–
Vegetation													
Roots, all sites	25	0.672	**0.879**	0.024	0.178	**0.826**	−0.398	−0.097	0.653	−0.148	**0.841**	–	–
Trunks, all sites	47	0.062	0.542	−0.178	0.363	**0.828**	−0.102	−0.207	0.399	0.082	**0.851**	–	–
Leafs, all sites	9	0.444	0.494	0.008	0.886	0.495	−0.706	−0.234	0.021	−0.566	0.050	–	–
Sap, all sites	6	−0.465	**0.900**	0.917	0.810	**0.952**	0.302	**0.939**	0.500	**0.907**	**0.883**	–	–

2003). We consider that the REE content of leaves and needles represent essentially soil-derived REE, because air-borne particles were removed with dilute acid prior to digestion. However, a slight contribution of REE derived from foliar uptake from airborne particles cannot be completely excluded.

Limestone site

Nd concentrations in spruce varied between 40 and 3,700 μg/kg for the roots, and 0.3 to 15 μg/kg for the trunk (Fig. 5). The patterns of the REE plant/soil transfer factors were very similar for root, trunk and needles with a LREE enrichment and a slight negative Ce anomaly. Medium and large roots showed positive Eu anomalies, whereas the anomaly was negative for the trunk (Fig. 6). The beech samples had Nd concentrations between 600 and 3,500 μg/kg for the roots, and 4 to 10 μg/kg for the trunk (Fig. 5). The REE patterns showed, as for spruce, a slight LREE enrichment and negative Ce anomalies for some root samples (Fig. 6). Two sap samples were retrieved from small beech branches of the plateau plot. They showed strong positive Eu and Ce anomalies, and LREE enrichment.

The REE root/soil transfer factors varied between 10^{-3} and 10^{-2} for spruce. For the beech roots from the plateau and slope plots the values were significantly higher, ranging between 10^{-2} and 10^{-1}. This difference between spruce and beech disappeared in the trunk where the transfer factors varied between 10^{-4} and 10^{-3} for both species (Fig. 6).

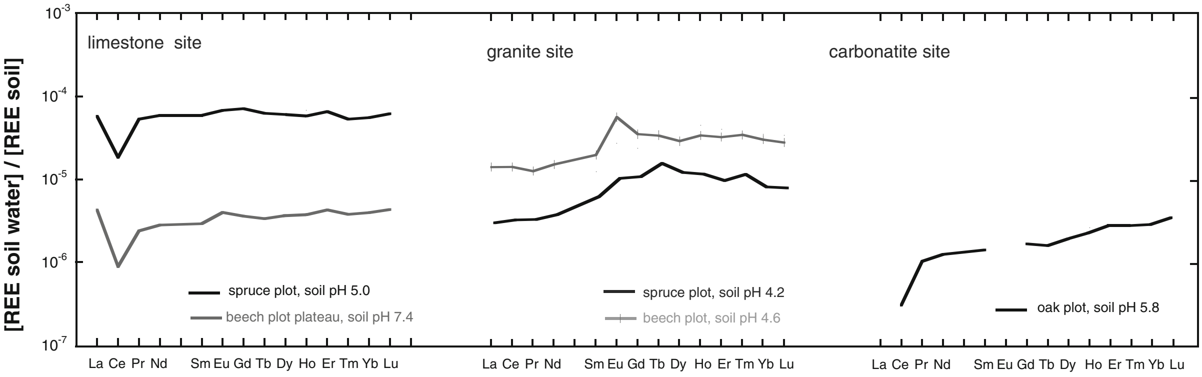

Fig. 4 REE distribution patterns of soil water of the 3 field sites. The patterns are normalized to local soil (<60 cm depth) and represent soil water/soil transfer factors. The soil pH values are the same as in Fig. 3

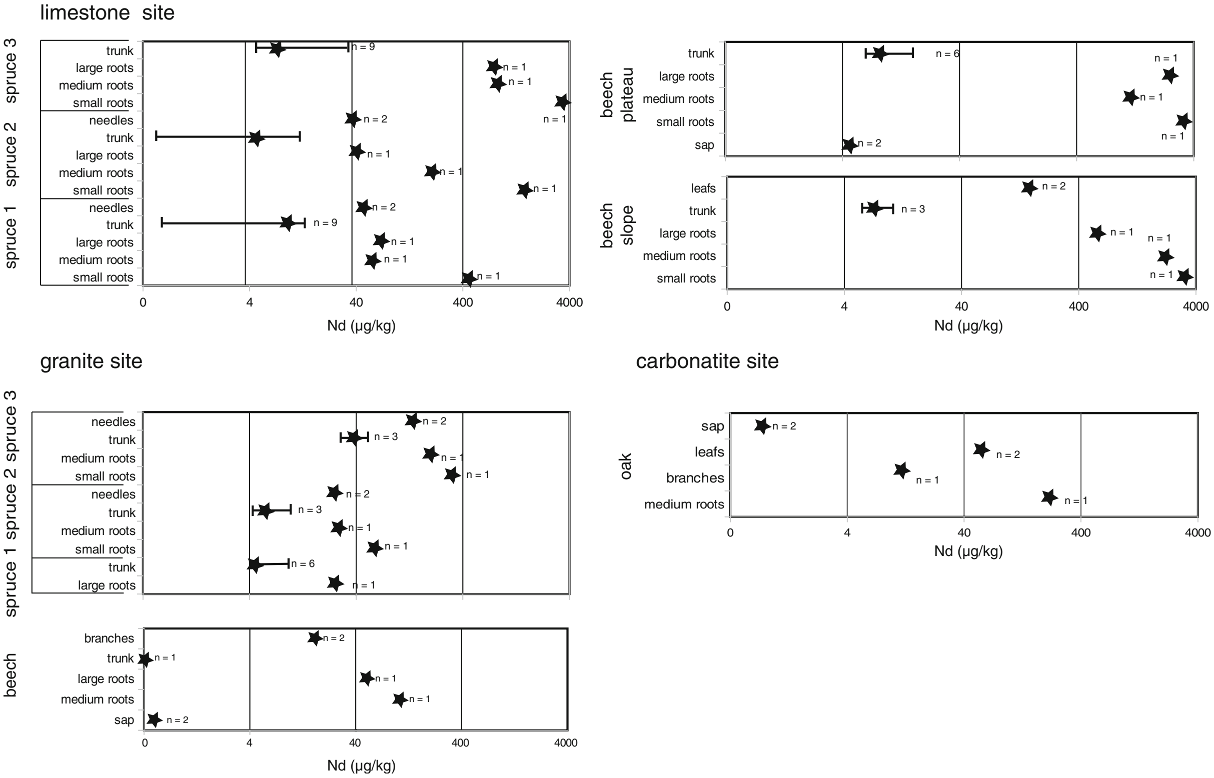

Fig. 5 Range of Nd concentrations of vegetation samples. The raw data are available in the supplementary data files. *Stars* represent simple or average values according to the number of samples "n". The bars associated with average values represent the absolute range of variation. Note the logarithmic scale of the x-axis

Granite site

The Nd concentrations in the beech and spruce roots ranged between 30 and 220 µg/kg, which is distinctly lower than for the limestone site. In contrast, the Nd concentrations for trunk and branches ranged from 4 to 17 µg/kg for both sites (Fig. 5). The patterns of the REE plant/soil transfer factors of the spruce and beech

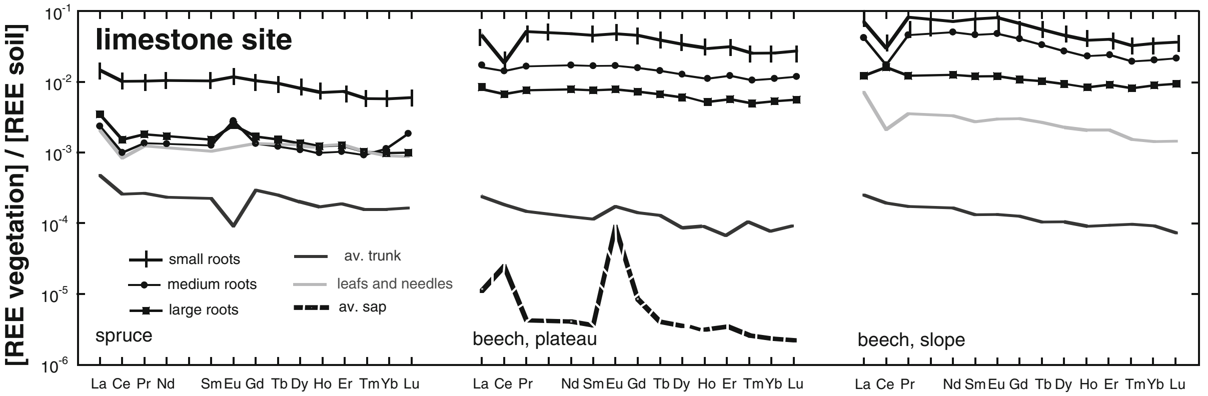

Fig. 6 REE distribution patterns of vegetation of the limestone site. The patterns are normalized to local soil in order to show fractionation at the plant/soil interface. The patterns represent average values. They are based on 27 samples for the spruce trunks, 6 samples for the beech trunks from the plateau, and 3 samples for the beech trunks from the slope and small beech and spruce roots. The data of sap, leaves and needles are based on 2 samples. Only 1 sample was available for medium and large roots

organs from the granite site differed from those of the limestone site by the presence of positive Eu anomalies and the absence of negative Ce anomalies. Furthermore, LREE enrichment was less pronounced than for the limestone site and limited to roots (Fig. 7).

The REE root/soil transfer factors varied between 10^{-3} and 10^{-2} for spruce and were thus comparable with spruce from the limestone site. The transfer factors were slightly higher for beech, which, however, remained below those for the beech of the limestone site. The sap samples retrieved from young beech were very similar to those from the limestone site with strong positive Ce and Eu anomalies.

Carbonatite site

The vegetation data from the carbonatite site are shown in Fig. 8. No spruce or beech were present on this site and therefore parts of oaks were sampled. The absolute REE concentrations were, in comparison to the other sites, less variable for the individual plant organs (Fig. 5). As for the limestone and granite sites, the patterns of the REE plant/soil transfer factors were slightly enriched in LREE. The patterns of roots and leaves displayed negative Ce anomalies. On the other hand, the branches showed a positive Eu anomaly, which was absent in the other organs. The sap samples were, like for the limestone and granite sites, characterized by a strong positive Eu anomaly. But in contrast to the other sites, there was no positive Ce anomaly. The REE root/soil transfer factors were with values between 10^{-3} and 10^{-2} comparable with the limestone and granite sites.

REE stock of vegetation and soil

The total REE stock of vegetation and soil was calculated for each site. The biomass of vegetation was determined for each field plot based on the height and the diameter of the trees on an area of 30*30 m following the procedure described in detail by Lambert et al. (2005). The REE stock in soil was calculated on the basis of the soil depths and densities, and the average REE concentrations given in the supplementary data files. We were unable to measure accurately the soil depths of the granite site and therefore an average depth of 1 m was used. The results are presented in Table 4 and show that, with respect to soil, vegetation represents a negligible REE reservoir.

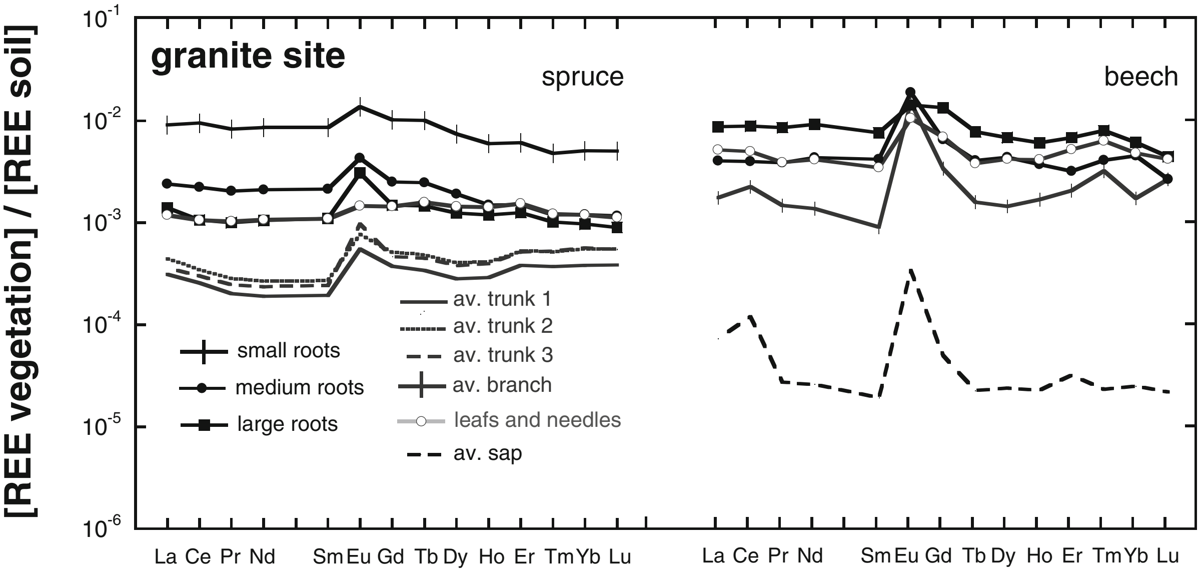

Fig. 7 REE distribution patterns of vegetation of the granite site. The patterns are normalized to local soil (<60 cm depth for the spruce plot and <70 cm for the beech plot) in order to show fractionation at the plant/soil interface. The patterns represent average values, which are based on 12 samples for the spruce trunks and 2 samples for the beech branches. The patterns of leaves, needles and sap are based on 2 samples, whereas only 1 sample was available for small, medium, and large roots

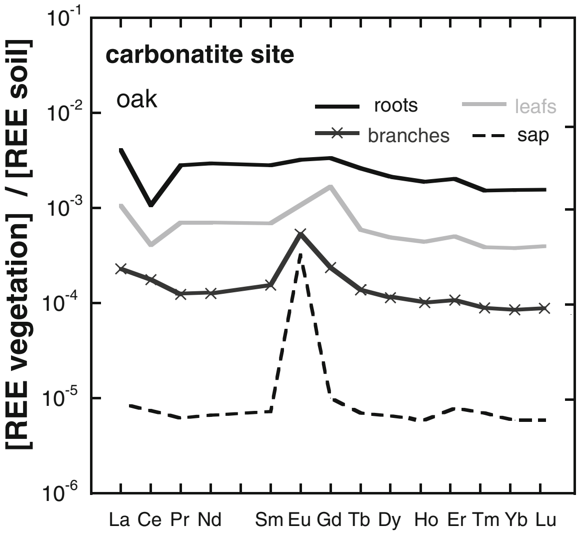

Fig. 8 REE distribution patterns of oak samples from the carbonatite site. The patterns are normalized to local soil in order to show fractionation at the plant/soil interface. The patterns represent average values, the number of samples is 2 for branches, leaves, and sap, and 1 for roots

Discussion

REE transfer from bedrock to soil

For the limestone site, the average soil/bedrock transfer factors were about 2 for most REE except for Eu with values of about 50. This REE enrichment of the soils is probably due to volume loss by decarbonatation during soil formation, which concentrates REE-bearing mineral particles. The strong positive Eu anomaly shows that this residual soil fraction contains Eu-rich feldspar particles or clay minerals resulting from feldspar weathering.

Previous studies on REE behavior in soils based on sequential extractions and electron microscopy have shown that a simple correlation analysis of bulk soil chemical data yielded a rough estimate for the mineralogical speciation of the REE (Aubert et al. 2001; Steinmann and Stille 1997; Stille et al. 2009). The strong correlation between REE and Fe (Table 3) suggests in the present case that the REE of the limestone soils are mainly located in Fe-oxyhydroxides. The additional correlation with Al may be due to Al located in Fe-oxyhydroxides or to an additional association of the REE with clay minerals of the clay-humus complex. Such a mixed speciation of the REE in Fe-oxyhydroxides and clays is typical for REE in soils (Land et al. 1999; Laveuf and Cornu 2009; Steinmann and Stille 1997).

For the granite site the soil/bedrock transfer factors were about 1, demonstrating that soil formation on granite has, in contrast to the limestone site, not led to a REE enrichment. The correlations between REE, Fe and Mn suggest that the REE are similarly to the limestone site mainly bound to Fe-Mn-oxyhydroxides. Aubert et al. (2001) furthermore identified igneous apatite and zircon as the principal REE source in the granite bedrock of the Strengbach catchment and showed that the REE budget of the soils is mainly controlled by dissolution of primary apatite. More

Table 4 Estimated REE stock of vegetation and soil of the granite and limestone sites

	Compartment	Soil depth [m]	Mass [10^3 kg/ha]	∑ REE [mg/kg]	REE stock [g/ha]	% of total stock (Soil + vegetation)
Limestone site						
Spruce plot	soil	0.7	10.5	147	1544	99.99 %
	vegetation		0.6	0.25	0.15	0.01 %
Beech plot plateau	soil	0.3	4.6	186	856	99.95 %
	vegetation		0.4	1.1	0.44	0.05 %
Beech plot slope	soil	0.4	6.3	258	1625	99.99 %
	vegetation		0.1	1.1	0.11	0.01 %
Granite site			0.0			
Spruce plot	soil	1	7.5	47	353	100.00 %
	vegetation		0.3	0.03	0.01	0.00 %
Beech plot	soil	1	10.5	96	1008	99.99 %
	vegetation		0.5	0.26	0.13	0.01 %

recently, Stille et al. (2009) identified newly-formed rhabdophane (REE-PO_4) in the surface soils of the Strengbach catchment and suggested that rhabdophane may, together with Fe-Mn-oxyhydroxides, represent an important secondary REE carrier phase of the surface soils.

The soils of the carbonatite presented a HREE enrichment with respect to the bedrock without specific anomalies. The REE soil/bedrock transfer factors were about 0.5, which is lower than for the other sites. Large amounts of REE, and in particular LREE, have thus been removed during soil formation. However, the REE concentrations of the resulting soils were still 5 to 10 times higher than for the other sites.

The soils of all sites were enriched in HREE with respect to bedrock. The fact that this HREE enrichment was common to the 3 sites, in spite of their completely different bedrock lithology, excludes preferential alteration of specific primary REE carrier phases of the bedrock as a fractionation process. A similar HREE enrichment has been described by Öhlander et al. (1996) for soils on moraines in northern Sweden. These authors showed that the HREE are enriched during soil formation, whereas the LREE are preferentially removed. Based on sequential extractions on the same soil material, Land et al. (1999) furthermore suggested that this HREE enrichment of soil is due to preferential scavenging of the HREE during precipitation of pedogenetic Fe-oxyhydroxides. This is in agreement with our observation that the REE of the LREE-enriched soils are mainly bound to Fe-oxyhydroxides. Land et al. (1999) also showed that the REE of the adsorbed soil pool as well as the particulate load of a nearby stream were enriched in the LREE, suggesting that there is a link between preferential scavenging of HREE in soils and preferential LREE export from a labile soil REE pool to surface and subsurface runoff. In a more recent study, carried out on soils on moraines in Wyoming, Harlavan et al. (2009) found similarly a higher mobility for the LREE during pedogenesis.

REE transfer from soil to soil water

The negative Ce anomaly of soil water of the limestone site can directly be related to the association of the soil-hosted REE with Fe-oxyhydroxides because Ce occurs under oxidizing conditions not in trivalent form as the other REE, but as Ce^{4+} in Fe-oxyhydroxides (Braun et al. 1990; Henderson 1984; Koeppenkastrop and De Carlo 1992). Ce is under these conditions less soluble than the other REE resulting in negative Ce anomalies in soil water and positive anomalies in the corresponding soil. The absence of such a negative Ce anomaly in the soil waters of the granite site may be related to soil pH, which is lower than for the limestone site. The positive Eu anomaly of soil water from the beech plot may be related to REE derived from feldspar alteration products.

The soil water/soil transfer factors were lower for the carbonatite site than for the two other sites, leading to similar REE concentrations for the soil waters of the 3 sites in spite of the very different concentrations in soil and bedrock. This shows that the REE concentrations of soil water were mainly controlled by solubility and not by the REE concentrations of soil. The slight HREE enrichments of soil water with respect to soil of the granite and carbonatite sites may similarly be solubility-controlled, because the HREE form more stable complexes with organic and inorganic ligands than the LREE (Brookins 1989; Ding et al. 2006b; Sonke and Salters 2006).

REE transfer at the soil/plant interface

Origin of the REE taken up by plant roots

The highest REE concentrations occurred in the oak roots from the carbonatite site, followed by beech and spruce roots from the limestone site. The lowest concentrations in roots were those of beech and spruce from the granite site (Fig. 5).

The REE patterns of the roots primarily reproduced the patterns of local soil particles, but with a slight enrichment of the LREE. The only similarities between roots and soil water were negative Ce anomalies for the limestone and carbonatite sites, and positive Eu anomalies for the granite site. Thus, one can infer that gravitational soil water, i.e. the soil water which percolates the soils vertically driven by gravity and which is sampled by lysimeter plates, was not the main source for REE uptake by plants. On the contrary, the close similarities between root and soil REE patterns strongly suggest that soil mineral particles present in the close vicinity of the root (rhizospheric zone) were the main source of REE for plants. Very likely, the rhizospheric acidification effect caused an enhanced physico-chemical alteration of the mineral particles present in the very vicinity of the root, resulting in the solubilization of REE which are then easily taken up by roots.

This hypothesis is supported by the correlation data from the limestone site (Table 3), where positive correlations occur between REE, Fe, and Al for soils and roots, but not for gravitational soil water. However, the negative Ce anomalies of the root samples resemble soil water and hint to the involvement of an aqueous phase during the transfer of the REE from soil to roots. As hypothesized above, this aqueous phase is most probably rhizospheric water. Indeed, it is well known that plants absorb poorly soluble elements mainly through the rhizospheric soil water pool (Hopkins and Hüner 2009).

Consequently, the comparison with the REE patterns of soil and soil water indicates that plant roots absorb the REE mainly through rhizospheric soil water adsorbed on REE-bearing soil particles. Based on the correlations between REE, Fe, and Al, these soil particles are mainly Fe-oxyhydroxides and possibly clay minerals. Unfortunately, it was not technically possible to sample this adsorbed soil water pool by suction cup lysimeters because our laboratory assays had shown that REE were fractionated by ceramic cups, while Teflon cups did not allow the recovery of sufficient volumes of water.

Origin of the LREE enrichment of plant roots

The REE patterns of the roots were slightly enriched in the LREE with respect to soil. This enrichment is strongest for the limestone site, followed by the carbonatite and granite sites (Figs. 6, 7 and 8). A similar LREE enrichment of vegetation has already been reported in the literature from field studies (Fu et al. 2001; Liang et al. 2008; Stille et al. 2006; Wyttenbach et al. 1998) and from laboratory studies with soil-grown plants (Aouad et al. 2006; Ding et al. 2006c).

We concluded in the discussion on the origin of the REE taken up by plant roots that they were mainly derived from the adsorbed soil water pool of Fe-oxyhydroxide and clay particles. The correlations between REE, Fe and Al in soils and plant roots show that uptakes of these elements are strongly linked. In contrast to Al and REE, Fe is known to be essential for plant growth and development. Plants have therefore developed specific strategies and processes to absorb Fe (Berner et al. 2003; Hinsinger 1998; Neilands 1981; Reichman and Parker 2005; Robin et al. 2008). The systematic association of the REE with an essential plant nutrient suggests that the REE are absorbed circumstantially during absorption of Fe. To check this relationship in more detail REE/Fe root/soil enrichment factors were calculated according to the following formula:

$$\mathrm{REE/Fe\ enrichment}[\%] = 100 * \left\{\left[(\mathrm{REE/Fe})_{\mathrm{root}} - (\mathrm{REE/Fe})_{\mathrm{soil}}\right] / (\mathrm{REE/Fe})_{\mathrm{soil}}\right\}$$

The resulting enrichment patterns are shown in Fig. 9. In the limestone site, except for spruce 1, plant roots absorbed preferentially the LREE with respect to Fe and there is almost no enrichment for the HREE. The plants of the limestone site thus favor LREE over Fe and do not discriminate between HREE and Fe. The enrichment patterns furthermore showed negative Ce-anomalies. For the granite site, the LREE enrichment was much less pronounced or absent, but there was systematically a positive Eu anomaly. For the carbonatite site the enrichment factors were negative without variations throughout the REE group.

In the discussion on REE transfer from bedrock to soil we hypothesize that the HREE enrichment of soil is probably due to preferential scavenging of the HREE in Fe-oxyhydroxides. The REE adsorbed on these Fe-oxyhydroxides are according to the sequential extraction data from Land et al. (1999) enriched in LREE. The LREE enrichment of the REE/Fe patterns is thus in agreement with the hypothesis that plant roots absorb the REE mainly from the adsorbed Fe-oxyhydroxide pool. However, this scenario cannot explain why the LREE enrichment of the REE/Fe patterns is much stronger for the limestone site than for the granite site.

This discrepancy may be explained by solution complexation of the REE in the adsorbed soil water pool. Dissolved organic and inorganic REE complexes are more stable for the HREE than for the LREE at low REE/humic acid ratios (Ding et al. 2006b; Sonke and Salters 2006; Marsac et al. 2010). Ding et al. (2006c) have shown, for hydroponically grown soybean plants, that increasing concentrations of organic ligands in the hydroponic solution led to the progressive enrichment of the LREE in the leaves. Ding et al. (2006c) concluded from this that plant roots preferentially absorb free LREE ions rather than dissolved HREE complexes. Similarly, Fu et al. (2001) found for the roots of soil-grown plants an enrichment of the LREE with respect to the labile soil reservoir. They

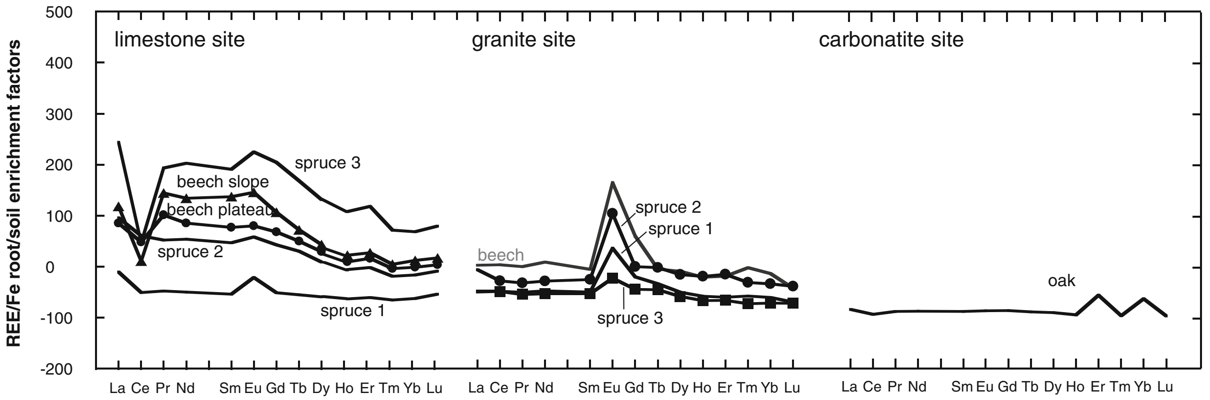

Fig. 9 Enrichment factors of REE/Fe ratios at the root/soil interface. The correlation data presented in Table 3 suggest that plant roots absorb the REE together with Fe. The REE/Fe enrichment factors shown here allow this relation with Fe to be detailed for the individual REE. Almost all roots at the limestone site absorb the LREE preferentially with respect to Fe and there is no similar enrichment for the other sites. Note the negative Ce anomalies for the limestone site and the positive Eu anomalies for the granite site. The enrichment factors were calculated according to the formula given in the text

related this enrichment, like Ding et al. (2006c), to the dominant speciation of the LREE as free ions, whereas the HREE were mainly present as dissolved complexes and therefore less absorbed. The stronger LREE enrichment of the REE/Fe patterns of the limestone site with respect to the granite site may be related to the higher soil pH of the limestone site, which leads to higher percentages of complexed HREE in the adsorbed soil water pool.

Moreover, cation transport across plant cell membranes is mediated through ion channels, carriers and pumps located in plant cell membranes (Taiz and Zeiger 2006). These membrane transport proteins usually display selectivity and are able to discriminate between different kinds of ions. Gao et al. (2003) have shown that Eu and La can be absorbed into the plant cell and bound to the inner membranes of the different organelles. Little is known about the transport proteins that can mediate REE uptake by plant cells, but we can readily hypothesize that ion channels may be involved in the passive diffusion of REE across the plasmalemma. The present results showed that plants preferentially absorb LREE. This indicates that plants may discriminate between free and complexed cations differing by diameter and charge. Further research is still needed in this field to better understand the underlying mechanisms.

In summary, we conclude that the LREE enrichment of plant roots may be related to 2 different factors: 1) The adsorbed soil water pool from where plant roots absorb the REE is enriched in LREE because pedogenic Fe-oxyhydroxides include preferentially HREE in their mineral structure. 2) The resulting LREE enrichment of plant roots is amplified by the preferential uptake of free LREE ions compared to HREE essentially present as complexed ions. Consequently, the HREE will preferentially be transferred towards the gravitational soil water pool, which could contribute to the HREE enrichment that we observed for gravitational soil water.

Specific behavior of europium during absorption by plant roots

Vegetation of the granite site is characterized by positive Eu anomalies, which are absent for most samples of the other sites. These Eu anomalies appear also in the REE/Fe enrichment factors presented in Fig. 9. Very similar positive Eu anomalies were described by Ding et al. (2006b) for soil-grown wheat. The anomaly was absent in the roots, appeared in the leaves, and was strongest in stem and grains. Ding et al. (2006b) related this Eu anomaly to precipitation of Eu-enriched phosphate particles in the different plants organs. However, phosphate precipitates with positive Eu-anomalies are not known from literature and we suggest therefore rather a link with the strong Ca depletion of the soils of the granite site where plants suffer from a marked Ca-deficit (Stille et al. 2009). Calcium and Eu have almost identical ionic radii (Shannon 1976) and previous studies have shown that

Eu can substitute Ca in plants, in particular in soils with elevated Eu/Ca ratios (Shtangeeva and Ayrault 2007; Zeng et al. 2003). The soils of the granite site have average Eu/Ca ratios of about 3.4 * 10^{-6} against 1 * 10^{-6} for the limestone site. Therefore positive Eu anomalies found in vegetation grown in the granite site by Ca deficiency may correspond to such Ca deficit. Whether or not Eu may be a Ca physiological substitute remains unknown.

Accumulation of the REE by the root system

REE concentrations are higher in small than in medium or large roots (Fig. 5). A similar preferential accumulation in small roots has been previously described by Thiry et al. (2005) for uranium. Complementary and non-exclusive mechanisms can be proposed to explain this enrichment. Absorption of mineral nutrients by plants is mainly localized in small roots (Hopkins and Hüner 2009), the higher concentrations may thus directly reflect higher nutriment fluxes. Moreover, the highest REE contents observed in small roots are consistent with the hypothesis that REE in plant tissues mainly accumulate in the primary cell wall during the early stages of cell growth (Bayer and Bayer 1991; Dong et al. 2009; Gao et al. 2003). Indeed, small roots display only primary cell walls which are thin and characteristic of young growing cells, whereas older roots have cells with thick lignin-rich secondary walls that are deposited when most cell enlargement has ended. Primary cell walls represent a larger fraction of the total root dry weight than in large roots, which may explain the higher REE concentrations of small roots. Furthermore it should be noted that most of the mass of small roots corresponds to active "living" tissues, with active growth and metabolism while large roots are mainly composed of inactive "dead" tissues.

REE transfer to the aerial plant organs

The REE concentrations of the aerial tree organs are about 10 to 100 times lower than in roots. Concentrations are similar for all field sites, in spite of the high variations observed in roots and soils. This indicates that the REE were not efficiently translocated from roots to shoots. The concentrations in the aerial organs seem to be independent of REE concentrations in soils and roots.

After absorption by the roots, trace elements may follow 2 different routes to reach the aerial plant organs: the apoplastic pathway ("through the cell wall") or the symplastic pathway ("through the cytoplasm") (Shan et al. 2003). Along the apoplastic pathway, REE moved into the cell wall by passive transport with respect to the diffusion gradient. In contrast, along the symplastic way, the transport of solutes occurred across the plasmalemma and ions entered into the cell within the cytoplasm (Hirano and Suzuki 1996; Hong et al. 2002; Klüsener et al. 1995). Both, apoplastic and symplastic routes are interrupted by the Casparian strip, which is an ion-selective cell wall located in the endoderm of the roots. Our results are in agreement with what is known about the role of the Casparian strip, which blocks or at least modulates the transfer of specific ions to the aerial parts of the plant. The large difference in REE concentrations between roots and aerial organs is very likely due to efficient filtering of the REE by the endoderm thanks to the Casparian strip. However, the REE/Fe ratios found in the aerial plant organs and sap remain similar to those observed in the roots except for Ce and Eu. This indicates that the endoderm similarly affects the REE and Fe fluxes. Furthermore, the shoot/root interface displays no systematic fractionation between LREE and HREE as for the root/soil interface.

The REE concentrations in the sap samples are strongly correlated with Fe (r=0.95, n=6), but also with other elements such as Al, Mg, K and P (r>0.9, n=6, Table 3). This demonstrates that the link observed between REE and Fe for root absorption still persists in sap. However, the new correlations with Mg, K, and P suggest that the transport of the REE and Fe in xylem sap is related to a mechanism which is common for macronutrients and trace metals. Cations taken up by plant cells form complexes with organic compounds (for instance organic acids) in which the cation becomes bound to the complex by non-covalent bonds (Taiz and Zeiger 2006). Plants are known to assimilate K and Ca, as well as micronutrients including Fe in this manner. The close link between sap concentrations of REE and mineral nutrients strongly suggests that REE form similar complexes in the xylem sap. This is in agreement with the studies of Ding et al. (2005a, 2006a) on hydroponic wheat who showed that the transport of REE in the xylem is mainly controlled by solution complexation with organic ligands. These authors furthermore found that some REE were immobilized during transport by chemical precipitation (mainly phosphate particles) and cell wall absorption.

The sap samples are also characterized by strong positive Ce and Eu anomalies (Figs. 7 and 8). Positive Ce anomalies in water samples are typical for REE transport by colloidal Fe-oxyhydroxide particles and incompatible with a transport as dissolved free ions (Steinmann and Stille 2008). So, REE in sap could also be associated to similar REE-oxyhydroxide particles. As previously said for the granite site, the positive Eu anomaly in sap could be related to the similarity of the ionic radii of Eu and Ca leading to an enrichment of Eu in sap with respect to the other REE.

The xylem is the principal route for the transport of metals from the roots to the aerial plant organs (Hopkins and Hüner 2009). For all tree species of our study we observed that the REE concentrations were lower for the trunk than for the roots or leaves, indicating that the trunk is a site of REE transfer rather than of REE accumulation. However, a more detailed look at the trunk data revealed no systematic evolution of the REE patterns, whether between individual growth rings, or with height above ground. This may be related to the fact that the REE signature of each trunk portion reflects the REE signature of sap during growth, which has been variable through time.

Leaves display higher REE concentrations than trunk samples. This is consistent with the behavior of other mineral nutrients: growing leaves are sinks for nutrients and known to accumulate them. This is also in agreement with the study of Ding et al. (2005a) who showed that REE concentrations in leafs of wheat increased with leaf age. Such effects may of course be enhanced by transpiration fluxes. As previously seen in other organs, REE contents of leaves are also correlated with Ca and Na (Shtangeeva and Ayrault 2007; Zeng et al. 2003).

Conclusions

The REE concentrations in soils are primarily controlled by pedogenetic parameters and the mineralogy of the REE carrier phases in the bedrock and in the soil rather than by the REE concentrations of the bedrock. For all the soils whatever the site enrichment in HREE was observed with respect to bedrock. In agreement with earlier studies, this fractionation can be related to preferential scavenging of the HREE by pedogenic minerals, most probably Fe-oxyhydroxides. LREE are consequently more mobile and preferentially exported by surface and subsurface runoff. This also implies that the LREE are more available for root absorption than the HREE.

The REE concentrations of gravitational soil water are similar for all sites, in spite of the strongly variable concentrations in soil. The REE content of soil water is therefore probably mainly solubility-controlled. The REE patterns of soil water are slightly enriched in the HREE with respect to soil as a consequence of the higher stability of dissolved organic and inorganic HREE complexes.

Plant roots absorb the REE from the adsorbed soil water pool rather than from gravitational soil water. The REE concentrations in roots vary with the REE contents in soil, but there was a slight enrichment of the LREE. This enrichment is probably related to the higher mobility of the LREE in soils mentioned before and amplified by the higher stability of dissolved HREE complexes in soil water. In fact, earlier studies have shown that roots preferentially absorb free ions rather than dissolved complexes. The preferential speciation of the HREE as dissolved complexes could therefore contribute to the LREE enrichment of plant roots. This is mainly the case for the limestone site.

The REE absorbed by the roots are efficiently filtered by the Casparian strip and only a small amount is transported by sap flow to the aerial plant organs. This leads to decreasing REE concentrations in the order roots > leaves/needles > trunk. Within the sap, the REE are, as in the roots, correlated with Fe, but further correlations occur with macronutrients (Mg, K, P), suggesting that the REE transport in sap is related to a mechanism which controls the general nutrient flux. The sap samples are additionally characterized by positive Ce anomalies suggesting that the REE may be associated with colloidal Fe-oxyhydroxide particles.

From the above observations it can be concluded that the transfer of the REE at the soil/root interface is not primarily controlled by the plant itself, but REE concentration and speciation in soil and the adsorbed soil water pool play significant roles. To absorb the REE, plant roots seem to use the same mechanisms as for Fe, which is an essential plant nutrient and like the

REE a poorly soluble trace metal. The detailed analysis of REE/Fe ratios shows that LREE/Fe ratios are higher in roots than in the adjacent soil, pointing to preferential absorption of the LREE. Within the xylem, the REE continue to follow the pathway of Fe, but now together with macronutrients such as Mg, K, and P. The transfer of the REE in soil-plant systems thus seems to be intimately coupled with the Fe cycle. The REE could therefore in the future, like Fe and other stable metal isotopes, be used to characterize the transport mechanisms during trace metal cycling within soil-plant systems.

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