

Plagioclase weathering by mycorrhizal plants in a Ca-depleted catchment, inferred from Nd isotope ratios and REE composition

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The neodymium isotope ratios ($^{143}\text{Nd}/^{144}\text{Nd}$) and rare earth element compositions of eight plant species in a well-studied Ca-depleted research forest (the Strengbach catchment) were measured. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios distributed between the higher ratio of apatite and the lower ratio of plagioclase. The ratio correlated well with the type of infected fungi. Ectomycorrhizae (EM)-infected plants tended to show lower isotope ratios than Ect-uninfected plants. This is supported by the REE abundance patterns: higher $^{143}\text{Nd}/^{144}\text{Nd}$ plants tend to show a more negative Eu anomaly. Based on the reported soil profile, the Nd isotope ratio of the surface soil is considered to be influenced significantly by Nd in plant litter. Combining Nd isotope and Eu anomaly data, the REE cycle in the catchment can largely be understood by mixing three endmembers of Ca-bearing plagioclase, apatite and carbonate in loess. EM-infected plants are estimated to incorporate 50–70% of Nd ultimately from plagioclase, whereas for non EM-infected plants, less than 30% of Nd is from plagioclase, perhaps indirectly from the recycled pool. Comparison of the results with reported mineral soil profiles and REE composition of acid leachates of soil indicates that plagioclase is dissolved by the symbiotic action of ectomycorrhizae, providing a direct evidence of active plant-induced weathering in a natural system. It is likely that plants dissolve plagioclase to compensate for insufficient Ca in soil.

Keywords: weathering, plagioclase, plants, Ectomycorrhizae, neodymium isotope, rare earth elements

INTRODUCTION

Chemical and mechanical weathering leads to the disaggregation of rocks and minerals and the formation of soil systems, and it allows the removal of chemical elements as well as larger and smaller particles from altered rocks and soils by rain-, pore-, ground-, and river water. Chemical weathering is the first reaction to release elements in rock to biogeochemical cycling and the determination of the rate of this process is an important issue because of its wide applicability in the various fields of geo- and environmental sciences. Many studies indicate that weathering rate increases with the presence of plants in field observations (Akagi *et al.*, 2012; Benedetti *et al.*, 1994; Derry *et al.*, 2005; Graustein, 1981; Moulton and Berner, 1998) and pot experiments (Akter and Akagi, 2005, 2006; Hinsinger *et al.*, 1993, 2001; Hinsinger and Gilkes, 1997; Rufyikiri *et al.*, 2004). Plants accelerate

the weathering rate of rocks and minerals by two principal mechanisms. The first is mechanical breakdown caused by root elongation. The other is chemical reaction associated with the physiological activity of the plants, in the form of respiration, hydration, inorganic ion nutrient ingestion, transpiration, and root exudations. All these processes are responsible for substantial changes in the rhizospheric conditions such as pH and redox conditions (Drever, 1994; Grinsted *et al.*, 1982; Haynes, 1990; Hinsinger, 1998; Jones and Darrah, 1995; Marschner, 1995; Nye, 1981; Römheld, 1986, 1991; Uren, 1981) and ultimately lead to significant dissolution of rocks and minerals. It has been reported that a mycorrhizal ecosystem plays an important role in weathering of minerals (Blum *et al.*, 2002; Koele *et al.*, 2014; Quirk *et al.*, 2012). An experiment shows that ectomycorrhizal infection influences the intake of Sr from minerals by tree seedlings using Sr isotopes as tracers (Wallander *et al.*, 2006). However, it is always somewhat vague whether the presence of plants influences weathering rate passively (resulting in physical and/or chemical condition changes to destabilize existing minerals) or actively (as a strategy to

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absorb certain nutrients), unless the elements released by mycorrhizae are shown to be *selectively* supplied to its host. For instance, mycorrhizal plants were shown to incorporate most of their calcium from apatite, and not just from soil solution with respect to Sr isotope and Ca/Sr ratios (Blum *et al.*, 2002). It is not certain yet whether plants are actively involved in weathering, because it is possible to interpret that such components are concentrated around roots. In fact it has been concluded that apatite is dissolved indirectly by acidification of soil and that mycorrhizae have a rather retarding effect on apatite dissolution (Smits *et al.*, 2014). This poses a real difficulty in understanding plant role in weathering.

This difficulty is partly due to the fact that Ca or Sr in the rhizosphere are readily soluble and highly mobile and partly due to uptake channels delegated to Ca ions from soil solution (Demidchik *et al.*, 2002). Most of the Ca is likely to be in the so-called recycle pool, to which Ca is supplied from litter by humification. The rhizospheric conditions altered by any indirect actions may eventually lead to the enhancement of ion uptake from the pool. To detect the active role of the plant-induced weathering, we require a more direct proxy than Sr.

Rare earth elements (REEs) are a group of chemically similar elements and behave coherently in the environment. REEs are not essential elements to plants and, similarly to Al, they are supposed to be rejected from the vascular system of plants during intake from a soil solution (Robards and Robb, 1974). REEs are much less mobile than alkaline elements. Therefore, REEs offer a more direct proxy of inorganic nutrient uptake. A set of REEs could be a good proxy for sources of the REEs plants take in. La/Er ratio was used as an index of mineral sources (Koele *et al.*, 2014). REEs are, however, vulnerable to fractionation during plant uptake or during transfer inside plant organs (Brioschi *et al.*, 2013; Fu *et al.*, 2001), which may degrade such a proxy for REE sources. However, the overall features of the REE patterns may be expected to be inherited from sources to plants (Fu *et al.*, 2001). In the rhizosphere condition Eu takes the same valency of 3+ as other REEs (Brookins, 1983) and a certain value of Eu anomaly in minerals can be transferred to plants; whereas Ce can have a valency of 4+ and Ce anomaly may develop in the course of plant uptake (Fu *et al.*, 2001). Therefore, Eu anomaly may be a promising proxy for sources of mineral nutrients. However, most studies reported the REE composition of plants using inductively coupled plasma mass spectrometry (ICP-MS) without separating REEs from Ba and most Eu data are erroneous due to BaO interference in the mass spectrum (Igarashi *et al.*, 2003; Stille *et al.*, 2009).

We have reported a series of cultivation experiments that showed plants do sometimes incorporate REEs from specific minerals to compensate for nutrient deficiency,

in which REEs were determined with ICP-MS following REE separation (Akagi *et al.*, 2006). Some K-bearing minerals can be sources of potassium (Dong *et al.*, 1998; Singh and Gilkes, 1991). Plants grown in a K deficient condition with a root mulch containing positive Eu anomalous muscovite themselves developed a slightly more positive Eu anomaly than that expected. Those grown in biotite with a negative Eu anomaly developed a somewhat more negative anomaly than those grown under the control conditions (Akagi *et al.*, 2006). This experiment indicated both that plants may selectively incorporate elements from K-bearing minerals. More importantly, an Eu anomaly in plants may be an indirect indicator for sources of inorganic nutrient such as K. This REE proxy can be useful in confining mineral sources in natural weathering systems, where several weatherable minerals and complicated vegetation are present.

Neodymium, a member of REEs, has a daughter nuclide (^{143}Nd) of radioactive samarium (^{147}Sm). As with the Eu anomaly, neodymium isotope ratio ($^{143}\text{Nd}/^{144}\text{Nd}$) in the environment can be employed as a faithful proxy of REEs in mineral sources. The Strengbach catchment, France, is an ideal experimental field for the study of plant-induced weathering using the Nd isotopes, since the Nd isotope signature of this catchment has been very well studied (Aubert *et al.*, 2001, 2002; Stille *et al.*, 2006; Tricca *et al.*, 1999). Since the Ca concentration in the soil is lower than 1/10 of that of common soil and the Ca/K ratio of the soil is much lower than common soil (Aubert *et al.*, 2001; Bowen, 1979), some plants are expected to take a strategy of carbon allocation to mineral-weathering mycorrhizae for maximizing growth and survivorship on a low-Ca site. In this catchment the association of higher plants in the weathering has been suggested to explain lighter REE (LREE) depletion in the stream water (Stille *et al.*, 2006). We measured the Nd isotope ratios and REE composition of some plants in the catchment with appropriate REE separation with the following objectives:

- 1) to examine whether Nd isotopes and REE abundance, especially Eu anomaly, can be used as proxies for the mineral sources of deficient nutrients in soil-plant systems, and

- 2) to find evidence to show plants *actively* participate in weathering of silicate minerals to compensate for nutrient deficiency.

MATERIAL AND METHODS

Sampling site

The Strengbach catchment, covering an 80-ha area, is located in the eastern part of the Vosges Mountains (north-east France), 58 km southwest of Strasbourg. The elevation ranges from 883 m ASL at the outlet to 1146 m ASL

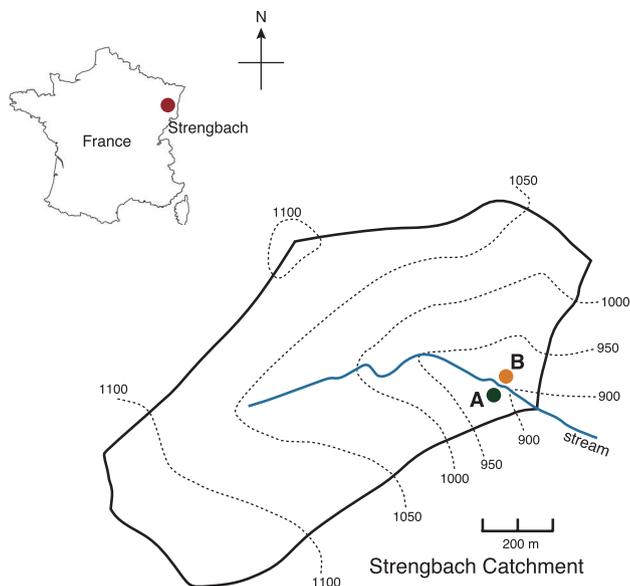


Fig. 1. Map showing the locations of sampling. A and B are sites where plants and soil samples were collected. Note that site A corresponds to site ZS in the earlier studies (Aubert *et al.*, 2001; Stille *et al.*, 2009).

at the highest point of the divide. The climate is temperate, oceanic mountainous, and a westerly wind is dominant. The monthly averages of daily mean temperatures range from -2°C to 14°C and rainfall is around 1400 mm/yr (Probst *et al.*, 1990). The mean annual stream discharge reaches 20 L/s (Probst *et al.*, 1995). The catchment is underlain by a base-poor leucogranite bedrock rich in quartz with plagioclase feldspar and mica covered by brown acid to ochreous podzolic soils about 60 to 80 cm in depth. Owing to the Ca-poor granitic bedrock, soils are depleted in Ca with the concentration typically as low as 0.05% (Aubert *et al.*, 2001) and with exchangeable Ca at a sub ppm level (Stille *et al.*, 2009). The concentration of K in the soil is about 4% (Aubert *et al.*, 2001) and relative depletion of Ca is noticeable. The pH of soil solutions ranges from 4 (surface) to 5 (at 200 cm) (Aubert *et al.*, 2001; Stille *et al.*, 2009). A small hydromorphic zone, which only represents 2% of the total catchment area (Probst *et al.*, 1990), takes up the valley bottom near the outlet. Common plants of this forested ecosystem are Norway spruce (*Picea abies* L. karst), Silver fir (*Abies alba* Mill) and Beech (*Fagus sylvatica* L.).

Samples were taken from two contrasting sites (A and B) in the catchment near to the stream in October, 2002 (Fig. 1). The two sites are selected for the contrasting thickness of O and A horizons, which are likely to act as pools of recycled elements. Site A is located in the hydromorphous area near the outlet. It is a dystic gleysol with a thick O-horizon of around 40 cm composed of or-

ganic matter, roots and quartz grains. This site corresponds to one of the well-studied sites by the French group, site ZS (Aubert *et al.*, 2001; Stille *et al.*, 2006, 2009). In contrast, site B is located at a sheer slope in the other side of the stream and composed of typical dystrochrept soil with thin O and A horizon (<10 cm).

Sampling

The sample plants from site A were fern (*Athyrium filix-femina*), moss (*Sphagnum* sp.), two grass species (*Graminaceous* genus) and spruce (*Picea abies* L. karst). From site B, the samples were stinging nettle (*Urticaceae* genus), maple (*Acer capillipes*), beech (*Fagus sylvatica* L.), and hazel (*Corylus avellana*). Foliage (approximately ten blades or leaves per species with varying sizes) of fern and herbaceous plants and trees, fresh moss (ten individuals), and pine cones (five cones) were collected in October 2002. Soil samples from O-horizon (site A) and A and B-horizons (site B) were collected from a depth of 10 cm on the same day using a plastic scoop. All samples were kept sealed in plastic bags. Mycorrhizal type was identified by microscopic observations of plant roots. The extent of infection was not measured.

Plant sample preparation

All laboratory equipment was cleaned by a sequential cleaning process using water purified using a Milli-Q (Millipore) system and acid. The acids HF, HNO₃, and HCl were of analytical reagent grade, purified by sub-boiling distillation in a silica glass or a PTFE still. Perchloric acid HClO₄ (suprapur grade, Merck) was used as received.

All plant samples were washed with distilled water using a supersonic tank and were dried at 80°C in France. The samples were again washed in the same manner and dried at 105°C for one day in the laboratory in Japan. After grinding each plant sample (several blades of fern, a few individuals of grass and nettle, a cone of pine, a few leaves of maple, beech, and hazel), about 3 g of each sample was combusted in a platinum crucible at 400°C for one hour and then at 700°C for five hours using a muffle furnace. After ashing, the residual ash was dissolved with water, HNO₃ and HF. This dissolution was performed on a hotplate at ca. 70°C overnight in a closed 15 ml polyfluoroalkoxy (PFA) vial. Excess HF and SiF₄ were removed by evaporating the sample to dryness and then 2 ml of water was added, which was again allowed to evaporate to dryness. Finally, the residue was dissolved in 3 ml of 2M HNO₃ whilst heating gently on a hotplate. The solution was cooled and kept in the PFA vial for later REE and Nd separations.

Soil sample preparation

The preparation was performed based on Fu *et al.*

Table 1. Nd isotope of plants and soil sampled in the Strengbach catchment

Sample ^{a)}	¹⁴³ Nd/ ¹⁴⁴ Nd ^{b)}	Mycorrhizal type ^{c)}	Reference
Plants			
Fern leaves (A)	0.512216 ± 4	AM?	this study
Maple leaves (B)	0.512175 ± 9	AM	this study
Moss (A)	0.512172 ± 7		this study
Grass leaves (A)	0.512164 ± 11	AM	this study
Stinging Nettle leaves (B)	0.512155 ± 17	AM	this study
Pine cone-1 (A)	0.512135 ± 8	EM	this study
Pine cone-2 (A)	0.512126 ± 22	EM	this study
Beech leaves (B)	0.512129 ± 16	EM	this study
Hazel leaves (B)	0.512111 ± 7	EM	this study
136 (bark wood; beech)	0.51212		Stille <i>et al.</i> (2006)
LP2 (leaves; beech)	0.51225		Stille <i>et al.</i> (2006)
LP19 (branch wood; beech)	0.51209		Stille <i>et al.</i> (2006)
PRH (roots wood; beech)	0.51217		Stille <i>et al.</i> (2006)
Lichen	0.51205		Stille <i>et al.</i> (2006)
Soil			
Water soluble (A)	0.512226 ± 5		this study
HCl+HNO ₃ soluble (A)	0.512185 ± 10		this study
HF soluble (A)	0.512091 ± 7		this study
Water soluble (B)	0.512240 ± 9		this study
HCl+HNO ₃ soluble (B)	0.512133 ± 9		this study
HF soluble (B)	0.512086 ± 5		this study
Soil solution (surface)	0.512185		Aubert <i>et al.</i> (2002)
Loess	0.51210		Aubert <i>et al.</i> (2002)
Apatite	0.51228		Aubert <i>et al.</i> (2001)
Plagioclase	0.51205		Aubert <i>et al.</i> (2001)

^{a)}(A) and (B) stand for the sampling sites. The two sites are located at opposite sides of the stream (Fig. 1). Site A is wetter than site B.

^{b)}Errors in the final digits are 2σ of 100 ratio measurements.

^{c)}EM: ectomycorrhizae, AM: vesicular arbuscular mycorrhizae

(2001) with a minor modification. The soil samples were dried at 80°C and sieved through a stainless mesh to obtain <2 mm sized soil particles. Approximately 5 g of soil was treated with 50 ml of water and an extract was collected by filtering using a membrane filter of pore size 0.45 μm. After drying the soil on filter paper, approx. 0.5 g soil was taken in a platinum crucible and ashed at 400°C for one hour in a muffle furnace to combust the organic matter. The ash was transferred into a PFA vial and treated successively with 10 ml of water, 6M HCl and 10M HNO₃ at a 2:1:1 ratio on a hot plate for one hour. This acid solution was separated from the residue by filtration and collected in a clean polyethylene bottle. This step was done three times and all the acid solutions were combined. After this step, the residue on the filter paper was further decomposed with 10 ml mixture of 1:1:1 10M HNO₃, 6M HF and 6M HClO₄ acids in a PFA vial. After dissolution, the solution was evaporated to dryness. Finally, the residue was again dissolved with 2M HNO₃. All the portions

were kept for further steps. All acid solutions used were purified by sub-boiling distillation. The procedural blank except sieving was negligibly small (<1%) for all REEs.

REE separation

To obtain consistent results between Nd isotope and REE composition, it is important to perform Nd and REE separation using single sample solutions. Two extraction resins, TRU.Spec and Ln.Spec, with 50–100 μm particle size obtained from Eichrom Technologies Inc., were used to separate Nd in the solutions. The Nd separation using TRU and Ln resin columns was done using the method of Pin *et al.* (Pin *et al.*, 1994; Pin and Zalduegui, 1997). REEs in the plant and soil solutions were pre-concentrated by solvent extraction using a bis[2-ethylhexyl] phosphate (HDEHP) and 2-ethylhexyl phosphate (H₂MEHP) mixture (Fu *et al.*, 2001). This is necessary to remove Ba, whose presence could seriously interfere with Eu measurement by forming BaO in inductively coupled plasma



Fig. 2. Photographs of roots of beech, pine and hazel showing EM-infection. Arrows highlight typical positions of infection. Roots of EM-uninfected maple are shown as a reference.

mass spectrometry (ICP-MS) measurements. The blank of the procedure is typically as small as 1% and at the most <5% (in the case of Beech) for all REEs except Ce (<10%) and the recovery of the separation is >99% for all REEs except La, Ce, Yb and Lu, which was as low as 90–95%.

Nd isotopic ratio and REE measurement

The Nd fraction prepared in Subsection “REE separation” was dissolved using 2 μl of 1M HNO_3 and loaded on the side filament of an outgassed Ta-Re double filament assembly. The neodymium isotopic ratio was measured by thermal ionization mass spectrometry (TIMS; MAT262, static multi-collector mode). Typically, 100 ratios were collected. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio was measured for the correction of Sm isobaric interferences on Nd. The Nd isotope ratio was normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The typical precision of 100 ratio measurements is 0.00001 in $^{143}\text{Nd}/^{144}\text{Nd}$. The accuracy of the isotope ratio measurement was checked using JNd-1 standard; the

results were within the range of the certified ratio. REEs of plant samples were determined with ICP-MS (Agilent 4300).

REE abundance patterns are shown by normalizing the concentration of each of REEs, Ln, to that of Post Archean Australian Shale composite (PAAS) (McLennan, 1989). The Eu anomaly in an REE pattern is expressed as

$$\text{Eu anomaly} = \frac{(\text{Eu})_N}{\sqrt{(\text{Sm})_N(\text{Gd})_N}}, \quad (1)$$

where $(\text{Ln})_N$ is the normalized concentration of Ln.

RESULTS

Infected fungus types and Nd isotope ratios of plants

Table 1 lists the Nd isotope ratios of the plants with mycorrhizal type sampled by us in the Strengbach catchment together with the data on beech and lichen reported

Table 2. Rare earth element compositions (ng/g) and Eu anomalies of plant sample and possible calcium sources

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Eu/Eu*
Plants															
Fern	1190	564	485	1740	373	44.7	210	16.8	65.4	9.9	25	2.3	11	1.3	0.75
Maple	116	129	20	73	15	2.8	10.4	2.6	11.2	1.9	5	0.51	2.9	0.4	1.06
Moss	334	798	143	569	207	37.5	292	39.1	200	32.8	83.8	9.5	44.5	4.9	0.72
Grass	49.6	78.2	14.5	53.4	16.2	3.2	19.1	2.5	14	2.4	6	0.7	4.3	0.6	0.86
Nettle	77.8	174	18.2	58.4	13.3	3.3	16.9	2.3	11.4	2.3	5.6	1.0	3.7	0.8	1.04
Pine	67.6	86.7	14.1	50.9	11.8	2.2	15.4	2.8	13.6	2.5	6.6	0.71	3.8	0.45	0.77
Beech	28.2	61.2	6.9	21.1	4.7	1.2	5.8	1.2	5.4	1.2	3.1	0.93	3.7	0.85	1.07
Hazel	76.1	28.3	16	51.4	9.3	2.2	13.4	1.8	9.4	1.4	3.9	0.4	0.9	0.1	0.93
Lichen ^{a)}	184	354	42	166	36	(7) ^{b)}	29	4	22	5	13	2	12	2	(1.02) ^{b)}
Sources															
Apatite ^{c)}	103.28	298.05	51.21	276.8	132.83	9.99	109.1	16.8	71.36	9.37	16.93	2.33	11.87	1.45	0.39
Plagioclase ^{c)}	7.74	17.19	2.03	7.4	1.58	0.33	1.03	0.14	0.64	0.1	0.23	0.03	0.2	0.03	1.22
Loess ^{b)}	25	52	4.67	25.2	5.07	0.82	3.24	0.57	3.44	0.73	2.21	n.d.	2.05	n.d.	0.95
Orthoclase ^{c)}	3.97	8.94	1.01	3.71	0.83	0.48	0.59	0.08	0.33	0.05	0.11	0.01	0.09	0.01	3.23
Soil solution ^{a,d)}	188.4	114.5	12.8	58	17.6	3.9	19.8	3.6	19	3.2	8.7	1.7	10.9	1.3	(0.98) ^{b)}

^{a)}Cited from Aubert *et al.* (2002). ^{b)}The Eu datum or Eu anomaly value may be erroneous due to BaO interference and likely to be overestimated. ^{c)}Cited from Aubert *et al.* (2001). ^{d)}0.001N HCl leachate of soil.

by Stille *et al.* (Stille *et al.*, 2006). The Nd isotope ratios of soil leachates are also summarized. The Nd isotope ratios varied significantly among plant species. They distributed between the reported ratio of apatite and estimated ratio of plagioclase in this catchment, typical Ca-bearing minerals (Aubert *et al.*, 2001). The isotope ratio of fern was the highest. Fern and grass were small shallow-rooted plants grown in organic-rich site A. The variation of $^{143}\text{Nd}/^{144}\text{Nd}$ in an individual plant species is not the focus of this study, but it can be as great as 0.0001 from the present study of two pine cones and from the previous study using beech (Table 1) (Stille *et al.*, 2009).

The mycorrhizal type of pine, beech and hazel is ectomycorrhizal (EM). We observed that pine, beech and hazel were actually infected with EM (Fig. 2). All of them showed lower Nd isotope ratios ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512125 \pm 0.000010$ ($n = 4$)). However, the species that were not infected with ectomycorrhizae (fern, grass, moss, nettle and maple) showed higher isotope ratios without exception ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512178 \pm 0.000023$ ($n = 5$)), close to the value of soil solution ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51218$, Aubert *et al.*, 2002) (Table 1). The mycorrhizal type of the five plants is not EM. Microscopic observations show that maple was not infected with EM (Fig. 2) and was considered to be infected with vesicular arbuscular mycorrhizae (AM). The mycorrhizal infection of the other four species (fern, grass, moss and nettle) were not checked, but grass and nettle are likely AM symbiosis; moss is non-mycorrhizal. The difference of Nd isotope ratio between plants of two types was statistically significant ($p < 0.005$), although considerable variation in Nd isotope ratio should be considered for individual plant species. The soil showed lower $^{143}\text{Nd}/^{144}\text{Nd}$ values for stronger acid treatments for both the sites, with the difference between two sites very small (Table 1). Nd isotope ratios of plants seem to depend in the first order more on mycorrhizal infection than on soil difference between two sites (Table 1).

REE composition of plant samples

The REE compositions of the plant samples studied are summarized in Table 2, together with those of apatite, loess and plagioclase (Aubert *et al.*, 2001). Figures 3a and b exhibit the shale-normalized patterns of these components. Moss and fern gave higher concentrations of REEs than the other plants (Fig. 3a). The two species displayed distinct negative Eu anomalies. The overall REE patterns of the two species show a break at Gd. Nettle and grass are low-shoot plants and their REE compositions are much lower than those of moss and fern (Fig. 3a). The patterns of nettle and moss also show some negative Eu anomalies and breaks in the REE patterns, but they are subdued. Some of the non-EM-infected plants, maple and nettle (Fig. 3a), seem to exhibit some features

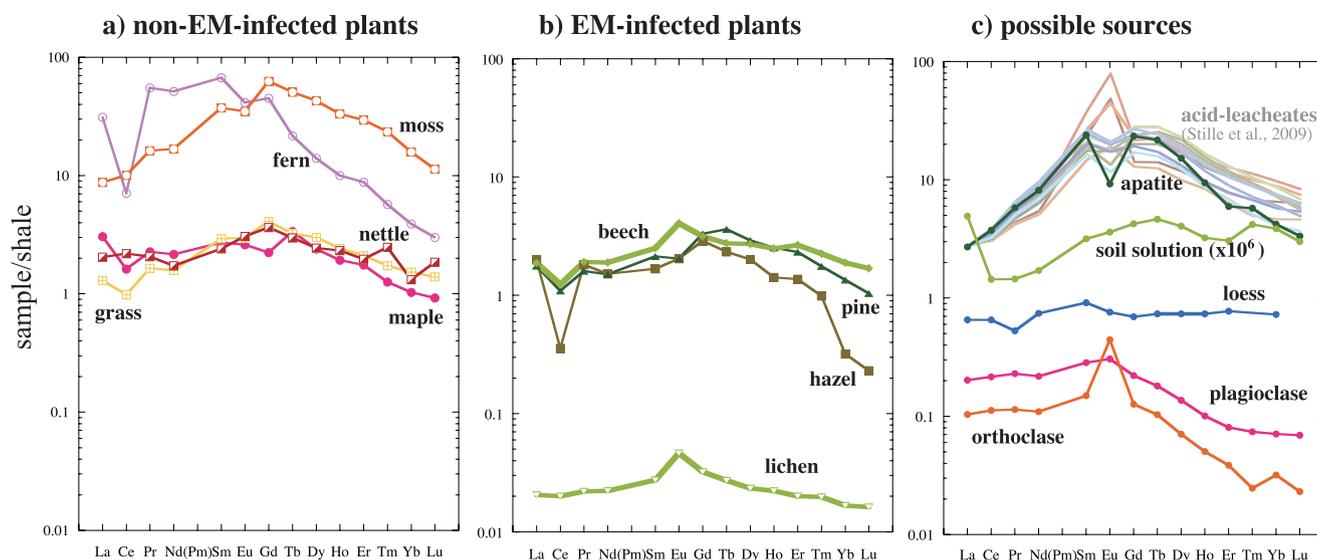


Fig. 3. PAAS-normalized REE patterns of non-EM-infected plants (a) and EM-infected plants and lichen (b), together with those of possible REE sources (c). Soil solution indicates REEs leached by 0.001 N HCl. Acid-leachates are the REEs leached from ZS soil (10 cm to 80 cm depth, brighter line for deeper soil) by 0.05 N acetic (reddish), 1N hydrochloric (greenish) and 1N nitric (bluish) acids (Stille *et al.*, 2009), and are shown in the background after normalizing La values to a certain value for easier comparison with apatite. Note that Eu data of the acid leachates might be erroneous due to BaO interference (Igarashi *et al.*, 2003; Stille *et al.*, 2009). Data of lichen and some sources are cited from previous work (Aubert *et al.*, 2001, 2002; Stille *et al.*, 2009). Normalizing values of shale is PAAS (McLennan, 1989).

seen in soil solution (Fig. 3c). Beech, pine and hazel (Fig. 3b) showed similar REE concentrations to maple, nettle and grass. Beech showed a distinct positive Eu anomaly (Fig. 3b). Negative anomalies of Ce were seen in the REE patterns of fern and hazel (Figs. 3a and b).

DISCUSSION

Consistency in mineral characteristics of soil

The results of this study are dependent on the geological setting of the sites. The geology of the catchment is rather simple with a single bedrock type with the exception of the very top (Probst *et al.*, 1990). However, the depth profiles of minerals (Aubert *et al.*, 2001) and REE composition of acid leachates (Aubert *et al.*, 2002) are reported only for a different site within the catchment. It is therefore a requirement to check the consistency of geological setting. Nd isotope ratios of water, HCl+HNO₃, and HF treatments for two soils at sites A and B were measured to examine the consistency between the two studied sites. The Nd isotope ratios for each treatment are almost identical between the two sites; the ¹⁴³Nd/¹⁴⁴Nd ratios are smaller in the order of water, HCl + HNO₃, and HF treatments (Table 1). The Nd isotope ratios of water treatment is closest to that of apatite and those of HF treatment is closest to that of plagioclase (Table 1), which is in a good agreement with reported Nd isotope ratios and weatherability of the minerals. We consider the geologi-

cal setting between the two sites is identical and also not different from that of other sites in the catchment.

Variation in Nd isotope ratio and fungal infection of plants

In this study the limited sample numbers of each plant species ($n = 1$ or 2) weaken any discussion on the taxonomical differences in REE incorporation. Here we employed a strategy of measuring both Nd isotope and REE composition in identical solutions prepared from samples to understand the consistency in REEs during their uptake.

In this study deep-rooted trees tended to give a lower Nd isotope ratio than shallow-rooted plants. The soil profile of the catchment shows that apatite with a high Nd isotope ratio is more abundant with increasing of depth, and apatite/plagioclase ratio increases accordingly (Aubert *et al.*, 2001). The mineral composition of soil is 5.4% plagioclase and 0.05% apatite at a depth of 0–20 cm and is 8.1% plagioclase and 0.43% apatite at a depth of 40–60 cm (Aubert *et al.*, 2001). If the two minerals are somehow dissolved, the amount of Nd from both the minerals were calculated about Nd-plagioclase : Nd-apatite = 3:1 (shallow) – 1:2 (deep), which corresponds to 0.51211 (shallow) – 0.51220 (deep) in ¹⁴³Nd/¹⁴⁴Nd. Based on the solubility of minerals (White and Brantley, 1995) and the abundance of minerals, the Nd isotope ratio of the soil solution can be estimated, which again shows a trend of increased Nd isotope ratio with increasing depth. The

hydrochloric acid leach of the soil profile, in fact, also shows an REE composition closer to that of apatite at deeper depth (Aubert *et al.*, 2002). Although we did not observe the mineral profiles of soil at the two sites, a relative increase of readily-weatherable apatite content with depth over less-weatherable minerals is commonly seen in soil profiles (Blum *et al.*, 2002; Smeck, 1973). Any estimation based on abiotic acid dissolution of REEs from soil accounts for the adverse trend and seems difficult to explain the observed lower Nd isotope of the deeper-rooted plants.

It was observed that EM-infected pine, beech and hazel showed lower Nd isotope ratios than AM-infected or non-mycorrhizal plants. In this study we did not sample a statistically high number of specimens for a species and therefore discussion of species difference should be avoided. However, it is considered that a specific type of ectomycorrhizae takes part in the decomposition of silicate minerals and consequently permits the subsequent intake of elements. Feldspar and hornblende are reported to be partly dissolved by organic acids of small molecular weights secreted from hyphae of ectomycorrhizae (Griffiths *et al.*, 1994; Jongmans *et al.*, 1997; Quirk *et al.*, 2012; Van Breemen *et al.*, 2000; Van Hees *et al.*, 2002) and importance of the mycorrhizal symbiosis at ecological scales has been discussed (Koele *et al.*, 2014). It is interesting that the Nd isotope ratio of plants corresponds to that leached from soils by very strong acids like HCl or HF (Table 1). Incidentally, ectomycorrhizae are reported to associate in dissolution of apatite (Blum *et al.*, 2002; Koele *et al.*, 2014), but this association can also be superficial or passive being caused by soil acidification (Smits *et al.*, 2014).

Implications of REE composition of plants on REE sources and soil environment

Fern and moss displayed negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.72\text{--}0.75$) (Fig. 3a). Apatite is a Ca & P-bearing mineral, whose REE abundance is the greatest with a negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.39$) (Fig. 3c). It is likely that the major sources of REEs in the two species may be apatite. This is supported by their highest $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (fern 0.512253, moss 0.512172). Further, a break at Gd in the overall REE patterns of the two species seems to mirror that of apatite. The REE composition of hazel seems to strongly reflect that of plagioclase (Fig. 3c), a Ca-bearing silicate, with low REE abundance. This is also supported by the low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.512111). The intake coefficients, or biological concentration factors, of an element may differ among different species. We treated the REE concentration data as just subsidiary information. Distinct negative Ce anomalies seen in most of the plants (Figs. 3a and b) may reflect a high pH and/or redox potential of soil or vessel environment (Akagi

and Masuda, 1998) and should not be taken as a proxy of source minerals. Unlike fern, moss is well known to lower the pH environment by releasing H^+ from their roots to exchange cations (Clymo, 1963), which is favorable for the disappearance of Ce anomaly (Akagi *et al.*, 2002). The variation observed consistently among REE abundance, REE pattern except Ce anomaly and Nd isotope ratio implies that REE may be a potent tool to discuss which minerals REEs in plants are sourced from.

Acid-leachates by any acid (acetic, hydrochloric and nitric acids) from soil (Stille *et al.*, 2009) always show a similar pattern resembling that of apatite except for Eu, whose data may be erroneous without proper REE separation being employed (Fig. 3c). Apatite is the most influential of minerals in the catchment with respect to REE abundance (Aubert *et al.*, 2001). It is interesting to note that plants do not show the stereotypical patterns of the acid leachates from soil: a break around middle REEs is observed in different extents (Fig. 3a), mostly much subdued compared with that seen in apatite (Fig. 3c).

Other atmospheric inputs from rainwater or sea salt particles could have as low an Nd isotope ratio as plagioclase (Aubert *et al.*, 2002). However, the dissolved concentration of REEs in rainwater is about one hundredth that of the stream water according to Tricca *et al.* (1999), implying that rainwater explains only a small proportion of REEs in the catchment. Even if chloride in the streams (Tricca *et al.*, 1999) originated entirely from sea salt, such particles explain only 1/50,000 of the Nd in the water. None of the lower $^{143}\text{Nd}/^{144}\text{Nd}$ plants displayed REE patterns similar to those of rainwater (Aubert *et al.*, 2002). We consider that an input from rainwater and sea salt particles are not influential with respect to the REE budget in the catchment. Our new identification of the source of REEs in the catchment implies the presence of a new route to supply low $^{143}\text{Nd}/^{144}\text{Nd}$ components to the catchment system.

Incidentally, a lichen sample from beech bark shows a Nd isotope ratio of 0.51205 (Stille *et al.*, 2006), which was usually taken as a value representative of the atmospheric input. This may be correct, but it is also possible that by using hyphae, the lichen takes in some of the REEs from those taken in by the beech, which shows a Nd isotope ratio as low as 0.5121 (Table 1). In fact, REE patterns of lichen (Aubert *et al.*, 2002) seem rather different from that of rain (Aubert *et al.*, 2002) or loess (Fig. 3c), but similar to that of beech (see Fig. 3b).

Nd isotope and Eu anomaly variation in the catchment

The previous section (Subsection “Implications of REE composition of plants on REE sources and soil environment”) indicates a consistent linkage between REE compositions and Nd isotope ratios, encouraging a comparison of an Eu anomaly with a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. Fig-

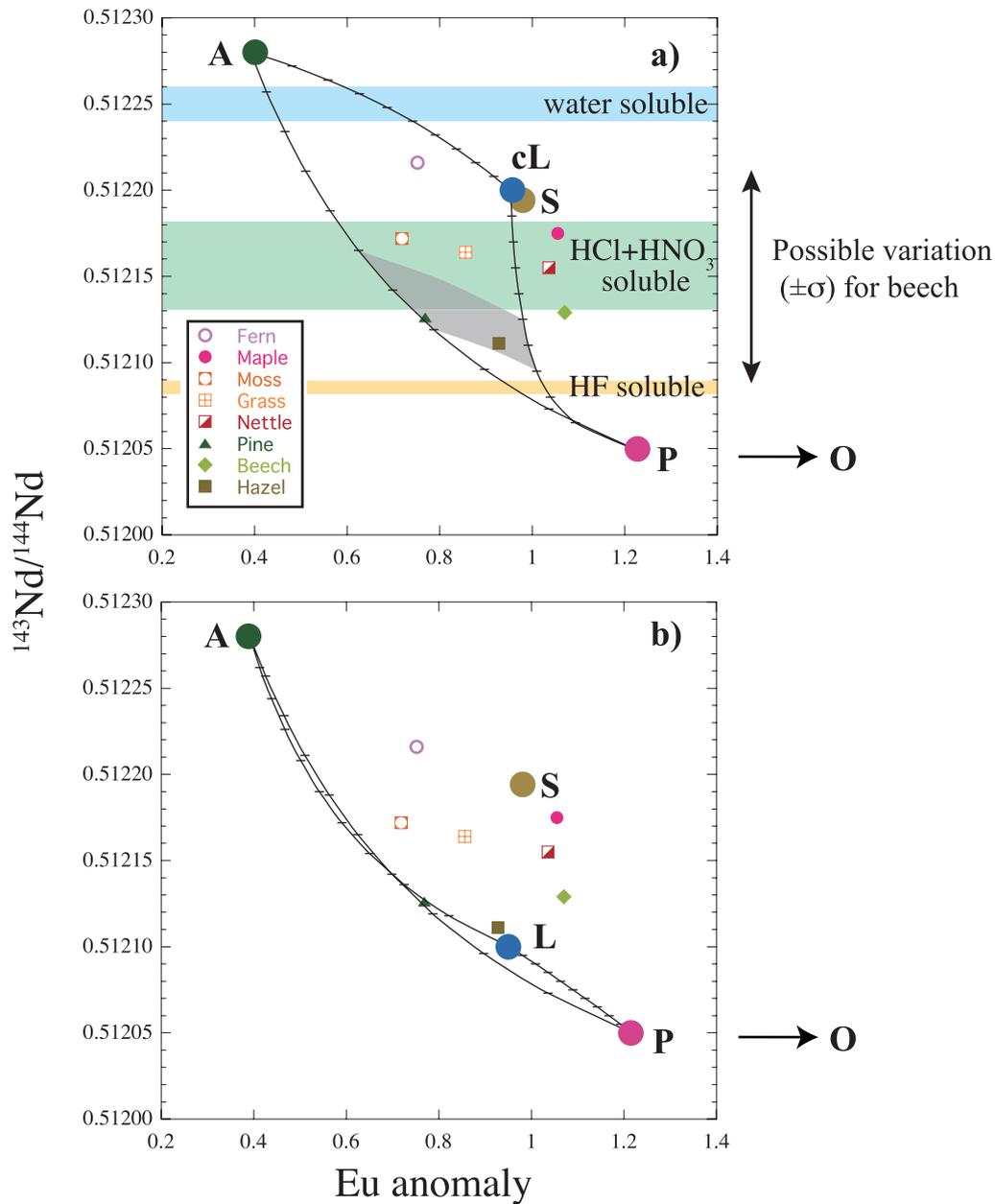


Fig. 4. Nd isotope ratio and Eu anomaly of plant samples from the Strengbach catchment. Three barbed curves are mixing lines between the two of three end members. Each barb corresponds to mixing as ten-percent units on the basis of Nd. PAAS (McLennan, 1989) are used for normalization to calculate Eu anomaly. (a) A (apatite), cL (carbonate in loess) and P (plagioclase) endmembers. The gray zone represents the mixing of 50–70% Nd of plagioclase. (b) A, L (loess) and P endmembers. The $^{143}\text{Nd}/^{144}\text{Nd}$ values and concentration data of the end members are from Aubert *et al.* (2002) and Stille *et al.* (2009). O and S are the plots for orthoclase by Aubert *et al.* (2001) and soil solution (0.001N HCl leachate) by Aubert *et al.* (2002), respectively. Note that Eu anomaly of S might be overestimated due to BaO interference (Igarashi *et al.*, 2003; Stille *et al.*, 2009) in which case its correct position would lie to the left. The three horizontal bars indicate the results of the sequential leaching of soil for both the sites (Table 1). The arrowed bar indicates the size of variation (average $\pm \sigma$) in Nd isotope ratio (this study and Stille *et al.* (2006)) for beech.

Figure 4 plots the Nd isotopes and Eu anomaly of our data for eight plants collected in the same catchment (Table 1).

The Nd-Sr isotopic system of the catchment can be

well-described by three endmembers of apatite, plagioclase and atmospheric inputs (Aubert *et al.*, 2002; Stille *et al.*, 2009). Seawater salts, rainwater and loess are candidates for atmospheric inputs (Aubert *et al.*,

2002). We considered only loess as the atmospheric input for the reason stated earlier (Subsection “Implications of REE composition of plants on REE sources and soil environment”). Loess is, however, not a homogeneous substance, but comprises a variety of minerals and its isotopic signature is not unique. Loess contains considerable amounts of carbonate minerals (Jacobson and Holmden, 2006) and we assumed that readily-weatherable carbonates in loess is considered as a supplier of REE and Ca here. The $^{143}\text{Nd}/^{144}\text{Nd}$ of carbonate in loess is systematically higher by about 0.00008 than that of loess silicate (Jacobson and Holmden, 2006). A similar size of difference was observed in $^{143}\text{Nd}/^{144}\text{Nd}$ between acetic acid leach (likely to be carbonate) and residue after HNO_3 treatment (likely to be silicate) of European Soil (Steinmann and Stille, 1997). As the end-member, we adopted $^{143}\text{Nd}/^{144}\text{Nd} = 0.5122$ (0.5121 (Aubert *et al.*, 2002) + 0.0001). Although Sm/Gd ratios differ significantly, no systematic difference is observed in Eu anomaly between carbonate and bulk of loess (Jun *et al.*, 1996) and the same Eu anomaly data as loess was adopted. The three lines in Fig. 4a are the mixing lines of apatite and plagioclase (A-P), carbonate in loess and plagioclase (cL-P), and apatite and carbonate in loess (A-cL). We have only used the plant Eu anomaly data obtained with proper REE separation in this study and have not employed the previously-reported Eu anomaly data of plant samples, which is likely to be interfered with BaO in ICP-MS measurement due to considerably high Ba contents in plant samples (Igarashi *et al.*, 2003; Stille *et al.*, 2009).

It is interesting to note that eight points of plants plot inside or just outside the region enveloped by the three mixing curves (Fig. 4a). If bulk loess is used rather than carbonate in loess (Fig. 4b), or if orthoclase is introduced instead of plagioclase (not shown), most plant sample data would not be enveloped by the mixing curves. Fern is located closest to apatite; the values of moss, and grass are near each other in the upper-middle of the envelope; those of nettle and maple are just outside the envelope and close to the mixing line of cL-P. The soil solution (0.001N HCl leach, Aubert *et al.*, 2002) is plotted near the plot of maple, although the Eu anomaly of the soil solution may be overestimated due to BaO interference. Hazel and beech lie the closest to the plagioclase position; pine nearly on the midpoint between apatite and plagioclase. The three samples just outside of the envelope are from site B. The reason is not clear due to a shortage of data and somewhat ambiguous information of plagioclase and loess, but the small influence from orthoclase weathering may be one of the reasons. The site difference seems to be unimportant (Subsection “Consistency in mineral characteristics of soil”). The three EM-infected plants are located in a zone where 50–70% of Nd are from plagioclase, whereas the non-EM-infected

plants are in a zone where less than 30% of Nd is from plagioclase. Despite this, we should recognise that we have a low number of samples for a species, so whether this is statistically valid remains to be seen. It is considered that an EM-infected plant can have a wide range of REE sources depending on the extent of the infection of individual trees. The variation in the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of beech reported by Stille *et al.* (2006) and in this study for this catchment is as large as 0.0001 (Table 1 and Fig. 4). In the case of non-EM-infected plants, the Nd of plagioclase origin is likely to be supplied indirectly from litter of EM-infected plants judged from the similarity of $^{143}\text{Nd}/^{144}\text{Nd}$ between plants and soil solution.

Our discussion indicates that plagioclase is mostly weathered by the action of vegetation in the Strengbach catchment. Orthoclase, another abundant feldspar in the catchment, has a Eu anomaly as high as 3.2 (Aubert *et al.*, 2001). If a significant proportion of REEs in plants are from orthoclase, plant data would plot far to the right from the envelope of the three end members (A-P-cL). The contribution of K-bearing orthoclase is therefore considered to be unimportant. In addition, orthoclase may be less-weatherable than plagioclase (Loughnan, 1969). There also may be physiological reasons as discussed later (Subsection “Implications for plant induced weathering”).

It is interesting to note that the surface organic-rich soil at site A (or ZS) has lower $^{143}\text{Nd}/^{144}\text{Nd}$ than the deep layer and that litter tends to represent the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51211–8) in the profiles (Stille *et al.*, 2006, 2009). This low Nd isotope ratio of the organic-rich soil contrasts with that of soil water (Aubert *et al.*, 2001). The low Nd isotope ratio of organic-rich soil has been attributed to the atmospheric origin in earlier papers (Stille *et al.*, 2006, 2009). As discussed in Subsection “Implications of REE composition of plants on REE sources and soil environment” we argue that the atmospheric input of Nd with low isotope ratio is rather unlikely. Pine cones have the lowest Nd isotope ratio observed in this study and significant amounts of cones and pine needles cover the soil surface at site A. Other than pine, the leaves of many plant species revealed a Nd isotopic ratio as low as that in soil leachate 0–10 cm ($^{143}\text{Nd}/^{144}\text{Nd} = 0.5122$, Stille *et al.*, 2009) (Table 1). It is reasonable to consider that REEs from plagioclase are transferred to the soil system via decomposition of this vegetation litter. It was reported that plants were likely to be important phases in explaining the mobility of REEs in the catchment (Stille *et al.*, 2006). The remaining silicate minerals in granite are likely to escape from plant-induced weathering, forming large grains in soil as were observed (Aubert *et al.*, 2001).

Implications for plant induced weathering

In Strengbach catchment, apatite and carbonate are two of the most readily weatherable minerals; plagioclase is

one of the most weatherable silicate minerals (Loughnan, 1969). Therefore, it may be natural that REEs in plants are sourced from those three minerals. Unlike apatite and carbonate, however, to release REE from plagioclase at a laboratory time scale, a fairly caustic condition such as that by HCl, HNO₃, HF acid solutions was needed (Table 1). However, there are three observational facts, which favor for the *active* contribution of plants. 1) Lower Nd isotopes for deeper-rooted plants are incompatible with the increase in content of the low-Nd-isotopic apatite with increasing depth (Aubert *et al.*, 2001) and with depth profiles of HCl leachate of soil (Stille *et al.*, 2006). They are hard to explain without selective uptake of Nd in plagioclase. 2) Acid leachates of soil with different acidities only exhibited the stereotypical patterns of apatite at any soil depths (Stille *et al.*, 2009) (Fig. 3c) and fail to capture the variation seen in plants (Fig. 3a). 3) The plant Nd isotopes are observed to correlate with mycorrhizal types. All three observations lead to the idea that low-isotope-ratio Nd in plants originates from plagioclase through a physiologically-selective process.

In the Strengbach catchment where Ca-bearing apatite is at sub-percent level and Ca concentration in soil is much smaller than that of K (Aubert *et al.*, 2001), vegetation may seek other Ca sources. This may explain the physiological motivation of plant-induced weathering of plagioclase. Compared with Ca-bearing plagioclase, which is one of the most readily-weatherable minerals, K-feldspar is less weatherable (Loughnan, 1969). These explain why K-bearing orthoclase should not be an influential source of REEs in the catchment as shown in the previous section (Subsection “Nd isotope and Eu anomaly variation in the catchment”). It is interesting to note that biotite, which is more weatherable than plagioclase, in this catchment has a high REE concentration with a negative Eu anomaly as strong as 0.096 (Aubert *et al.*, 2001). It is likely that K-bearing biotite seems to exert only a minor influence in the REE in plants, judged from the size of negative Eu anomaly of REEs. This may be explained by the lack of physiological motivation in weathering of non-Ca bearing biotite.

Plants have evolved different mechanisms to take in ions mainly depending upon valences, thereby blocking the passage of toxic trivalent metal ions like Al into the cells. The toxicity of trivalent ions is alleviated by coexistence of silicate (Cocker *et al.*, 1998). Trivalent ions have much greater constants of complex formation with silicic ions (Akagi, 2013; Thakur *et al.*, 2007). Consequently, trivalent ions are often taken in by plants in the form of less toxic silicic complexes in close proximity to silicate minerals. This may explain why REE patterns of plants rather faithfully reflect those of silicate minerals, from which REEs are sourced.

Divalent Sr can, however, be absorbed, most probably

via ion channels (Demidchik *et al.*, 2002), from aqueous media. Considering the above-mentioned physiological background and the fact that two of the three Ca sources in the present case (apatite and carbonate in loess) are not silicate minerals, the strong linkage between REE and Si seen in this study is interesting. REEs in plants were reported not to be directly inherited from bedrocks, but pedogenetic processes could be important to determine the transfer of REEs from soil to plants (Brioschi *et al.*, 2013). However, the present study indicates a somewhat stronger linkage between REEs in plants and REEs in minerals. One of the most important aqueous media in soil to vegetation is likely to be soil solution, whose Si concentration is as high as 10² ppm (3 mmol) (Beckwith and Reeve, 1963; McKeague and Cline, 1963). Our tentative calculation indicates that at pH 5 and [Si] = 3 × 10⁻³ mol more than 60% of LREEs to 90% of HREEs are complexed with silicic ion (OSi(OH)₃⁻). It is our hypothesis that most REEs in soil solution are in a state of silica-complex and therefore like Ca, are not readily blocked by plants. Sr isotope and Ca/Sr ratios have been used to discern Ca of apatite origin from Ca of soil solution origin in plants (Blum *et al.*, 2002). As REEs are much less soluble than Ca and Sr in soil solution, closer proximity of roots to silicate minerals would seem to be necessary to explain the observed linkage between REEs and Ca.

Incidentally, this study does not necessarily indicate the importance of direct uptake of elements from minerals in the plant community in this catchment. The importance of direct uptake of elements in the community depends not only on the input rate, but also on the residence time of elements in the recycled pool. The residence time of calcium in the recycled pool is likely to be longer by several times than that of REEs, which accordingly reduces the importance of direct mineral uptake. The reason is the smaller range of isotope variation of ⁸⁷Sr/⁸⁶Sr in plants (mostly 0.725–0.730), which corresponds to only one fifth of the variation of endmembers (from 0.716 to 0.745) (Stille *et al.*, 2006), implying that Sr is much well mixed in the catchment.

CONCLUSION

In the Ca-depleted Strengbach Catchment, the REE sources in plants could be understood by three Ca-bearing minerals: apatite, carbonate in loess and plagioclase. The ectomycorrhizae (EM)-infected plants showed a distinctively lower Nd isotope ratio than the non-EM-infected plants ($p < 0.005$). This cannot be explained by soil profiles of minerals (Aubert *et al.*, 2001). From combined consideration of Nd isotopes and Eu anomaly, it was estimated that 50–70% of Nd in EM-infected plants and less than 30% of Nd in non-EM-infected plants are sourced ultimately from plagioclase. K-bearing

orthoclase, another abundant feldspar in this site, is not an important supplier of REEs in the Ca-depleted catchment.

Soil solution in the Strengbach catchment contains elements only from easily weathered minerals like apatite and carbonate in loess, and in addition, elements in litter, and the REEs in non-EM-infected plants show $^{143}\text{Nd}/^{144}\text{Nd}$ similar to that of soil solution and are likely to *passively* reflect the composition of such easily soluble matter, while the action of EM-infected vegetation upon more resistant minerals like plagioclase *actively* takes in and eventually releases elements into the catchment system. This action by plants should help the growth of EM-infected plants when the recycled pool contains only limited amount of calcium. The results could be one of the most straightforward evidences of plant-induced weathering in a natural system.

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