

The impact of vegetation on fractionation of rare earth elements (REE) during water–rock interaction

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Abstract

Previous studies on waters of a streamlet in the Vosges mountains (eastern France) have shown that Sr and rare earth elements (REE) principally originate from apatite dissolution during weathering. However, stream water REE patterns normalized to apatite are still depleted in light REE (LREE, La–Sm) pointing to the presence of an additional LREE depleting process. Speciation calculations indicate that complexation cannot explain this additional LREE depletion. In contrast, vegetation samples are strongly enriched in LREE compared to water and their Sr and Nd isotopic compositions are comparable with those of apatite and waters. Thus, the preferential LREE uptake by the plants at the root–water–soil (apatite) interface might lead to an additional LREE depletion of the waters in the forested catchment. Mass balance calculations indicate that the yearly LREE uptake by vegetation is comparable with the LREE export by the streamlet and, therefore, might be an important factor controlling the LREE depletion in river waters.

Keywords: Rare earth elements; Fractionation; Vegetation; River water; Speciation; Water–rock interaction

1. Introduction

The fractionation of the rare earth elements (REE) in river water, as well as the immobilization of REE in the river sediment, between dissolved and particulate load can be extensive and is strongly controlled by weathering reactions, surface adsorption and solution chemistry. The REE react quickly to form complexes and

from the literature it is known that competition between the complexes and free ions as well as colloidal particles (adsorption to surface sites) may strongly fractionate the relative lanthanide concentrations (Byrne and Sholkovitz, 1996). Besides weathering and solution–surface chemistry, other factors like vegetation have never been considered to be of importance for the REE fractionation of river water although some plants are known to accumulate REE under natural conditions (e.g. Ozaki and Enomoto, 2001). The aim of the present study is to determine how far vegetation can fractionate the relative lanthanide concentrations in natural surface waters. To do this, the small Strengbach stream in the

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Vosges mountains (France) has been chosen, because the isotopic and REE characteristics of its catchment have already been previously extensively studied (Amiotte-Suchet et al., 1999; Riotte and Chabaux, 1999; Tricca et al., 1999; Probst et al., 2000; Aubert et al., 2001).

The forested Strengbach catchment covering an 80 ha area is located on the eastern part of the Vosges mountains at altitudes ranging from 883 at the outlet to 1146 meters a.s.l. at the top. The bedrock of the catchment is a base-poor, hercynian leucogranite. The average annual stream discharge is about $680\,000\text{ m}^3\text{ year}^{-1}$. After leaving the catchment, the Strengbach stream flows over a distance of about 10 km down to the Rhine valley and incorporates other streamlets from other catchments with different basement lithologies.

The sampling and the REE concentrations and Sr, Nd isotopic compositions of waters, suspended loads and soils are given in previous papers (Aubert et al., 2001; Tricca et al., 1999). The tree samples (mainly

beech) have been collected in summer (May–September) in the Strengbach catchment (Fig. 1). After drying, the samples were powdered and digested in $\text{HNO}_3\text{--H}_2\text{O}_2$. The REE concentrations of beech samples (Table 1) were measured by inductively coupled plasma–mass spectrometry (ICP–MS, VG PlasmaQuad PQ2+) and Sr and Nd isotopic analysis were performed on a fully automatic VG Sector thermal ionization mass spectrometer with a 5-cup multicollector (Aubert et al., 2001).

The speciation calculations for the dissolved load REE (filtered waters $<0.45\ \mu\text{m}$) have been done using the CHEAQS code (Janssen and Verweij, 2003) and saturation index have been calculated with AQUA-CHEM (www.waterloohydrogeologic.com).

2. Results and discussion

In a previous study, it has been shown that the Strengbach waters close to their source in the catchment

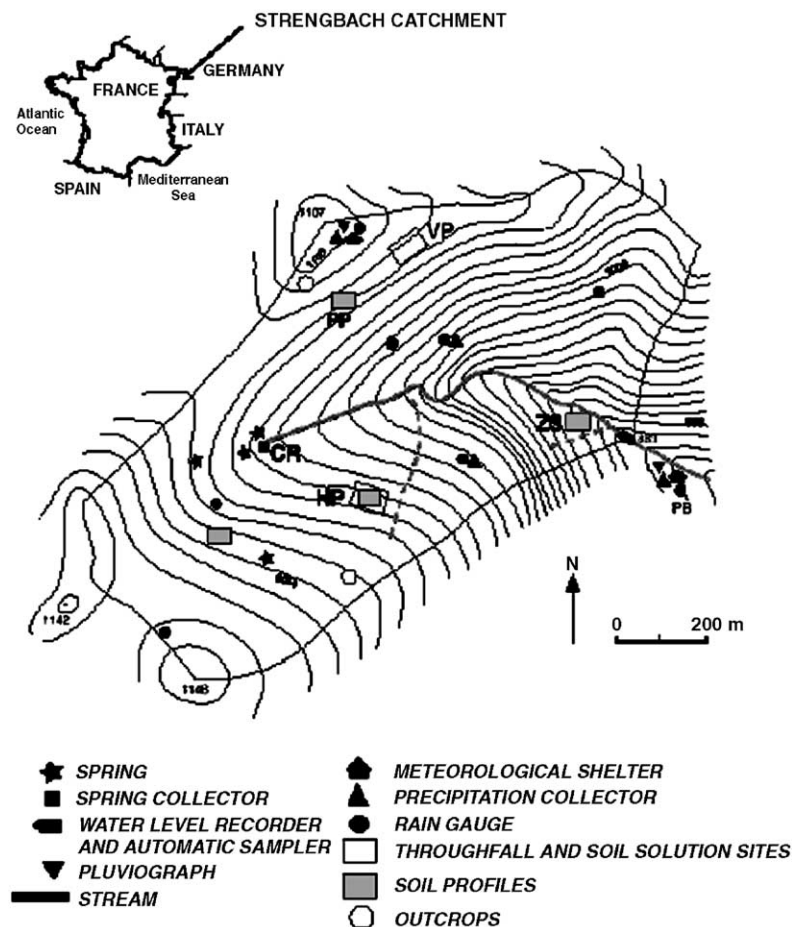


Fig. 1. Map of the Strengbach catchment.

Table 1
Rare earth elements concentrations in beech ($\mu\text{g kg}^{-1}$)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	SREE
3 leaves	64.7	62.1	6.9	24.9	4.1	2.7	4.6	0.7	3.3	0.6	1.6	0.2	1.1	0.3	177.8
Bark	25.7	37.9	4.5	18.4	3.7	17.4	3.9	0.5	1.9	0.5	1.7	0.3	0.8	0.3	117.5
Branch	50.9	62.0	7.4	26.9	5.3	11.9	6.6	0.7	3.4	0.6	1.5	0.3	1.3	0.2	179.3
Bark (not washed)	75.1	163.3	19.4	70.3	14.5	5.0	13.5	1.8	8.0	1.6	4.1	0.5	2.9	0.4	380.4
Small root (LP25; 1 mm)	190.2	411.4	49.1	181.8	39.7	15.8	39.4	5.4	24.7	4.5	11.0	1.5	8.4	1.4	984.3
Small root (PR; 1 mm)	985.8	2038.9	244.6	877.7	172.9	33.0	160.0	18.9	82.4	13.7	39.0	4.6	30.6	4.5	4706.6
Large root (5–8 mm)	26.0	54.1	6.1	23.3	5.3	8.4	5.5	0.7	3.4	136.0	0.2	1.1	0.2	1.2	0.6
Root (intermediary)	279.2	603.0	69.4	248.2	48.7	12.8	48.0	6.1	27.7	4.7	12.4	1.7	11.5	1.6	1375.1

have Sr and Nd isotopic compositions very similar to the values of primary apatite from the granitic basement rock and the overlying soils (Aubert et al., 2001). However, apatite normalization of the Strengbach waters points to an additional depletion in LREE after the process of apatite dissolution in the soil. What is the reason of this strong LREE depletion?

2.1. Lanthanide complexation in the Strengbach waters

During its travel down to the Rhine valley, the Strengbach crosses different lithologies and mixes up with smaller affluents from other catchment basins. As a consequence, pH and the major element composition of stream water evolve from upstream to downstream and also the solution chemistry of the REE. However, our data indicate that there is no direct link between the evolution of the calculated speciation of the REE and the observed REE fractionation.

The saturation shows that all Strengbach water samples from the source to the confluence with the plain rivers are undersaturated with respect to mineral phases such as Fe–Mn oxides that could, in form of newly formed minerals or colloidal particles, potentially re-

move REE from solution or fractionate the dissolved REE patterns. In summary, the LREE depletion of stream water seems in the present case not to be primarily controlled by solution chemistry, coprecipitation with newly formed minerals or colloidal phases.

The Sr and Nd isotopic compositions of the leachates (adsorbed) of the suspended load samples and bottom sediments are similar to those of the waters. However, compared with water they are slightly LREE enriched. Thus, adsorption suspended particles might to some extent be responsible for the LREE depletion in the waters, but both pools, leachates and dissolved loads remain LREE depleted with respect to their source (apatite).

2.2. REE fractionation in waters due to preferential LREE uptake of plants

The Sr and Nd isotopic composition data of the Strengbach waters from the catchment are compared with root samples and a wood–bark mixture of a beech. The plant's Sr and Nd isotopic compositions are close to those of apatite but very different from those of the other granite and soil bearing minerals analyzed previ-

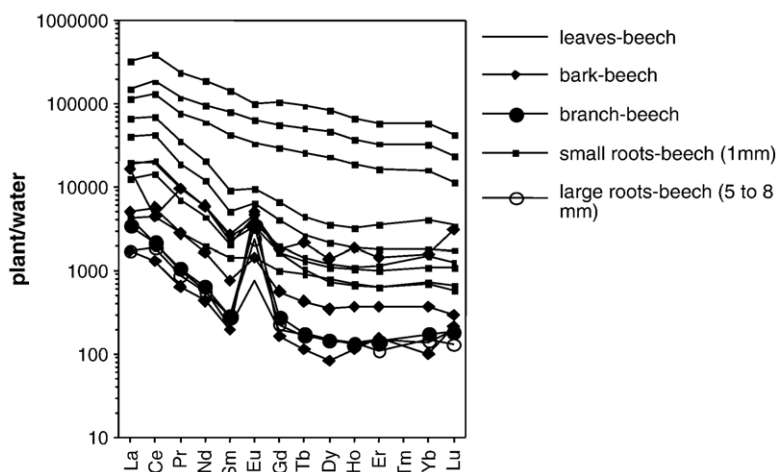


Fig. 2. Water (Strengbach)-normalized REE distribution patterns of beech samples.

ously (Aubert et al., 2001). It appears that the plants have taken up Sr and Nd from the circulating catchment waters. We therefore normalized the REE concentration data of the trees to those of the Strengbach water (Fig. 2). The trees are strongly REE enriched. Most enriched (up to 100 000 times the stream water) are the very small roots (1 to 2 mm in diameter). Larger roots are up to 1000 times enriched. Wood and bark of branches and trunks show lower REE concentrations however much stronger *Eu** anomalies. Striking is the LREE enrichment (compared with water) with highest La_N/Yb_N ratios in some of the wood, bark and leaf samples (5–30). The leachable reservoir in the soil representing REE, which precipitated from circulating waters and became adsorbed on mineral surfaces and edges, might be another important nutritive source for the plants. Isotopically the roots and the leachable reservoir in the soil are very similar. Compared to soil leachates the plants are less fractionated but still LREE enriched with La_N/Yb_N ratios ranging between 2 and 10. The REE distribution patterns of plants normalized to apatite, the most important REE source for plants and waters point to even smaller LREE enrichments. Leaf and wood have most fractionated La_N/Yb_N (<7). The very small roots show low La_N/Yb_N (<1.6) and very small *Eu* anomalies. Thus, the apatite-normalized REE distribution patterns of the very small roots are least fractionated and emphasize together with the Nd and Sr isotope data the idea that most of the REE in the plants of the Strengbach catchment originate from apatite dissolution.

Balance calculations clearly indicate that the LREE uptake by the vegetation from the water of the soil system during a year is comparable with the LREE export by the streamlet. However, the HREE discharge by the Strengbach stream is always more important than the uptake by plants. The results imply that at least at a local scale LREE uptake by

the vegetation was of importance leading to a fractionation and additional LREE depletion in the waters.

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