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Distribution of light lanthanides (LREE) in Cambisoils evolved on volcanic rocks of the Eastern Carpathians (Romania)

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DISTRIBUTION OF LIGHT LANTHANIDES (LREE) IN CAMBISOILS EVOLVED ON VOLCANIC ROCKS OF THE EASTERN CARPATHIANS (ROMANIA)

Angela Lupașcu[1] Daniela Chelariu[2]

Abstract. This paper shows the distribution of light lanthanides: La, Ce, Nd, Sm evolved in soils of volcanic rocks in the Gutai and Oaş Mountain (Northern Romania). We have analyzed three subtypes of soil located at different heights which led to different physico-chemical properties: chemical reaction, organic accumulation amount exchangeable bases, acid-hydrolytic and quantitative values studied lanthanides

Keywords: lanthanides, volcanic soils, Gutai and Oas Mountain (Northern Romania)

Introduction

General geochemical characters of the rare earths. The rare earths named as lanthanides include similar series of 15 chemical elements with atomic numbers in the periodic table between *Z*=51 and *Z*=71: La, Ce, Pr, Nd, Pm, Sm, Eu (Ceric subgroup or light rare earths: *LREE*) şi Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (Ytrice subgroup of heavy rare earths: *HRE*) *E*. In this paper we analyzed the presence and distribution of the four elements lanthanum profile (La, Ce, Nd, Sm) in three subtypes volcanic soil evolved on volcanic parent material evolved, respectively: an andic eutricambosoil (Ecan), taken from Oas Mountain, Târna Mare village (400 m alt), an andic skeletal eutricambosoil (Ecan-qq) taken from Oas Mountain, Cămârzana village (490 m alt) and an andic districambosol (DCum-an) taken from Gutâi Mountain, Săpânța village (930 m alt).

Materials and methods

For each soil profile were analyzed by 5 samples, taken according to soils horizons. For each soil sample was determined the pH of the aqueous suspension of the ground, the total organic carbon by wet oxidation method and dosage titration Walklay-Blak in Gogoaşă modification and humus (total organic C x 1,724).

The components of humus were determined by the method developed by Kononova M. M. and Belcikova N. P. (1961) where the soil sample is divided into several sub-samples and extraction make the solution mixture of sodium pyrophosphate (Na4P2O7 x 10H2O) 0,1 m – NaOH 0,1 n, pH aprox. 13. The solution based on sodium pyrophosphate is considered the best for extracting humic fractions. The extract obtained is used to determine the total

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extractable carbon and carbon in the determination of the humic acids, having first washed fulvic acids.

Determination of the total fraction of heavy metals in soil.

Quantitative determination of the chemical components was carried out in Department of Geology from the Alexandru Ioan Cuza University of Iasi using X-ray fluorescence spectroscopy ***(XRF)*** (PANalytical Epsilon 5) (elements: Si, Ti, Al, Fe, Mg, Ca, Na, K, P, S, Sc, Rb, Nb, Mo, La, Ce, Nd, Sm, Cd, As) using energy dispersive technique (ED-XRF) using pellets pressed, so the total fraction (<2mm) and the fine fraction (<0,150mm). Geochemical data obtained were processed statistically using programs NCSS (produced by the company with the same name) and XLStat (produced by Addinsoft). At the same time, they were used and free software DAS+R and GCDkit.

Results and discutions

1. Andic Eutricambosoil (Ecan)(400 m alt.) was taken from Oas Mountain, near the Târna Mare village (Satu Mare county), from Berii valey floor, vegetating under a format of a beech forest (*Fagus silvestris)* with *Luzula sylvatica* in herbaceous layer. Parental material consists of an andesitic deluvia, andesite and pyroxene hialoandezite hiperstenice. The thickness of the profile is 77 cm, and its morphology is as: Aou (0-10 cm), Ao/Bv (10-21 cm), Bv1 (21-33 cm), Bv2 (33-52 cm), C+R (52-77). Analyses carried out a chemical reaction reveals all acidic soil profile (4,34 – 4,87) and a reduced organic accumulation arranged on a curve showing decrease with depth (Table 1).

Soil subtype	soil Horizon	Depth (cm)	pH (H_2O)	Corg.	Humus	SB	SH	T	V
				(%)		(me/100 g sol)			(%)
Andic ECand (1)	Aou	0-10	4,34	3,39	5,84	3,6	6,4	10,0	36,0
	Ao/Bv	10-21	4,30	1,27	2,18	2,4	3,7	6,1	39,0
	Bv1	21-33	4,45	1,10	1,89	4,8	2,6	7,4	64,8
	Bv2	33-52	4,83	0,24	0,41	4,0	2,6	6,6	60,1
	C+R	52-77	4,61	0,19	0,32	3,6	1,5	5,1	69,9
	R+C	77-90	4,87	0,24	0,41	5,6	1,5	7,1	78,3
Andic scheletic ECan-qq (2)	Ao	0-12	4,96	2,82	4,86	10,7	6,8	17,5	61,1
	AB	12-22	4,99	1,35	2,32	6,8	4,8	11,6	58,3
	Bv1	22-40	5,29	0,96	1,65	6,0	2,4	8,4	71,1
	Bv2+R	40-55	5,89	0,47	0,81	7,5	1,5	9,1	83,0
	BC+R	55-65	5,92	0,45	0,77	11,5	1,5	13,0	88,1
	R+C	65-75	5,90	0,43	0,74	9,1	0,8	10,0	91,2
Umbric DCum (3)	Au	0-13	3,92	9,67	16,67	6,8	37,7	44,5	15,2
	Au	13-21	4,15	5,95	10,26	6,0	29,6	35,6	16,8
	BA	21-33	4,50	3,81	6,57	5,6	20,7	26,3	21,2
	Bv1	33-54	4,70	2,06	3,55	4,9	16,1	21,0	23,3
	Bv2	54-78	4,83	1,09	1,88	3,8	15,2	19,0	20,0
	Bv3	78-100	4,67	0,75	1,29	2,7	14,5	17,2	15,6
	Bv4	100-120	4,80	0,54	0,93	2,0	13,0	15,0	13,3

Table 1. Physico-chemical properties of soil analyzed subtypes

Thus, the humus is 5,84% in Aou horizon and gradually decreases to 0,32% at the basis of the profile C+R. The degree of humification varies on profile: 36,87 , 33,07 in the first 20 cm, 75 in Bv2 horizon and slightly lower in C+R. In the process of humification result slightly higher amounts of fulvic acids, which are accumulating in Bv1 horizon, that exceed 4,77 times on the humic part. Particle size analysis shows a low clay (0,12 – 3,28%), an increase of the sand in C+R horizon and an increase in the amount of dust in the upper layers.

Measurements of light lanthanides show a build of La, Ce şi Nd in intermediate în Bv1 horizon and a decrease to the bottom of profile. Sm has a uniform representation without dramatic changes in any horizon (Figure 1).

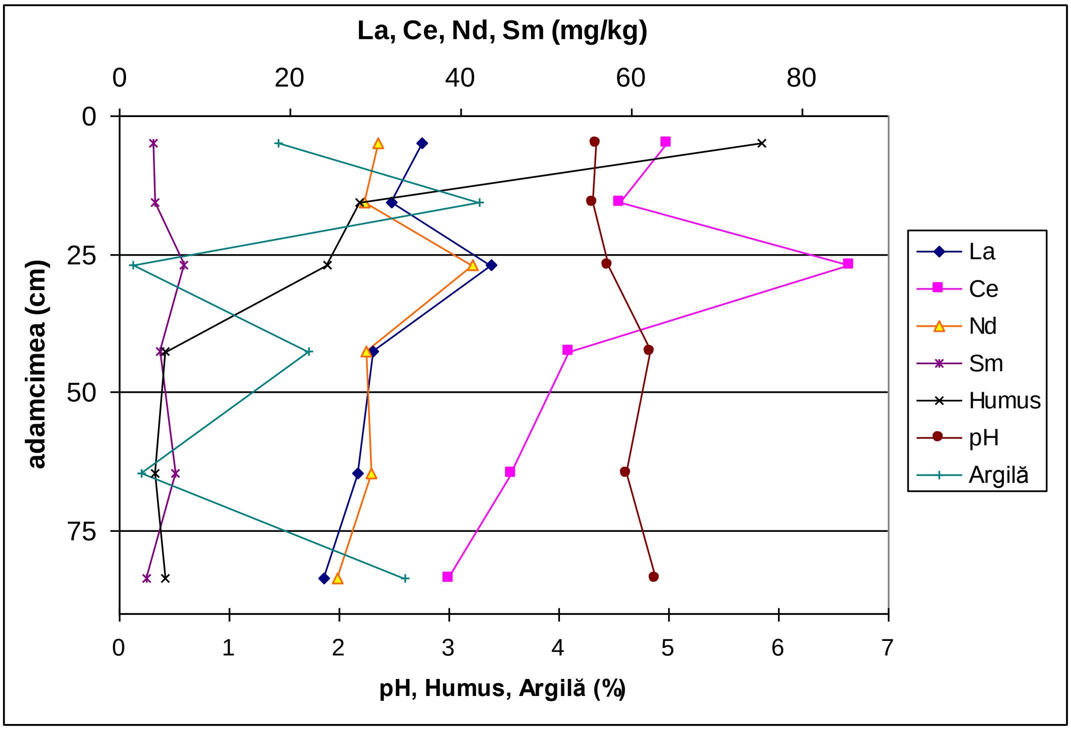
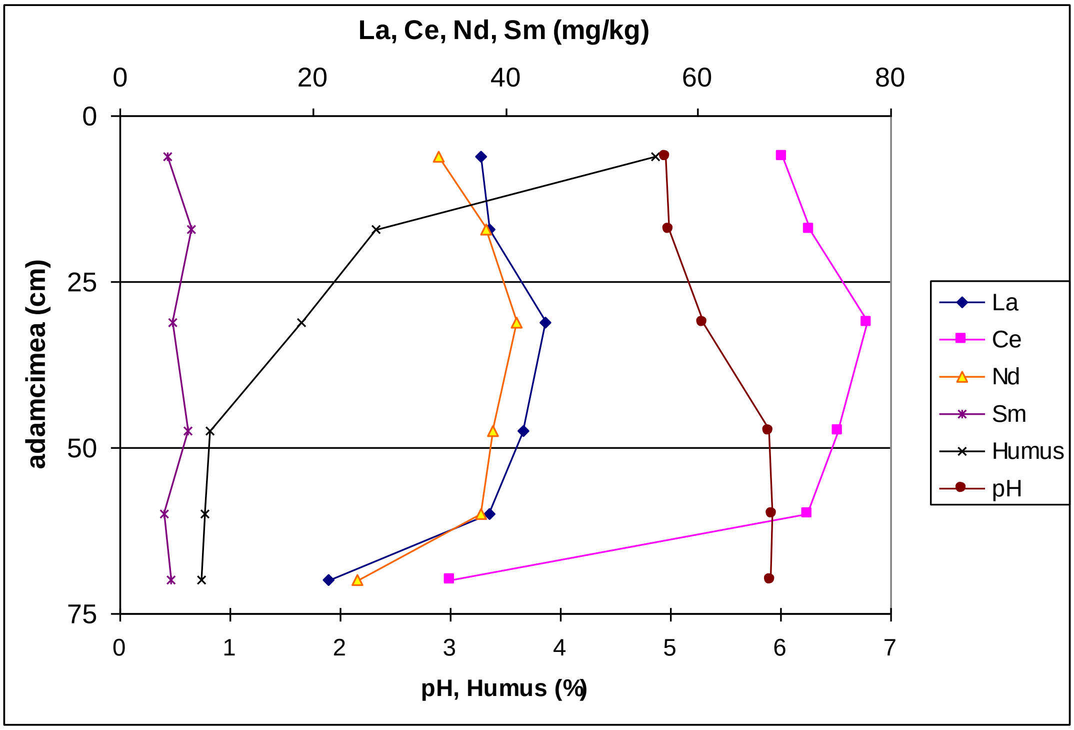


Figure 1: Distribution on profile of La, Ce, Nd, Sm in an eutricambosol (EC) From Oas Mountain (Tarna Mare village)

2. Andic Skeletal Eutricambosoil (ECan-qq)(490 m alt.) was taken also from Oas Mountain, Cămârzana village from the western slope of Geamăna Mare Top. The soil evolves under spontaneous vegetation represented by a beech forest (*Fagus silvatica*). Parental material is represented by dacite and hialodacite hiperstenice. Morphology of profile is as follows: Ao (0-12 cm), AB (12-22 cm), Bv1 (22-40 cm), Bv2+R (40-55 cm), BC+R (55-65 cm). The chemical reaction is variable on profile, with slightly decreasing pH to base profile - 4,96 - 5,92 (Table 1). Physico-chemical analisis reveal an reduced organic accumulation and a good mineralization with values decreasing with depth (2,82 – 0,43% C.org.total, respectively 4,86 – 0,74% humus).

The physico-chemical properties and low values for both variable amount easily exchangeable bases and acidity hydrolytic.

a.



b.

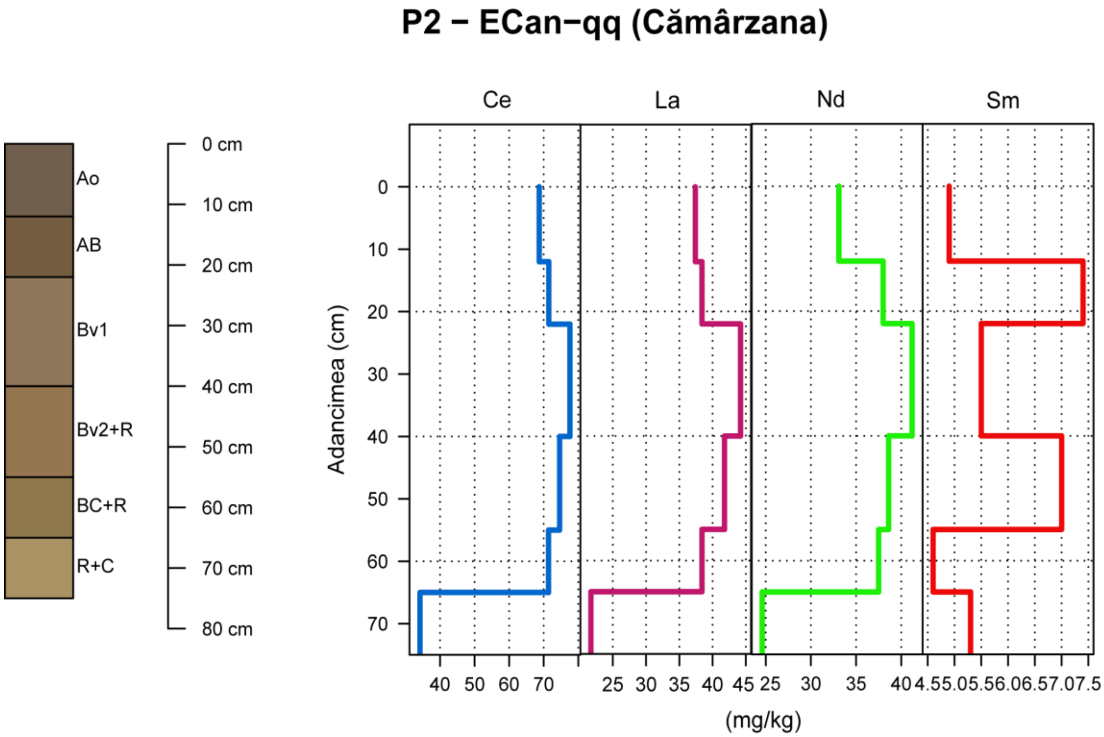


Figure 2: Distribution on profile (a.) and in depth (b.) of La, Ce, Nd, Sm an andic eutricambosoil (DCum-an) from Oas Mountain (Camarzana village, profile no. 9)

The physico-chemical features show a low values for both variable amount of exchangeable bases and hydrolytic acidity (Table 1).

Humification degree of organic matter varies between 35,1 and 53,19; humification processes favors the formation of humic acids that prevails on full profile, in Bv1horizon the humic acids exceed 5,4 times than fulvic acids.

Measurements of light lanthanides showed a distinct geochemical peculiarity of these elements in pedogenesis: their abundance decreased with increasing of the atomic number Z. The relative mobility of the lanthanide in the pedogenesis is controlled by the adsorption capacity of cationic exchange of the soil. The capacity of adsorption of lanthanides is higher in soils containing organic matter and clay.

The chemical analyzes in studied cambisoil highlights the following order of concentration: Ce > La > Nd > Sm. In fig ure below (Figure. 2a, 2b) it can be seen an accumulation of Ce, La, and Nd in Bv1 and Bv2+R intermediate horizons and a clear decrease in the base of the profile R+C. For SM the accumulation is in the Bv1 and BC+R horizon, and also a decrease in the base of the profile R+C.

3. Andic districambosoil (DCum-an) (930 m alt) was taken from Gutai Mountain, near Sapanta village (Varful Vezau, Maramures county). The vegetation consists of a mixed forest with predominantly *Fagus silvatica*; herbaceous layer is composed mostly of *Luzula silvatica* and *Oxalis acetosella.* Parental material is a pyroxene andesite deluvia. The thickness of the profile is 120 cm. The morphology of the profile is as follows: Au (0-13cm), Au (13-21cm), BA (21-33cm), Bv1 (33-54cm), Bv2 (54-78cm), Bv3 (78-100 cm), Bv4 (100-120 cm). Physico-chemical analyzes show a chemical reaction acidic soil in full profile, the pH values increasing with the depth from 3,92 in Au horizon to 4,83 in Bv2 horizon. SB values are comparable to the other two profiles analyzed, hydrolytic acidity is much higher (Table 1).

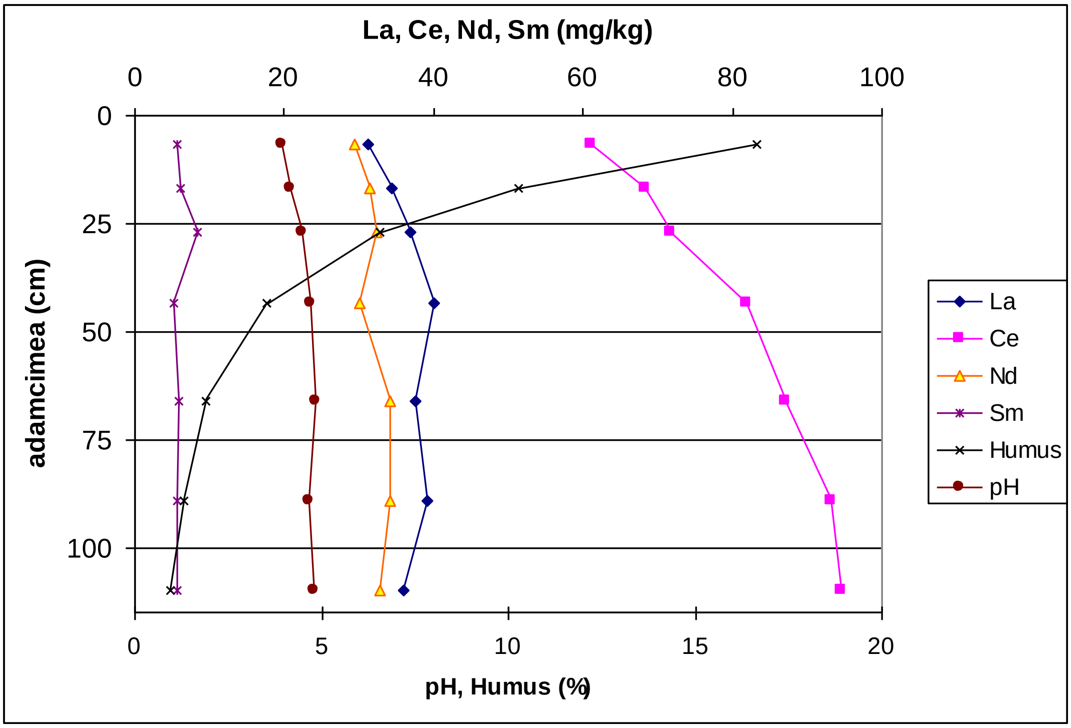
Organic matter, with accumulations down to depth profile reveals a slower mineralization of organic waste, thus a reduced biological activity ; org.total C decreases gradually from 9,67% in Au horizon to 0,54% in Bv4 horizon. Humification degree of organic matter or humic fractions extractability ranges between 45,81 in Au horizon and 84,4 in Bv2 horizon. Extractable material consists mainly of fulvic acids in the first 33 cm and humic acids in Bv1 and Bv2 horizons, whre the accumulation is very low.

Determinations of La, Ce, Nd and Sm plotted in two versions (Figure 3a and 3b) show that Ce has a clear accumulation curve starting from the Au horizon to the base profile in the BV4 horizon; lanthanum accumulation presents an Bv1 and Bv3 intermediate horizons, then slightly decreasing toward the base profile.

Conclusions

Results of the characteristics of the soil physico-chemical analysis highlights the following features: strongly acidic reaction frequency, with an increasing trend from surface to depth; humus content falls within large limits, with a decrease in concentrations below the upper; exchangeable bases (SB) have higher values in soils rich in humus and low in strong leachates soils (luvisoils) and andci soils; after the degree of base saturation (*V*) oligobazice the soils studied are oligobasic, mesobasic and eubazice; high humus content determines the presence of a cation exchange capacity (T) quite large.

a.



b.

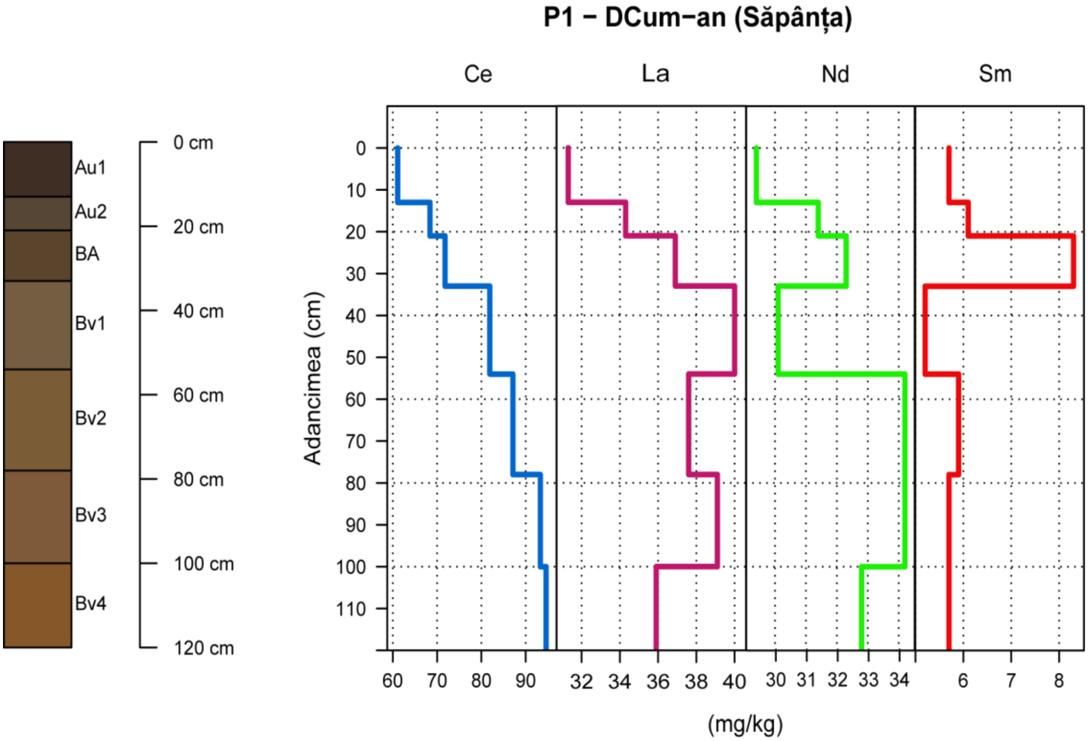


Figure 3: Distribution on profile (a.) and in depth (b.) of La, Ce, Nd, Sm an andic la districambosoil (DCum-an)from Gutai Mountain (Săpânţa village)

In terms of qualitative analyzes the humus fractionation indicates a variable content of humic acids (fulvic acids and humic acids) which is the result of the contribution of the vegetation cover rich in nitrogen which favor the accumulation of humic acids. Coniferous litter rich in debris with poor nitrogen favors the production of fulvic acids, compounds of low degree of polymerization, which are accumulated in certain horizons. Organic matter is a favorable environment for accumulation of microelements (Pb, Cu, Zn, Mn, Rb) due to high adsorption capacity.

Geochemical characters of magmatic rocks and how they have evolved over time indicate clearly their generation by subduction processes with the enrichment of rare earth elements and light litofile: Ce › La › Pr › Nd › Sm. Neogene magmatic mineral geochemical study of the Eastern Carpathians revealed some peculiarities related to magma differentiation processes, the nature and origin magmas.

Neogene magmatic contents of the TR of the Eastern Carpathians are characteristic of subduction zone rocks with enrichment in light lanthanides (TR-ceric). The data obtained for the content of the Carpathians volcanic soils reveals that the abundance of rare earths (REE) decreases with increasing atomic number Z and atomic number lanthanides are less abundant odd than their neighbors with atomic numbers appear.

References

1. Borcoş M., Peltz S., Stan N., Udrescu C., Vasiliu C., 1979. Consideraţii petrochimice şi geochimice asupra vulcanitelor neogene din Munţii Gutâi. , București, St.tehn.ec.I/16, p35-39. Fülöp
2. Kovacs M. A., 2000. Extrusive volcanism in Oaş-Gutâi Mts. An. Inst. Geol. Rom., București, 72, 35p.
3. Ilie I. 1987. Pământuri rare. Edit. Tehnică, București, 271p.
4. Ion A., 2014. Distribuția geochimică a lantanidelor, uraniului și thoriului în solurile Masivului Ditrău. Teză de doctorat. Univ. „Al.I.Cuza", Iași, 215p.
5. Kononova, M.M., Belcicova, N.P., 1961. Uskorenie metodî opredelenia sostava gumusa mineralnîh pociv, Pocivovedenie, 10
6. Lupaşcu A., Rusu C., Donisă C., 1998. Consideraţii privind materia organică din andosoluri şi soluri cu caracter andic din Munţii Oaş-Igniş, Lucr. Semin. Geogr. „D.Cantemir", Nr. 17-18.