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ATMOSPHERIC DEPOSITIONS OF RARE EARTH ELEMENTS IN ALBANIA STUDIED BY THE MOSS BIOMONITORING TECHNIQUE, NEUTRON ACTIVATION ANALYSIS AND **GIS** TECHNOLOGY

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INTRODUCTION

Since 1970 mosses have been regularly used in large-scale monitoring surveys, providing valuable information on the relative spatial and temporal changes of trace metal deposition in Europe (Rühiling et al. 1987; Rühiling 1994; Rühiling and Steinnes 1998; Buse et al. 2003; Frontasyeva et al. 2004; Steinnes 2008; Dam et al. 2010).

The carpet-forming moss species have not roots system, and take up nutrients and trace metals directly from atmosphere. It is the reason that made them a suitable tool for spatial and temporal monitoring of atmosphere (ICP Vegetation 2010).

The first monitoring results regarding the moss survey in Albania relate to 2010/2011, when Albania joined the European Moss Survey in the framework of the UNECE ICP Vegetation Programme (ICP Vegetation 2010). The results obtained by ICP-AES (Harmens et al. 2013) and the information on the following elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn, Al) were reported to the European Atlas (Harmens et al. 2013). The full set of the Albanian moss data (19 elements comprising also Li, Mg, P, K, Ca, Mn, Sr, Ba) was discussed and published in Qarri et al. (2013). Continuing this study, 39 elements (Na, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Sb, I, Ba, La, Ce, Nd, Sm, Eu, Tb, Gd, Tm, Yb, Hf, Ta, W, Au, Th, and U) of 64 moss samples (*Pseudoscleropodium purum* and *Hypnum cupressiforme)* collected over the whole territory of Albania were subjected to instrumental epithermal neutron activation analysis (ENAA). This paper is continuing to complete the previous study (Qarri et al. 2013; Bekteshi et al. 2015) with the rare earth elements (REE) not determined by ICP-AES.

REE in the atmosphere-soil interface are of importance because they have similar and conservative behavior and are scarcely derived from anthropogenic sources (Dominique et al. 2006). The REE group comprises 17 elements: 15 elements from lanthanides from lanthanum La ($Z = 57$) to lutetium Lu ($Z = 71$), yttrium Y ($Z = 39$) and scandium Sc ($Z = 21$) (Veronica et al. 2014). Due to their similar ionic radii and electron configuration (Taher 2006), these elements have very similar chemical characteristics. In general, REE are separated into two different groups: light lanthanides (La–Eu) and heavy lanthanides (Gd–Lu). Scandium has similar properties with La–Eu group of elements and is classified in the same group of light lanthanides. This classification is done basing on the electron configuration of these elements, which determines how they interact with other elements and compounds (Veronica et al. 2014). It is also based on the solubility of inorganic salts of REE. Light lanthanides are considered more soluble than the heavy ones (Sneller et al. 2000), but there is no worldwide accepted final definition regarding the elements of lanthanides that belongs to each group. The total REE content in soil surface is up to 100–200 $mg \cdot kg^{-1}$ (Liang et al. 2005; Tyler 2004). Higher contents are caused by human activity, low mobility of REE and their high adsorption to soils (Li et al. 2013; Cao et al. 2000). The use of the REE-rich phosphates fertilizers (Hu et al. 1998; Martin and McCulloch 1999; Volokh et al. 1990) is an important factor that causes the enrichment of REE in soil.

In this study, we have attempted to determine the content levels, distribution patterns and geochemical anomalies of REE accumulated in moss samples from Albania.

There are a number of objectives: i) to determine the levels of REE in mosses collected over the whole territory of Albania, ii) to compare those to the neighboring countries, iii) to obtain information on the spatial distribution of these elements in mosses in the form of GIS maps, iv) to compare those with the general pattern of reference values that are Upper Continental Crust (UCC) (Rudnick and Gao 2003), North American Shale Composite

(NASC) (Gromet et al. 1984), Average Post-Archaean Australian Shale (PAAS) (Taylor and McLennan 1985), since we have normalized the REE data with chondrite (Taylor and McLennan 1985), v) to investigate the geochemical origin of REE caused in Albania.

1. EXPERIMENTAL

1.1. Study Area and Sampling. The Republic of Albania (aprox. 28,000 km^2) is located in the south-eastern part of Europe and in the western part of the Balkan Peninsula. The first study of atmospheric deposition in Albania was performed in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation 2010) by using moss biomonitoring and ICP-AES analysis for 20 elements (Qarri et al. 2013).

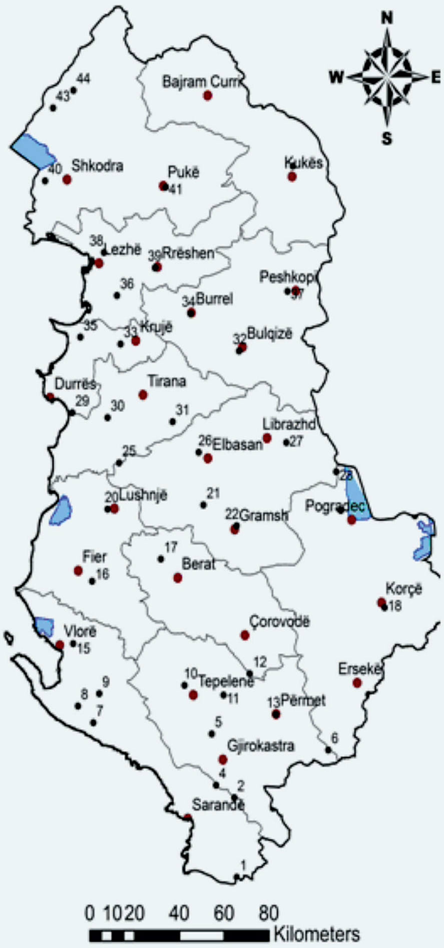
The moss samples were collected at 62 sampling sites positioned over the whole territory of the country during the dry autumn of 2010 and summer of 2011 (Qarri et al. 2013). To ensure a systematic sampling scheme (EPA QA/G-5S 2002) with a homogeneous distribution with more or less equal densities (1.5 moss samples/1000 km^2) (Qarri et al. 2014b), the number of sampling sites was reduced to 44 (Fig. 1). One of the recommended moss species, *Hypnum cupressiforme*, widely spread in Albania, was used as air pollution bioindicator in this study. Moss sampling was carried out according to the guidelines of the UNECE ICP Vegetation Protocol of the 2010/2011 survey (ICP Vegetation 2010). The criteria regarding the sampling points were respected during the sampling campaign (3 to 10 m away from the nearest projected tree; at least 300 m from main roads, villages and industries and at least 100 m away from smaller roads and single houses). The samples were collected within an area of about 50 m^2. About a liter of fresh moss composite samples was formed for each sampling point consisting of five to ten subsamples of only one moss species.

1.2. Sample Preparation and Analysis. The upper three fully developed segments of each *Hypnum cupressiforme* specimen and corresponding green or green-brownish parts of this moss species representing the last 2–3 years growth were cleaned from any extraneous material. Moss samples were dried for 48 h at 40 °C till the constant weight and were analyzed by instrumental neutron activation analysis (INAA). Neutron activation analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest (Biziuk et al. 2010). Previous experience of the use of INAA in moss biomonitoring has shown that *Hypnum cupressiforme* samples of 0.3 g are sufficiently large to be used without homogenizing (Steinnes et al.1994). Epithermal NAA (ENAA) at the IBR-2 pulsed fast reactor of FLNP JINR, Dubna, Russia, was used to determine contents of REE (Frontasyeva 2011). Neutron flux density characteristics in the channel equipped with a pneumatic system are given in Table 1 (Frontasyeva and Pavlov 2000).

Table 1. Characteristics of the ENAA irradiation channels (Frontasyeva and Pavlov 2000)

Channel	Neutron flux density φ, 10^{12} $cm^{-2} \cdot s^{-1}$		
Irradiation position	Thermal ($E = 0 \div 0.55$ eV)	Epithermal ($E = 0.55 \div 10^5$ eV)	Fast ($E = 10^5 \div 25 \cdot 10^6$ eV)
Ch1 (Cd-screened)	0.023	3.31	4.2

INAA has several advantages compare to other methods of elemental analysis. It differs from many methods of chemical analysis in that it depends on the properties of the nucleus and not on the behavior of electrons in out shells of the atom. This is a nondestructive method that provides precise and accurate results with high sensitivity and selectivity for



Site#	Latitude	Longitude	Site#	Latitude	Longitude
1	39°39'22.0"N	20°10'03.3"E	**23**	40°55'54.5"N	20°36'33.1"E
2	39°55'28.7"N	20°11'20.0"E	**24**	40°54'13.6"N	20°56'48.2"E
3	39°54'24.0"N	20°21'21.9"E	**25**	41°05'14.1"N	19°43'39.1"E
4	39°57'33.6"N	20°06'34.4"E	**26**	41°07'25.9"N	20°02'18.0"E
5	40°10'09.8"N	20°05'36.9"E	**27**	41°10'07.5"N	20°23'46.8"E
6	40°06'07.8"N	20°33'56.8"E	**28**	41°04'57.2"N	20°36'59.0"E
7	40°12'31.4"N	19°36'50.7"E	**29**	41°16'06.0"N	19°31'50.9"E
8	40°15'12.0"N	19°33'53.8"E	**30**	41°15'48.4"N	19°38'53.2"E
9	40°18'24.9"N	19°38'29.8"E	**31**	41°12'48.5"N	19°55'59.3"E
10	40°19'53.4"N	19°59'02.4"E	**32**	41°28'45.8"N	20°11'43.2"E
11	40°17'49.1"N	20°08'55.2"E	**33**	41°30'59.8"N	19°42'58.3"E
12	40°21'52.3"N	20°15'16.3"E	**34**	41°36'09.2"N	20°00'29.7"E
13	40°13'59.4"N	20°21'05.3"E	**35**	41°31'22.0"N	19°32'30.4"E
14	40°18'11.0"N	20°41'26.6"E	**36**	41°40'35.2"N	19°42'51.7"E
15	40°26'41.0"N	19°31'06.8"E	**37**	41°41'26.9"N	20°24'13.5"E
16	40°40'43.2"N	19°36'50.2"E	**38**	41°47'52.4"N	19°38'24.8"E
17	40°45'59.6"N	19°53'28.3"E	**39**	41°46'12.9"N	19°51'53.1"E
18	40°35'44.4"N	20°47'22.3"E	**40**	42°04'14.4"N	19°23'10.1"E
19	40°36'44.2"N	21°02'07.0"E	**41**	42°02'26.1"N	19°54'53.5"E
20	40°56'02.5"N	19°40'29.6"E	**42**	42°06'37.4"N	20°25'27.7"E
21	40°56'56.5"N	20°04'02.6"E	**43**	42°18'48.2"N	19°27'13.8"E
22	40°52'48.9"N	20°11'43.8"E	**44**	42°21'50.6"N	19°32'08.3"E

Fig. 1. The map of sampling sites of Albania with coordinates (centered at the latitude: 41° 00′ North; longitude: 20° 00′ East)

a large number of elements in the periodic table, making this technique most attractive for multi-element profiling (Frontasyeva and Steinnes 1997).

To determine elements in question, around 0.3 g of the moss samples were packed in aluminum cups for long-time irradiation. The content of REE in moss samples was determined by using the cadmium-screened irradiation Channel 1 with neutron flux density $\varphi_{epi} = 3.31 \cdot 10^{12}\ cm^{-2} \cdot s^{-1}$.

Samples were irradiated for about 100 h. The containers with samples were cooled for 4 days and then the samples were repacked and measured twice, using high-purity germanium detectors, the first time direct after being repacked and the second time after 20 days of the end of the irradiation. The measurement time was 0.5 and 1.5 h, respectively.

The processing of the spectral data was performed using the software developed at FLNP JINR (Ostrovnaya et al. 1993; Ostrovnaya 2000) and the content of each element in moss samples was calculated.

1.3. Quality Control. The quality control of NAA results was ensured by carrying out simultaneous analysis of the standard reference material (SRM) Montana Soil 2710, NIST (National Institute of Standards and Technology), trace elements in Coal 1632b from the US, NIST, and Estuarine Sediment BCR-667 from Sigma-Aldrich in Belgium, Institute for Reference Materials and Measurements (IRMM). The reference materials were packed together with 10–12 samples in each transport container. Certified values and NAA data of reference materials are shown in Table 2. As seen from Table 2, the mean content of the elements under investigation is in good agreement with the certified data.

Table 2. Certified and experimental values for the used reference materials (content in mg/kg of dry weight, BCR-667). Th* was determined from the reference 1632b

Element	Certified	Determined
Fe	44800 ± 986	44819 ± 2106
Sc	13.70 ± 0.69	13.69 ± 0.74
La	27.80 ± 1.00	27.83 ± 1.11
Ce	56.70 ± 2.49	56.63 ± 3.40
Nd	25.00 ± 1.40	24.98 ± 8.17
Sm	4.66 ± 0.20	4.65 ± 0.23
Eu	1.00 ± 0.01	0.99 ± 0.192
Gd	4.410 ± 0.119	4.416 ± 0.278
Tb	0.682 ± 0.017	0.681 ± 0.024
Tm	0.326 ± 0.025	0.325 ± 0.070
Yb	2.20 ± 0.09	2.19 ± 0.24
Th*	1.342 ± 0.036	1.339 ± 0.044

1.4. Data Analysis. The content data onto selected elements (Sc, Fe, REE, and Th) in moss samples from 44 sampling sites were subjected to Descriptive Statistics (min, max and median, see Table 3) and compared with those of the other Balkan countries and Northern Norway (Table 4) that is selected as a pristine area.

Arc-Gis 10.2 by Esri Inc. was used to generate the maps presenting the geographical distribution of the pollution patterns for several elements (Finkelshtein and Deev 1999). The contamination factor (CF) was calculated as a ratio of the median value of the element content in the area ($C_{\mathrm{med},i,A}$) under investigation and the respective median value of the element from Norway ($C_{\mathrm{med},i,N}$), that is selected as a pristine area (Fernandez and Carballeira 2002):

$$\mathrm{CF} = C_{\mathrm{med},\,i,\,A} / C_{\mathrm{med},\,i,\,N}.$$

The contamination scale presented first by Fernandez et al. (2000) was used to evaluate the contamination level. The nonparametric Spearman's rank-order correlation R_s was calculated to measure the strength of the association between the two ranked variables. The Spearman's rank-order correlation R_s is applicable to the monotonic relationship existing when either the variables increase in value together, or as one variable value increases, the other variable value decreases.

Different geochemical diagrams were constructed to investigate the geochemical origin of REE caused mainly by wind blown soil dust (Bekteshi et al. 2015).

2. RESULTS AND DISCUSSION

The results of Descriptive Statistics are shown in Table 3. The REE levels of the current moss samples ($N = 44$) indicated the following order of abundance: Ce $>$ La $>$ Nd $>$ Sm $>$ Gd $>$ Yb $>$ Eu $>$ Tb,Tm (Table 3). The same distribution was found in all of the natural compartments (Taylor and McLennan 1985). The REE contents in mosses: 10 ± 5 mg/kg, $N = 44$, are of the same order of magnitude as those found in the literature (Chiarenzelli et al. 2001; Dolegowska and Migaszewski 2013). The same conclusion can be found from the values of La/Yb ratios.

Table 3. Descriptive Statistics of experimental data. For comparison, the content of the same elements in the average Upper Continental Crust (from Taylor and McLennan 1985) is also listed. Contents are given in mg/kg

Elements	Maximum	Mean $\pm\sigma$	Median	Minimum	Coef. var., %	UCC
Fe	5800	1966 ± 1203	1482	601	61.2	–
Sc	3.09	0.92 ± 0.60	0.72	0.27	65.7	14
La	6.49	2.22 ± 1.21	1.83	0.69	54.5	31
Ce	10.60	4.15 ± 2.30	3.49	0.85	55.4	63
Nd	6.50	2.28 ± 1.63	1.63	0.65	71.5	27
Sm	0.75	0.32 ± 0.16	0.28	0.11	50.3	4.7
Eu	0.60	0.10 ± 0.09	0.08	0.04	90.6	1
Gd	2.23	0.29 ± 0.37	0.17	0.04	127.8	4
Tb	0.17	0.05 ± 0.03	0.04	0.01	60.6	0.7
Tm	0.24	0.05 ± 0.05	0.03	0.01	96.6	0.3
Yb	0.55	0.19 ± 0.11	0.14	0.06	59.8	2
Th	1.33	0.53 ± 0.28	0.46	0.18	51.9	10.5
ΣREE	24.34	9.65 ± 5.36	7.89	3.09	55.5	133.7
ΣL/ΣH*	28.42	18.19 ± 5.36	18.97	5.53	29.5	18.1
La/Yb	20.94	12.52 ± 3.37	12.96	6.06	26.9	15.5

Note. ΣL/ΣH* = ΣLREE/ΣHREE

The La/Yb ratio of the current moss samples of 12.52 ± 3.37 is similar to the same ratio of UCC (15.5) (Rudnick and Gao 2003), by indicating the same distribution pattern of REE in moss samples and UCC.

Most of the elements under investigation show moderate variation: their coefficient of variation (CV) is ranging between 25 and 75% and follows the lognormal distribution at $p < 0.05$ that is typical of mineral particles (Clarke and Washington 1924; Vinogradov 1962) mainly from wind blown soil dusts (Gjengedal and Steinnes 1990). The CV value is the highest one for Gd (128%), followed by Tm (97%) and Eu (91%) probably due to the fact that these elements are difficult to be detected and the error of measurement exceeds 30%.

Table 4 compares Fe, Sc, REE, and Th content (mg/kg) with neighboring countries and Norway, that is considered as a pristine area. The data for Fe, Sc, REE, and Th in moss samples in Albania were similar to those of the neighboring countries (Marinova et al. 2010; Barandovski et al. 2008; Stan et al. 2001; Frontasyeva et al. 2004), but were much higher than in Norway (Steinnes et al. 2007). It should be pointed out that the Albanian data refer to 2010/2011 sampling period and the data from the other Balkan countries belong to 2000/2001 moss survey. The content of most elements in soils tends to vary with time, while the rare earth elements are known to be stable in the geochemical environment (Taylor 1964).

From the data of the contamination factors (Table 5), it is evident that the area under investigation for most of REE belongs to the C5 level of contamination (sever polluted), except for Fe that remains at the C4 level of contamination (moderate polluted) as it is described by Qarri et al. (2013).

2.1. Correlation Analysis of the Elements. As shown in Table 6, there is a strong correlation between the presented elements. High correlation between these elements is mainly explained by the same geochemical properties of Sc and Th with ΣREE.

As it is expected from the high similarity of geochemical and chemical properties of REE, Table 7 illustrates that content of all REE appears significantly correlated, with the exception of Gd and Eu that showed from moderate to weak correlations.

Table 4. The comparison of content data of Fe, Sc, REE, and Th (mg/kg) with neighboring countries and Norway

Country	Albania (Present work)		Bulgaria (Marinova et al. 2010)		Macedonia (Barandovski et al. 2008)		Romania (Stan et al. 2001)		Northern Serbia (Frontasyeva et al. 2004)		Northern Norway (Steinnes et al. 2007)	
Number of samples	44		99		73		70		92		100	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Fe	1482	601–5800	3000	689–19400	2460	424–17380	3290	815–21340	3110	720–9230	209	77–1370
Sc	0.72	0.27–3.09	0.92	0.21–7.20	0.81	0.12–6.79	0.94	0.21–6.13	1.31	0.27–4.13	0.052	0.009–0.220
La	1.83	0.69–6.49	3.3	1–61.79	2.32	0.50–22	2.4	0.4–15.2	4.66	1.09–13	0.189	0.045–2.56
Ce	3.49	0.85–10.6	6.8	1.75–143	5.6	0.83–42	6.1	0.9–42.5	9.2	1.84–28	0.342	0.095–4.61
Nd	1.63	0.65–6.50	3.15	0.01–47								
Sm	0.28	0.11–0.75	0.6	0.19–8.30								
Tb	0.04	0.01–0.17	0.076	0.02–0.98	0.06	0.01–0.56	0.07	0.01–0.42	0.11	0.02–0.36	0.003	0.002–0.030
Eu	0.08	0.04–0.60										
Gd	0.17	0.04–2.23										
Tm	0.03	0.01–0.24	0.057	0.02–0.67								
Yb	0.14	0.06–0.55	0.22	0.05–3.32								
Th	0.46	0.18–1.33	0.86	0.27–23	0.67	0.12–7.6	0.81	0.21–4.16	0.82	0.18–2.4	0.033	0.004–0.24

Table 5. The values of the contamination factor (CF)

Element	Fe	Sc	La	Ce	Nd	Sm	Tb	Eu	Gd	Tm	Yb	Th
Median, Albania	1482	0.72	1.83	3.49	1.63	0.28	0.04	0.08	0.17	0.03	0.14	0.46
Median, Northern Norway	209	0.052	0.189	0.342			0.003					0.033
CF	7.1	13.8	9.7	10.2			13.3					13.9

Table 6. The matrix of the Spearman's correlation coefficients between Fe, Sc, Th, and ΣREE. Correlation is significant at $p < 0.05$

Element	Fe	Sc	Th
Sc	0.87		
Th	0.80	0.91	
ΣREE	0.73	0.86	0.88

Table 7. The matrix of the Spearman's correlation coefficients between REE. Correlation is significant at $p < 0.05$

Element	La	Ce	Nd	Sm	Eu	Gd	Tb	Tm
Ce	0.97							
Nd	0.74	0.73						
Sm	0.86	0.83	0.73					
Eu	0.28	0.30	0.29	0.26				
Gd	0.49	0.54	0.45	0.51	0.13			
Tb	0.97	0.95	0.75	0.84	0.29	0.44		
Tm	0.59	0.62	0.72	0.67	0.20	0.78	0.59	
Yb	0.84	0.86	0.76	0.76	0.22	0.40	0.86	0.63

To investigate the distribution of REE in moss samples, the GIS maps are plotted as shown in Fig. 2. Agnan et al. (2013) emphasized the comparison between the REE distribution patterns in organisms, and bedrocks showed a regional uniformity influence on dust particles originating from the bedrock and/or soil weathering that were entrapped by lichens and mosses.

Thus, the rare earth patterns indicate a lithogenic origin from weathering of regional bedrock (Bortolotti et al. 2002; Tashko et al. 2009; Saccani et al. 2011; Heba et al. 2009). The REE pattern in current moss samples more or less showed the regional influence on dust particles originating from the bedrock and/or soil weathering that confirms their origin from wind blown soil dust. The dry particles derived from bedrock chemical and physical erosion (Sugimae 1980) could be trapped by mosses during atmospheric deposition processes, e.g., wind and rain phenomena. For better understanding, the geochemical origin of REE in moss samples was investigated.

2.2. Geochemical Origin of REE. The REE distribution patterns using lichen and/or moss content analysis have been demonstrated as efficient in determining the origin of metals compared to bulk precipitation or local lithology (Markert and Zhang 1991; Chiarenzelli et al. 2001; Aubert et al. 2002, 2006; Rusu et al. 2006; Agnan et al. 2013). Recently, Agnan et al. (2013) emphasized the lithogenic influence on lichen and moss metal content in the southwest of France. The REE registered in lichens and mosses on a national scale remain scarce (Agnan et al. 2013). For a complete interpretation of the present moss data, corresponding literature values for the Upper Continental Crust (UCC) (Rudnick and Gao 2003), North American Shale Composite (NASC) (Gromet et al. 1984) and Average Post-Archaean Australian Shale (PAAS) (Taylor and McLennan 1985) were added.

For a better understanding of the geochemistry of the elements present in the moss samples of Albania, whose origin could be mainly attributed to wind blown soil dust (Bekteshi et al. 2015), we have used the Sc–La–Th ternary diagram (Condie 1993) (Fig. 3), the linear regression of UCC/chondrite vs. moss/chondrite (Fig. 4), as well as the chondrite-normalized REE spidergram (Fig. 5).

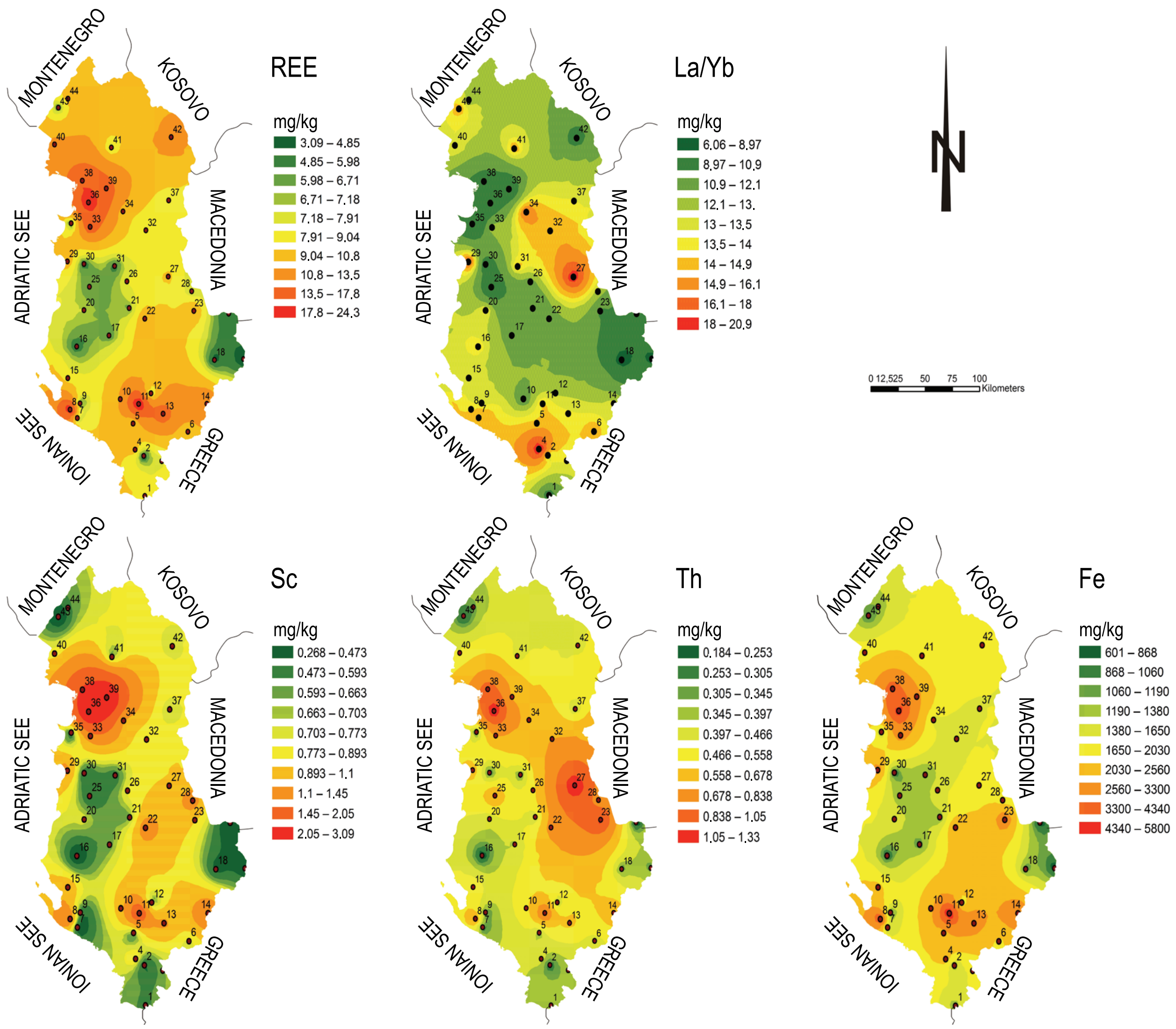


Fig. 2. The GIS maps for REE, La/Yb ratio, Sc, Th, and Fe

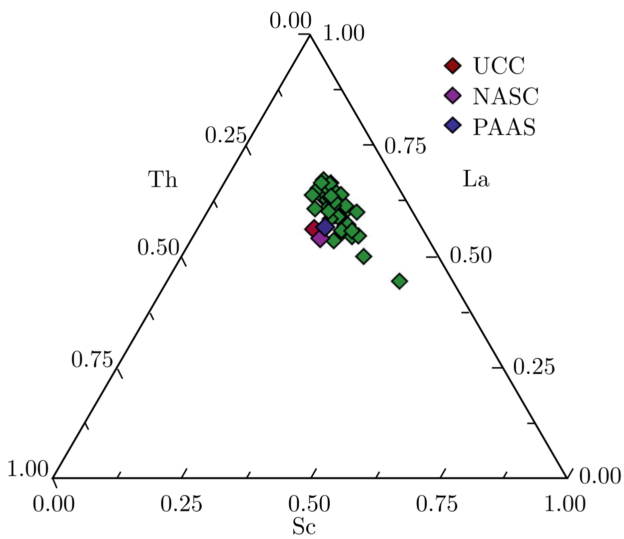


Fig. 3. Ternary diagram of geochemistry of Sc, La, and Th elements in moss samples and sedimentary Upper Continental Crust (UCC) (Rudnick and Gao 2003), North American Shale Composite (NASC) (Gromet et al. 1984), Average Post-Archaean Australian Shale (PAAS) (Taylor and McLennan 1985)

Accordingly, the distribution of these elements has confirmed the volcanic (felsic) origin of the investigated samples. Two outlier points were found at Station 28 (Lin) and Station 39 (Rrësheni). Station 28 (Lin) is characterized by the Jurassic South Albanian ophiolites: MORB vs. SSZ-type ophiolites (Hoeck et al. 2002) and the basalts and mantle peridotites (Saccani et al. 2011; Tari 2002), while the Mirdita region with its capital Rrësheni (Station 39) is characterized by the ophiolite sequences and MORB magmatism (Bortolotti et al. 1996, 2004, 2006; Dilek et al. 2008; Chiari et al. 1996). In the Sc–La–Th ternary diagrams (Pearce et al. 1984) (see Fig. 3), the elements present in soil dust of moss samples are more or less positioned close to the most common continental average samples and thus show the origin from the mixed sources.

The REE/chondrite moss samples pattern is similar to those of (PAAS, NASC and UCC)/chondrite. The observed Eu and Tm anomalies depend on the chemical behavior of Eu and the geochemistry of the area. The Eu ions exist in two different oxidation states Eu^{2+}

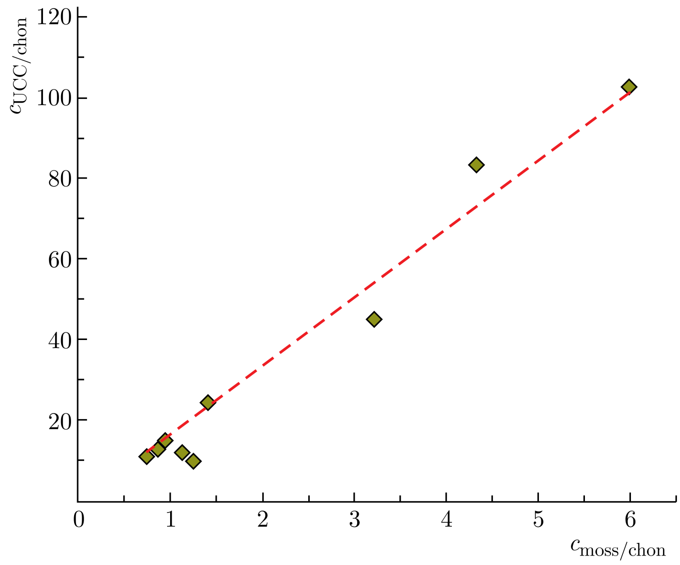


Fig. 4. The linear regression of UCC/chondrite vs. moss/chondrite of the Albanian moss samples. Chondrite normalizing factors are taken from Taylor and McLennan (1985)

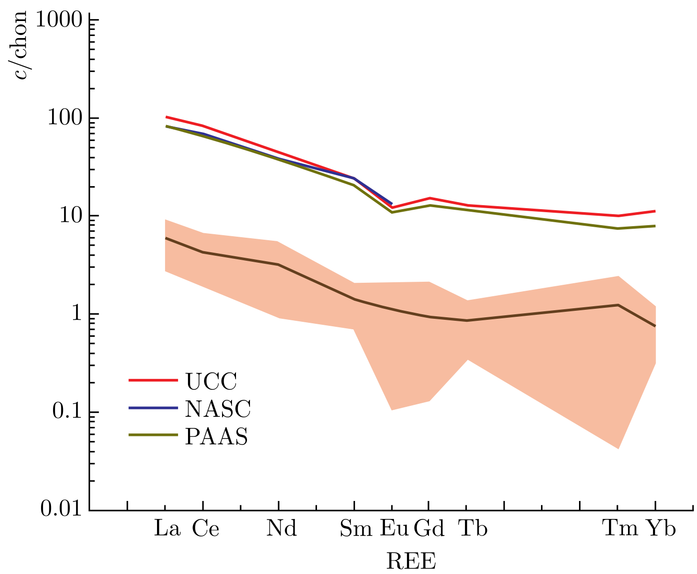


Fig. 5. The chondrite-normalized REE spidergram in moss samples, UCC (after Rudnick and Gao 2003), NASC (after Gromet et al. 1984), and PAAS (after Taylor and McLennan 1985). Chondrite normalizing factors are taken from Taylor and McLennan (1985)

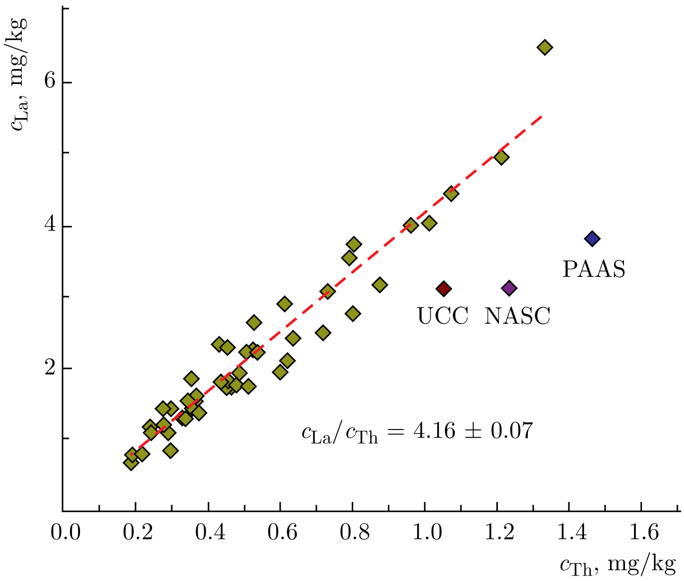


Fig. 6. Plot of La vs. Th illustrating the existing differences between moss samples and sedimentary UCC, NASC, and PAAS

and Eu^{3+}. The Eu^{2+} ion is different to the other trivalent REE that enables incorporation into minerals, especially of calcic minerals such as plagioclase feldspars, by the substitution of Eu^{2+} for Ca^{2+} (Weill and Drake 1973).

Both diagrams of the UCC/chondrite vs. moss/chondrite linear regression (Fig. 4) and the chondrite-normalized REE pattern (Fig. 5) in the case of Albanian moss samples show a REE/chondrite ratio about 14 times lower than in the case of PAAS, NASC, and UCC, but present a similar pattern. Similar results were published by Agnan et al. (2014) and Chiarenzelli et al. (2001) showing that the REE contents in lichens and mosses are of 1 to 3 orders of magnitude less than those of the UCC, but yield identical patterns.

Another parameter that might sustain this statement is the La/Th ratio (see Fig. 6) that is higher from the corresponding values of 2.73, 2.52, and 3.05 reported for UCC, NASC, and PAAS, respectively, by showing the presence of more volcanic rocks in Albania than the continental ones (Tashko et al. 2009).The Triassic volcanism of Albania consists mainly of basaltic pillowed and massive flows locally associated with dolerites and trachytes (Monjoie et al. 2008).

CONCLUSION

The order of the elements according to their abundance is Fe > Ce > Nd > La > Sc > Th > Sm > Gd > Yb > Eu > Tm > Tb. They follow the lognormal distribution ($p < 0.05$) that is typical of mineral particles.

The contents of Fe, Sc, REE, and Th in moss samples of Albania were similar to those of neighboring countries, but lower than those of Norway elected as a pristine area.

The data of the contamination factors indicate that the area under investigation for most of REE belongs to the C5 level of contamination (sever polluted), except for Fe that belongs to the C4 level of contamination (moderate polluted).

Significant correlations ($0.7 \leqslant r \leqslant 1$) between most of the pairs of REE, except for Gd and Eu, indicate similar origin and/or behavior of REE in moss samples of Albania.

The GIS maps of REE and the registered geochemical signatures (such as the general trend of REE distribution patterns and Eu or Tm anomalies) indicated a regional lithological source of dust particles derived from bedrock and/or soil weathering entrapped by lichens and mosses that erased any anthropogenic influence.

Both diagrams of the chondrite-normalized pattern and the linear regression of UCC/chondrite vs. moss/chondrite in moss samples show that the chondrite-normalized REE pattern in moss samples is about 14 times lower than in the case of PAAS, NASC, and UCC, but it showed to have a similar pattern.

Ternary diagrams and La/Th ratio showed that in spite of the fact that the majority of investigated elements present contents close to the Upper Continental Crust, their relative distribution points to the presence of fragments of volcanic (felsic) rocks.

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Аллайбеу Ш. и др. E18-2015-64
Изучение атмосферных выпадений редкоземельных элементов в Албании с помощью метода мхов-биомониторов, нейтронного активационного анализа и ГИС-технологии

Вряд ли можно предполагать, что редкоземельные элементы (РЗЭ), являющиеся консервативными, имеют антропогенное происхождение. Подвижность РЗЭ в окружающей среде требует их мониторинга в матрицах окружающей среды, в которых они в основном присутствуют в следовых количе-ствах. Представлены результаты определения одиннадцати элементов с помощью эпитеплового нейтронного активационного анализа (ЭНАА) на реакторе ИБР-2 в Дубне в природных мхах вида *Hypnum cupressiforme*, собранных в 44 точках пробоотбора на всей территории Албании. Статья посвящена определению редкоземельных элементов, таких как Sc и лантаноиды. Fe и Th, которые хорошо коррелируют с лантаноидами, также включены в статью. Эти элементы (за исключением Fe) никогда не были ранее определены в атмосферных выпадениях в Албании. Для интерпретации полученных результатов использовалась описательная статистика программного пакета STATISTICA™ 10. Средние значения содержания изучаемых элементов сравнивались с аналогичными значениями в соседних странах, таких как Болгария, Македония, Румыния, Сербия, а также в Норвегии, которая считается чистой территорией. Изучено геохимическое поведение РЗЭ в пробах мха, в частности РЗЭ, нормированных на хондриты. Выявлено, что основной причиной накопления РЗЭ во мхах является выветривание почв, обогащенных металлами.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ и в Университете в Тиране, Албания.

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Allajbeu Sh. et al. E18-2015-64
Atmospheric Depositions of Rare Earth Elements in Albania Studied by the Moss Biomonitoring Technique, Neutron Activation Analysis and GIS Technology

Rare earth elements (REE) are conservative elements, scarcely derived from anthropogenic sources. The mobilization of REE in the environment requires their monitoring in environmental matrices, where they are mainly present at trace levels. The results on determination of the content of 11 elements by epithermal neutron activation analysis (ENAA) at the IBR-2 reactor in Dubna in carpet-forming moss species *Hypnum cupressiforme* collected from 44 sampling sites over the whole Albanian territory are presented and discussed. The paper is focused on Sc and lanthanides, as well as Fe and Th, the last ones showing correlations with the investigated REE. With the exception of Fe, all other elements were never determined in the air deposition of Albania. The STATISTICA™ 10 software was used for data analysis. The median values for the content of elements under investigation were compared to those in Bulgaria, Macedonia, Romania and Serbia, as well as Norway selected as a pristine area. Therefore, it was shown that the accumulation of REE in mosses is associated with the wind blown metal-enriched soils that are pointed out as the main emitting factor.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, and in University of Tirana, Albania.

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