



# Anomalous concentrations of rare earth elements in the moss–soil system from south-central Poland



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## ABSTRACT

Fourteen rare earth elements were determined in mosses (*Pleurozium schreberi*) and soils (subhorizon-Ofh and -Ol, mixed horizon-AE and AEB) from south-central Poland. The results were normalized against North American Shale Composite (NASC) and Post-Archean Australian Shales (PAAS). The distribution of REEs in the moss–soil system differed considerably, but all the samples showed the average percent of increase of medium rare earth elements. The shale-normalized concentration ratios calculated for selected elements ( $La_N/Yb_N$ ,  $Gd_N/Yb_N$ ,  $La_N/Sm_N$ ) were in the range of 1.22–2.43, 1.74–3.10 and 0.86–1.09. Both subhorizon-Ofh (-Ol) and horizon-AE (-AEB) showed a weak enrichment of Gd. The shale-normalized patterns of soils showed a somewhat negative Eu anomaly in the horizon-AE (-AEB), and a slightly negative Ce anomaly in the subhorizon-Ofh (-Ol). A strongly positive Eu anomaly and a somewhat negative Nd anomaly were found in the moss samples.

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## 1. Introduction

Rare earth elements (REEs) include lanthanides or lanthanoids from lanthanum ( $Z = 57$ ) to lutetium ( $Z = 71$ ) or according to IUPAC even Y ( $Z = 39$ ) and Sc ( $Z = 21$ ). These elements undergo fractionation during crystallization of minerals (e.g. monazite, bastnaesite, gadolinite) in residual magmas, pegmatites and hydrothermal deposits or during regional metamorphism of volcano-sedimentary rocks. The REEs have widely been used in cosmo-geochemistry, petrology and sedimentology for tracing geochemical processes or in environmental studies as indicators of geogenic or anthropogenic pollution sources. They can also record subtle geochemical processes in natural systems (Fu et al., 2001; Lee et al., 2003; Laveuf et al., 2008; Zhou et al., 2010).

The REEs can be divided into two groups: light rare elements (LREEs) from La to Eu and heavy rare elements (HREEs) from Gd to Lu. The former group includes elements with lower atomic numbers, larger ionic radii, higher solubility and alkalinity, whereas the HREEs encompass sparingly soluble elements with higher atomic numbers, smaller ionic radii and lower alkalinity. Lanthanides occur as trivalent ions ( $Ln^{3+}$ ), except for Ce, which can be both tri- or tetravalent and Eu which can occur as di- or trivalent ions. In

biogeochemical processes the fractionation of REEs between the LREEs and the HREEs is very often observed, as well as non-redox (Gd, Yb, Lu) and redox (Ce, Eu) sensitive anomalies. Due to very similar chemical properties, the REEs occur in the environment as geochemical associations. Some differences in chemical behavior result from the decreasing size and increasing atomic number. Thus, the REEs can undergo in-between fractionation (Wytenbach et al., 1998a; Ding et al., 2005a,b; Castor and Hedrick, 2006; El-Taher, 2010).

The REE abundance in the Earth's crust varies from 0.5 mg/kg (Tm) to 66 mg/kg (Ce) with a mean of about 215 mg/kg. The elements with an even atomic number (e.g. Ce, Nd, Sm) are more common than those with an odd atomic number (e.g. La, Pr, Eu), and this property is known as the Oddo-Harkins rule (Vernadsky, 1980). The elements with an odd atomic number have one unpaired proton, and are more likely to capture another thus increasing their atomic number, whereas the elements with an even atomic number are more stable because their protons are paired (Tyler and Olsson, 2001a,b; Zhang and Liu, 2004; Ferreira et al., 2006). To compare graphically the REE abundances in environmental samples, it is necessary to eliminate the Oddo-Harkins effect by normalizing concentrations of individual REEs in samples to those in different standards, for example: Chondrite, Post-Archean Australian Shales, North American Shale Composite, World Shale, Upper continental crust and Clay from the Russian Platform (Haskin and Haskin, 1966; De Baar, 1983; Markert et al., 1989; Pourmand et al., 2012).

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Nowadays, most studies have focused on REE concentrations in sediments, soils and vascular plants (Liang et al., 2005; Chen and Yang, 2010; Miao et al., 2011; Zhu et al., 2012). The mechanisms of assimilation and transportation of REEs in nonvascular plants is still less known. The results derived from bioindication studies suggest that lichens and mosses may accumulate higher concentrations of REEs than shrubs or coniferous trees (Chiarenzelli et al., 2001). So far, the distribution patterns and chemical behavior of REEs in different moss species have been studied by Berg and Steinnes (1997), Chiarenzelli et al. (2001), Rühling and Tyler (2004), Tyler (2004) and Prudêncio (2007).

The principal objectives of this study were as follows: (i) to present the baseline concentrations of REEs in moss species *Pleurozium schreberi* and soil samples from the organic fermentative-humic (Ofh) subhorizon and the mixed humic-eluvial (AE) horizon, (ii) to compare concentrations of these elements in the samples examined, and (iii) to normalize measured values against North American Shale Composite and Post-Archean Australian Shales in order to find anomalous REE concentrations.

## 2. Materials and methods

### 2.1. Study area and fieldwork

The city of Kielce is a capital of the Holy Cross Mountains region (south-central Poland). The southern part of the city is mostly wooded. There are two ranges extending west–east, i.e. the Postowice Range in the southern part and the Białogon Range in the west-central part (Fig. 1). The Białogon Range is located within the Kielce-Łagów synclinorium. This tectonic unit consists of Lower Devonian quartzites and quartzitic sandstones, limestones, dolomites, marls, Middle/Upper Devonian marlaceous shales, clayey and siliceous shales, and Lower Carboniferous sandstones and mudstones. The Postowice Range belongs, in turn, to the Cępczyń-Klimontów synclinorium. This geologic structure is built of Lower Cambrian, Ordovician and Silurian clayey shales, sandstones, mudstones with subordinate tuffites. The Paleozoic bedrock is covered with Pleistocene and Holocene sediments composed of tills and fluvio-glacial sands.

The biogeochemical study was carried out in May, 2011. All sampling sites were located within wooded area: sites 1–5 in the Białogon Range and sites 6–20 in the Postowice Range (Fig. 1). During the fieldwork 20 moss (*P. schreberi*) samples, 18 soil samples from the subhorizon-Ofh (sites 1–4, 6–15, 17–20), 2 soil samples from the subhorizon-OI (sites 5, 16), 16 soil samples from the mixed horizon-AE (sites 1, 6–20) and 4 soil samples from the mixed horizon-AEB (sites 2–5) were collected. The soil samples from the subhorizon-OI (organic litter) and the mixed horizon-AEB (humic-eluvial–illuvial) were collected at sites devoid of well-developed horizons-Ofh and -AE. The subhorizon-Ofh consists of organic matter (humic and fulvic acids),

clayey colloids and Fe, Mn, Al oxides and hydroxides and it varies from 1 to 10 cm in thickness overlying directly the humic (A) horizon. The humic (A) is a mineral horizon, and it contains less than 20% of organic matter and averages about 10–20 cm in thickness. The horizon-E is a mineral horizon which underlies the horizons-O or -A. These two horizons commonly occur as the mixed humic-eluvial horizon (AE), which exhibits the properties of both horizons-A and -E (Czępińska-Kamińska, 2000). In general, we collected samples down to 20 (30) cm.

Moss samples (about 25 g each) of apical green parts with no sporophyte and dead parts were collected from an area of about 10 m<sup>2</sup> each. To avoid the influence of throughfall precipitation and stemflow, moss samples were taken outside of the crown projection of trees. Alien organic matter (bark, leaves, spider's web) was removed during sample collection. The soil samples (about 1 kg each) were collected from the same sites. Each composite sample consisted of five sub-samples taken within an area of about 1 m<sup>2</sup>. The soil samples were cleaned from oversized particles ( $\phi > 2$  mm) and foreign organic matter (leaves, bark, twigs) using FRITTSCH Analysensieb Test Sieve 200 mm DIA  $\times$  50 mm ISO 3310-1  $\phi = 2$  mm. All samples were placed in polyethylene bags and dried at ambient temperature (about 18 °C) to avoid developing fungi.

All samples were collected according to the PN-EN ISO/IEC 17025 standards and guidelines of OSWER Directive 9285.7-25A, EPA 540/R-97/028, PB97-963239, biological (1997) and OSWER Directive 9360.4-10, EPA 540/R-95/141, PB96-993207, soil (1995).

### 2.2. Chemical reagents

During the digestion process Merck Millipore Poland concentrated nitric acid 65% Suprapur<sup>®</sup>, concentrated chloride acid 30% Suprapur<sup>®</sup> and hydrogen peroxide 30% Suprapur<sup>®</sup> were used. The ICP-MS was calibrated using ELAN DRC Setup/Stability/Masscal Solution (for use with ELAN DRC/DRS<sup>plus</sup>/DRC II) with ratio Matrix/Vol. 5% HNO<sub>3</sub>/1000 ml, and the following concentrations of elements: 1  $\mu$ g/l Al, Cd, Ce, Cr, Cu, In, Pb, Mg, Mn, Rh, Th; 10  $\mu$ g/l Ba. The calibration solutions (from 0.1 ppb to 100 ppb) were prepared using Perkin Elmer Pure Plus Standards for ICP-MS, Multi-Element Calibration Standard 2 with ratio Matrix/Vol. 5% HNO<sub>3</sub>/100 ml and the following concentrations of elements: 10  $\mu$ g/ml Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Yt, Y.

### 2.3. Sample preparation and analysis

Because the REEs are linked to various mineral phases, so the most crucial procedure prior to measurements by an ICP-MS method is complete digestion of samples, separation of complex matrix and elimination of interferences (Wei et al., 2001). For the purpose of this study, the moss and soil samples were prepared separately. The preparation of moss samples encompassed:

1. Triple rinsing with deionized water to remove outer contamination;
2. Drying at ambient temperature (about 25 °C);
3. Disaggregation using a MF10 basic IKA<sup>®</sup>WERKE blender for plants;
4. Digestion with nitric acid (1:1) (8 ml) and hydrogen peroxide (1 ml) in a close microwave system (Multiwave 3000).

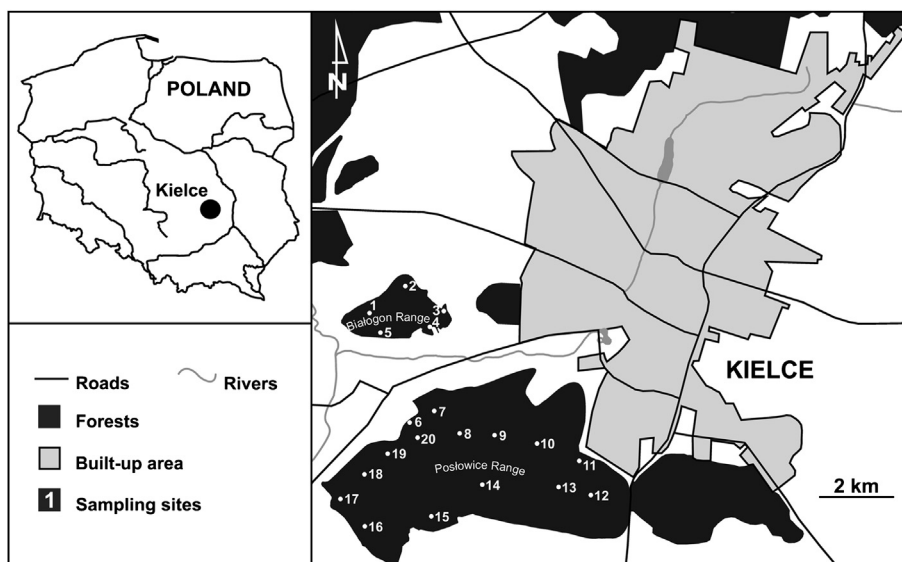


Fig. 1. Localization of investigation sites (south-central Poland).

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