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Controls on transport and fractionation of the rare earth elements in stream water of a mixed basaltic–granitic catchment basin (Massif Central, France)

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ABSTRACT

We present rare earth element (REE) patterns of small streams from a catchment basin in the Massif Central (France) in order to characterize the individual fractionation stages for the dissolved REE from the source to the catchment outlet. The upper part of the catchment is located on a basalt plateau, followed downstream by deep and narrow valleys within granitic and orthogneissic bedrock. Basalt-normalized 0.45 μm filtered stream water has REE patterns slightly depleted in the light REE (La–Sm, LREE) on the basalt plateau close to the source, followed by a continuous amplification of this LREE depletion downstream. At the same time also a negative Ce anomaly develops in the adsorbed fraction of >0.45 μm particles, which has been isolated by leaching with 1 M HCl. Strontium and Neodymium isotope ratios of stream water demonstrate that the dissolved REE are essentially of basaltic origin, even in the lower, granitic and gneissic part of the catchment. Mixing with gneiss or granite derived REE thus cannot explain the observed evolution of the REE patterns.

Our data suggest that the REE of the <0.45 μm fraction are associated to Fe colloids, which grow during transport downstream to Fe oxyhydroxide particles exceeding 0.45 μm in size. Precipitation of these oxyhydroxide particles leads to selective removal of LREE from 0.45 μm filtered stream water, and of Ce adsorbed on >0.45 μm particles. In contrast to earlier studies, we found no link between REE behavior and organic colloids or organic complexes. This scenario is confirmed by a detailed analysis of the REE patterns at 3 stream confluences. The results show that the REE do not behave conservatively during mixing at stream confluences, but that the LREE and Ce are preferentially removed similarly to what has been observed at catchment scale. Our study thus underlines the importance of Fe colloids for the transport and fractionation of the REE in stream water.

1. Introduction

The rare earth element concentrations in river water, river suspensions and in marine fine grained detrital sediments are extensively used to trace the erosional history of continents and to establish erosion budgets (Goldstein et al., 1984; Goldstein and Jacobsen, 1987, 1988a,b; Allègre et al., 1996; Gaillardet et al., 1997). Several studies have dealt with the evolution of dissolved rare earth elements (REE) in streams from large scale catchment basins and shown that there is no direct link between the REE distribution patterns of the dissolved load and bedrock (e.g. Dupré et al., 1996; Gaillardet et al., 1997; Sholkovitz et al., 1999). Other studies however indicate that REE distribution patterns and Eu anomalies of stream water in small catchment basins might be strongly lithology dependent (Tricca et al., 1999). Preferential dissolution of REE minerals during weathering, variable complex stabilities for the individual REE, and preferential removal of certain REE from solution by colloids and newly formed minerals are the most cited processes to explain the behavior of REE in aqueous solutions (e.g. Öhlander et al., 1996; Tricca et al., 1999; Dia et al., 2000; Ingri et al., 2000; Andersson et al., 2001; Aubert et al., 2001; Hannigan and Sholkovitz, 2001; Stille et al., 2003; Gruau et al., 2004). More recently, it has been shown that vegetation might be another important factor controlling REE fractionation and especially LREE depletion in river water (Stille et al., 2006).

The aim of the present study is to characterize in detail REE transport and fractionation processes within a small catchment situated on a mixed basaltic–granitic–orthogneissic bedrock. This catchment basin has been chosen because the contrasting lithologies allow to trace basalt derived REE from the source area downstream, and to quantify the exchange of stream water with the different bedrock lithologies using Sr and Nd isotopes.

2. Setting and methods

2.1. Regional setting

The catchment basin is located in the southern part of the French “Massif Central” (Fig. 1). The basin is underlain by Quaternary basalts

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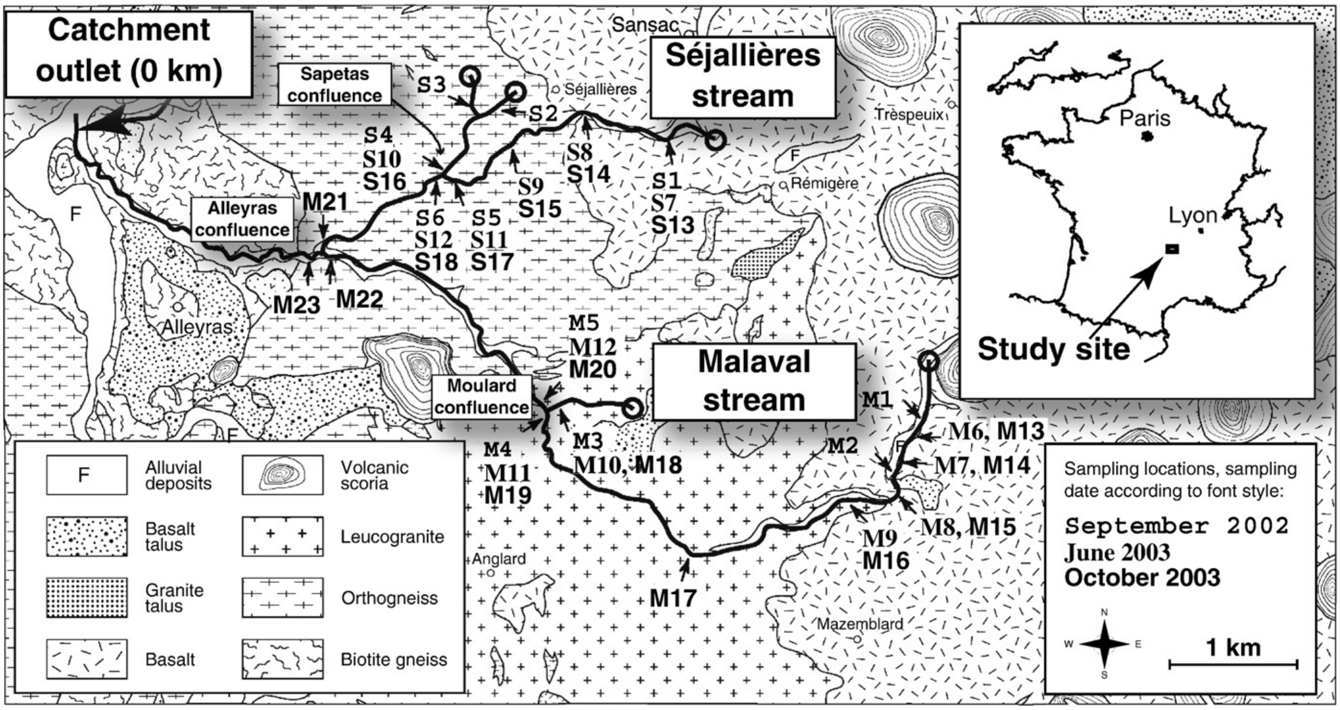

Fig. 1. Geographic location and simplified geological map of the study site according to Bouiller et al. (1978) with the sampling sites of the Séjallières and Malaval streams. The altitude of the basaltic plateau to the east is about 1200–1300 m, the outlet of the catchment basin of both streams into the main river named "Allier" to the west is located at 714 m.

in its upper part to the east and by Hercynian granites and orthogneisses in its lower part to the west. The catchment covers an area of about 68 km^2 at altitudes ranging from 1301 m on the basalt plateau to the east down to 714 m at its outlet to the Allier river to the west. The low inclination of the basalt plateau favors the formation of well developed soil profiles and swampy areas. In contrast, the slopes in the granitic and orthogneissic terrains to the west are steep, the soils are poorly developed and covered by forest. The climate is temperate oceanic mountainous with dominating west winds. The mean annual precipitation is about 800 mm and the annual mean temperature 10 °C. The basalt plateau is mainly covered by pastures and conifer forests (mainly spruce and pine), whereas mixed deciduous (beech, oak) — conifer forests and only little pasture areas occupy the steep slopes to the west.

2.2. Field sampling and analytical methods

Field sampling was realized in 3 campaigns in September 2002, June 2003, and October 2003 during dry periods with low stream discharge. The sampling order was from upstream to downstream, the stream Séjallières was sampled in 1 day and the stream Malaval in 2 days. The location of the sampling points is given in Table 1 as the upstream distance from the catchment outlet in kilometers, which is common for both streams (Fig. 1). This labeling has been chosen in order to plot the data of both streams together with a common kilometer scale. Table 1 gives furthermore the bedrock lithology for each stream water sampling point.

Sample aliquots for trace elements, REE and Nd–Sr isotope analysis were filtered on site using 0.45 μm Sartorius cellulose acetate filters of 47 mm diameter and a Nalgene filtering unit with a manual vacuum pump. Typically, 2 L of stream water were filtered and the filters were changed up to 16 times per sample depending on the particle load. The filtered samples were immediately acidified to pH 1–2 with sub-boiled distilled HCl and stored in acid-cleaned HDPE bottles for major cation and trace element analysis. Filtered, but non-acidified aliquots were kept to determine major anions. For DOC analyses an additional filtered aliquot of 100 mL was treated in the field with 5 drops of concentrated H_3PO_4 in order to stop microbial activity and stored at −18 °C after arrival in the laboratory. Conductivity, pH and Eh were measured on site using a portable WTB MultiLine P3 device and are given in Table 1. Bicarbonate was determined in the evening of each sampling day by titration with H_2SO_4.

The major cation and anion composition of the water samples was determined at the department of Geosciences, University of Franche-Comté, Besançon (France). Ca^{2+} was measured by potentiometric titration with a TitraLab 90 apparatus from Radiometer Analytical. The cations Na^+, K^+, Mg^{2+} were analyzed with a Perkin Elmer 1100 atomic absorption spectrophotometer, and the anions F^-, Cl^-, NO_3^-, and SO_4^{2-} with a Dionex DX100 high-pressure ion chromatograph. The DOC analyses were done at the common analytical center (SERAC) of the University of Franche-Comté, Besançon (France) using a Dohrmann carbon analyzer according to the method NF EN 1484.

All trace metals including the REE were determined by ICP-AES (Jobin Yvon) and ICP-MS (Fisons VG-Plasma Quad PQ2+) at the Centre de Géochimie de la Surface at CNRS Strasbourg (France). The REE concentrations of the waters range between 0.5 and 10 ng/L for Lu and 50 to 250 ng/L for Nd and are below the detection limit of traditional quadrupole ICP-MS. Therefore, a liquid–liquid extraction technique using HDEHP as organic solvent was used to enrich the REE by a factor of at least 100 (Shabani et al., 1990; Shabani and Masuda, 1991; Tricca et al., 1999). Typically, 1 L of filtered stream water was necessary to achieve concentrations above detection limit. This sample enrichment was realized in a clean lab at the department of Geosciences in Besançon. A detailed description of the procedure and reagents used is given by Steinmann and Stille (1998). This liquid–liquid extraction removes efficiently Ba and other matrix elements from the REE fraction leading to a significant reduction of mass interferences, in particular between BaO and Eu on mass 151 (Shabani and Masuda, 1991). The total procedure blank was determined by running the complete extraction procedure with 18 MΩ ultrapure water from a Millipore Simplicity system. Only La, Ce, and Gd were present in detectable amounts in the 14 blank samples and the blank contribution to stream