Genesis of anomalies of Ti, Zr, Nb and rare-earth elements in Lithuanian soils

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The reasons for higher concentrations of Ti, Zr, Nb, Y, Yb and La in Lithuanian soil have been analysed. The main minerals and grain-size fractions responsible for anomalous concentrations of these trace elements have been determined.

Keywords: trace elements, anomalies, accessory minerals, soil, glaciolacustrine basins

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INTRODUCTION

Geochemical mapping of Lithuanian soils allowed to reveal areas with increased concentrations of some trace elements. Such zones were distinguished as geochemical anomalies (Kadūnas, 1998). Many of such anomalies are formed by a group of trace elements (Ti, Zr, Nb, Y, Yb, La), which are closely correlated in the soil and associated with weathering-resistant allothigenous accessory minerals (Kadūnas et al., 1999). This group is distinguished as a paragenetic accessory association in surface sediments, but in some works referred to as clastogenic (Baltakis, 1993). The contents of trace elements of this association in the soil mostly depend on natural factors. For this reason the knowledge of the genesis of their anomalies is important for the evaluation of the influence of the composition of soil-forming rocks and soil-forming processes on the content of trace elements in the soil. Though the contents of these trace elements in the soil are low (except Ti and Zr), they participate in biogeochemical processes. The influence of rare-earth trace elements on cereal productivity and intellectual development of children (Соловов и др., 1993) implies that these trace elements have impacts on the quality of natural environment.

METHODS

Investigations were carried out in the most contrasting polyelement anomalies where the content of accessory association elements was one of the highest in Lithuanian soil (Table 1). The sum of concentration coefficients of these elements in these anomalies exceeded 8 and the concentration coefficient of at least one of these elements exceeded 1.2 (Table 2). Soil samples of the A-horizon were examined for a total content of trace elements at the Laboratory of Spectral Investigations of the Institute of Geology and Geography by method of direct current arc-emission spectrometry (DC-Arc ES). Soil samples were divided into three groups (1–0.1, 0.1–0.01 and < 0.01 mm grain fractions) using the sieve method. The silt fraction of some of the samples was additionally subdivided into coarse-grained (0.1–0.05 mm) and fine-grained (0.05–0.01 mm) silt fractions, whereas the sand fraction was subdivided into coarse-grained (1–0.25 mm) and fine-grained (0.25–0.1 mm) fractions. The fine sand fractions of soil samples taken from Medininkai Upland and the Kaunas–Kaišiadorys glaciolacustrine basin were divided into three parts according to the density of minerals (<2.8, 2.8–3.3 and >3.3 g/cm^3). All grain-size and mineral density fractions were also examined for the total content of trace elements. The loam and sandy loam samples taken from the Kaunas–Kaišiadorys glaciolacustrine basin were analysed in detail at the laboratories of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements of the Russian Academy of Sciences. X-ray spectrography was applied to determine the contents of Ti, Zr, Nb, Y, Yb, La, Ce and Nd. The X-ray structural and X-ray stadial analysis was used to determine the mineral composition of the fine-grained silt–pelite fraction (<0.04 mm). The sand and coarse-grained silt fraction was split in a bromoform into the light (<2.8 g/cm^3) and heavy (>2.8 g/cm^3) fractions and these fractions were examined mineralogically, too. The heavy (concentra-

Table 1. **Anomalous values of trace elements of accessory association in Lithuanian soils, ppm**
1 lentelė. **Anomalus akcesorinės asociacijos mikroelementų kiekis Lietuvos dirvožemiuose ppm**

No. of anomaly in Fig. 1	Locality of anomaly	Soil	Trace elements					
			Ti	Zr	Nb	Y	Yb	La
1	Mūša–Nemunėlis glaciolacustrine basin							
		Clay	5168	360	12.9	44.3	4.4	60.9
2	Kaunas–Kaišiadorys glaciolacustrine basin							
		Clay	8869	480	21.7	47.1	6	48.9
3	Kaunas–Kaišiadorys glaciolacustrine basin							
		Sandy loam	3252	823	17.2	23	3.8	28
4	Vievis–Širvintos glaciolacustrine basin							
		Clay	4580	651	14.3	25.8	3.8	26.7
5	Jūra–Šešupė glaciolacustrine basin							
		Sand	3210	262	16.9	12.7	2.1	26.2
6	Medininkai Upland	Loam	3707	760	17.1	28.5	4	35.2
7	The Merkys river valley	Sandy loam	3152	458	25.8	21	2.4	23
8	The Grūda river valley	Organic	2975	226	10.3	38	3.7	30.6
		Loam-clay	2875	263	13.6	18.8	2.4	26.5
Background (median) values in soil of Lithuania		Sandy loam	2512	280	13.7	16.1	2.1	23.0
		Sand	1716	222	12.5	10.7	1.5	17.2
		Organic	1670	142	6.8	15.4	1.5	19.2

Table 2. **Coefficients of concentration and sequence of accumulation of trace elements in soil anomalies**
2 lentelė. **Mikroelementų koncentracijos koeficientai ir jų kaupimosi eilės dirvožemio anomalijose**

No. in Fig. 1	Locality of anomaly	Soil	Coefficient of concentration						Sum	Sequence of accumulation
			Ti	Zr	Nb	Y	Yb	La		
1	Mūša–Nemunėlis glaciolacustrine basin	Clay	1.8	1.4	0.9	2.4	1.8	2.3	10.6	Y–La–Ti–Yb–Zr
2	Kaunas–Kaišiadorys glaciolacustrine basin	Clay	3.1	1.8	1.6	2.5	2.5	1.8	13.4	Ti–Y–Yb–Zr–La–Nb
3	Kaunas–Kaišiadorys glaciolacustrine basin	Sandy loam	1.3	2.9	1.3	1.4	1.8	1.2	9.9	Zr–Yb–Y–Ti–Nb–La
4	Vievis–Širvintos glaciolacustrine basin	Clay	1.6	2.5	1.1	1.4	1.6	1.0	9.1	Zr–Ti–Yb–Y–Nb
5	Jūra–Šešupė glaciolacustrine basin	Sand	1.9	1.2	1.4	1.2	1.4	1.5	8.5	Ti–La–Yb–Nb–Y–Zr
6	Medininkai Upland	Loam	1.3	2.9	1.3	1.5	1.7	1.3	9.9	Zr–Yb–Y–Ti–Nb–La
7	The Merkys river valley	Sandy loam	1.3	1.6	1.9	1.3	1.1	1.0	8.2	Nb–Zr–Ti–Y–Yb–La
8	The Grūda river valley	Organic	1.8	1.6	1.5	2.5	2.5	1.6	11.5	Y–Yb–Ti—Zr–La–Nb
	Soil of glaciolacustrine basins		1.9	2.0	1.2	1.8	1.8	1.6	10.3	Zr–Ti–Y–Yb–La–Nb
	Soil of all anomalies		1.7	2.0	1.4	1.8	1.8	1.5	10.1	Zr–Y–Yb–Ti–La–Nb

te), fine-grained light (<0.04 mm) and residual (sand–silt and heavy minerals) fractions were separated by the inert-dynamic method. In constituent minerals of these fractions the content of trace elements was determined by the method of stadial emission–spectral scintillation analysis.

Statistical parameters of the distribution of trace elements were calculated and their graphic expression obtained using Excel software.

RESULTS

Distribution of anomalies. Anomalies of trace elements of the accessory association have been found throughout Lithuania in all types of soil (Fig. 1). The content of these trace elements in them is a few times higher (Table 2) than the median values for Lithuanian soils (Kadūnas et al., 1999). More intensive anomalies of these trace elements have been detected in glaciolacustrine basin sediments of the last Nemunas (Weichselian) glaciation. According to concentration coefficients in the graded accumulation sequence of these components, Zr, Y, Yb and Ti are the most readily accumulating ones. An anomalous content of these elements was also found in the soils of Medininkai Upland, which have formed on glacial sediments of the penultimate glaciation (Saalian). The highest values were determined for Zr, Yb and Y (Table 2). Anomalous concentrations of these components have also been detected in soils formed on alluvial sediments (the Merkys and the Grūda river walleys).

Anomalous contents of ***titanium*** were observed in all samples. According to the concentration coefficients its anomalies were not very intensive (Kk < < 2d) in most cases. Its intensive anomaly has been found only in the clay soils of the Kaunas–Kaišiadorys glaciolacustrine basin (Kk = 3.1) (Table 2). The content of Ti in grain-size fractions increases with the amount of fine mineral particles (Fig. 2) and reaches its maximum in pelite fraction. Consequently, the anomalous concentration of Ti in clay-loam soils depends on the content of pelite fraction (<0.01 mm), which is the dominant in clay soil (over 50%). Increased contents of Ti were found in some samples of the silt fraction of soil. In all these cases the content of Ti was ~1.5 times higher in fine-grained (0.05–0.01 mm) than in coarse-grained silt. The silt fraction in clay-loam soil did not exceed 20–30%. Therefore the accumulation of Ti in it made up 15–20% of the total in the soil sample. In the sand fraction the concentration of Ti was minimal (Md = 460 ppm) and did not affect its concentration in anomalous samples, reaching only a few per cent of the total. Differentiation of fine-grained sand fraction (0.25–0.1 mm) into three groups of

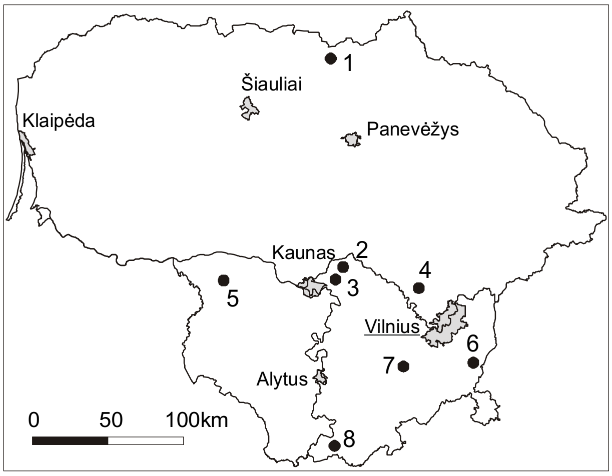

Fig. 1. Anomalies of trace elements of accessory association in soil of Lithuania. For names of anomalies, see Tables 1 and 2

1 pav. Akcesorinės asociacijos mikroelementų anomalijos dirvožemyje. Vietovių pavadinimai – 1 ir 2 lentelėje

mineral density revealed an almost equal accumulation of Ti in both groups of heavy minerals, where its concentration exceeded the concentration in the group of light minerals 20–40 times (Fig. 3). The content of minerals in sand–silt fraction of soil did not exceed 1%. Therefore their influence on the total amount of Ti in a sample is not decisive, though the mentioned fraction contains Ti minerals such as ilmenite (up to 35% of the content of heavy minerals) and rutile (up to 0.8%). These minerals most probably predetermine the anomalous Ti contents when they are accumulated in pelite fraction. Increased contents in these fractions were determined by stadial emission scintillation analysis. In this fraction, ilmenite is often replaced by leucoxene or authigenous anatase (Berrow, Mitchell, 1991). Replacement of ilmenite by leucoxene has been also observed in the soils of Medininkai Upland, where anomalous concentrations of Ti and other elements of the association are related to the long-term weathering processes (Vareikienė, 2001). Presumably, part of Ti in pelite fraction is contained in the intergrowths of Ti minerals and other minerals and in sorbed form ($Ti(OH)_3$), especially in hydromicas. A comparatively high content of Ti observed in the group of minerals with a density 2.8–3.3 g/cm^3 implies that the main Ti minerals, ilmenite (density 4.7 g/cm^3) and rutile (4.3 g/cm^3), exist as not independent mineral individuals but as an isomorphous impurity in crystals or minerals (biotite, hornblende).

Zirconium is one of the most intensively accumulating trace elements in this kind of anomalies. Its concentration coefficients in the soils of glaciolacustrine basins vary from 1.2 (sand) to 2.9 (sandy

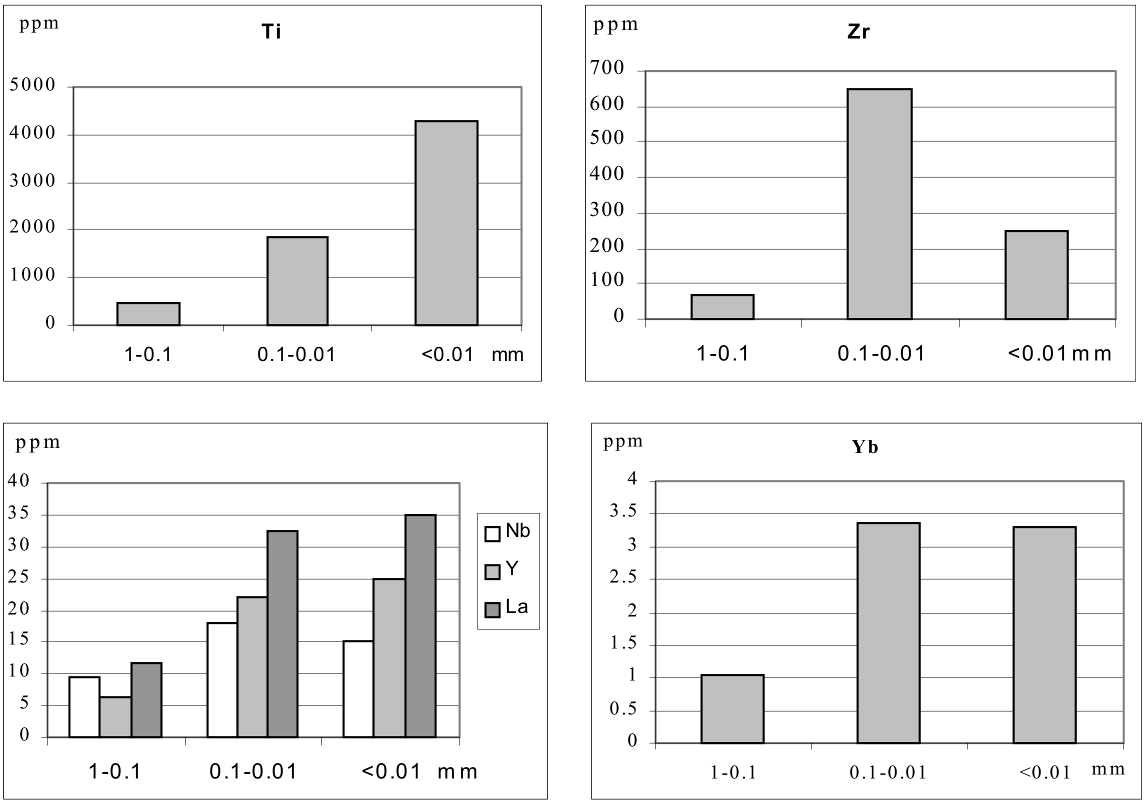

Fig. 2. Content of trace elements of accessory association in soil granulometric fractions
2 pav. Akcesorinių mineralų mikroelementų kiekis dirvožemio granuliometrinėse frakcijose

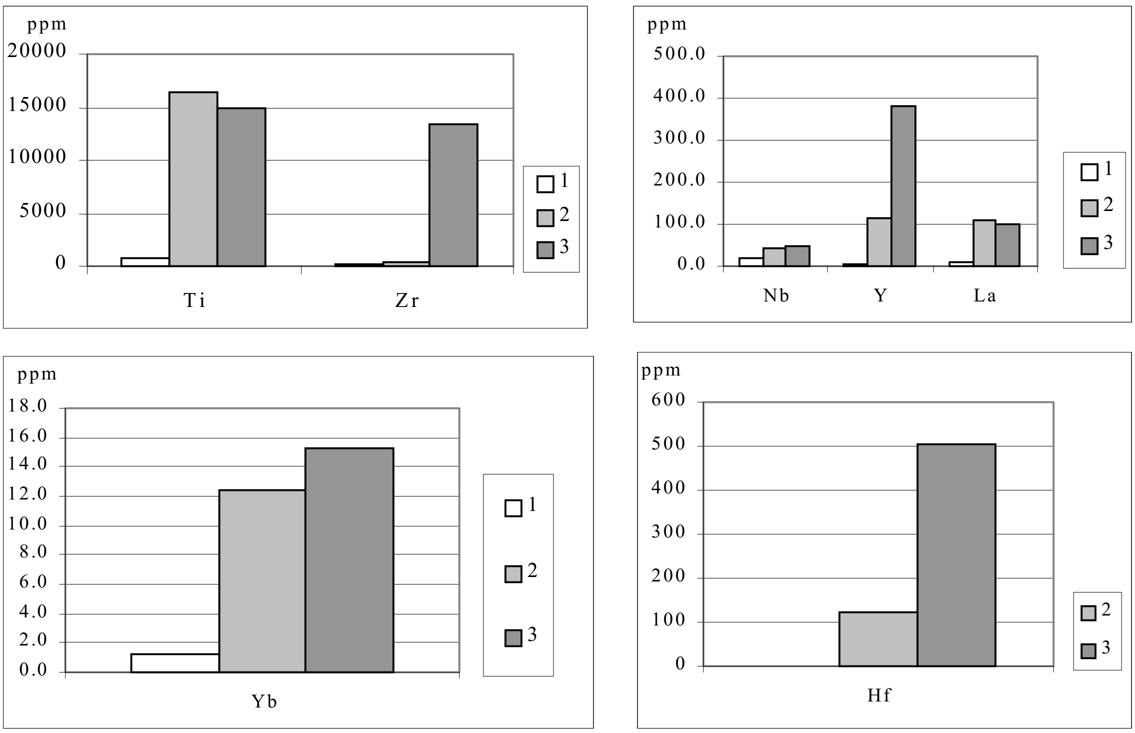

Fig. 3. Content of trace elements in fine-grained sand (0.25–0.1 mm) fraction of soil, divided by density into: *1* – <2.8; *2* – 2.8–3.3; *3* – 3.3 g/cm^3
3 pav. Mikroelementų kiekis dirvožemio smulkaus smėlio frakcijoje (0,25–0,01 mm), suskirstytoje pagal tankį: *1* – <2,8; *2* – 2,8–3,3; *3* – 3,3 g/cm^3

loam). In the loam of Medininkai Upland it reaches 2.9. According to concentration coefficients, Zr occupies the leading position in the graded sequence of these components (Table 2). In contrast to Ti, zirconium mostly accumulates in the silt fraction of soil (2.6 times as much as in clay fraction and 9.6 times as much as in sand fraction) (Fig. 2). This distribution pattern of Zr has been determined in all types of Lithuanian soils (Kadūnas, Gregorauskienė, 1999).

Increased contents of Zr mostly depend on the content of mineral zircon in the soil, which in anomalous soil samples makes up 5–8% of the content of heavy minerals (Table 3). Its certain portion is also associated with rutile and ilmenite (Table 4). In contrast to other trace elements of this group, Zr accumulates only in the group of the heaviest minerals (density >3.3 g/cm^3), where Zr concentration in some anomalous samples reaches 1.5–2%. Despite the fact that these minerals account for not more than 0.5% of the total mineral mass of soil, their influence on the formation of anomalous Zr concentrations is great. Zircon tends to exist in silt as an independent mineral individual and almost does not participate in intergrowhts with light minerals or rarely occurs in other minerals as microcrystal spots. Therefore its concentration in the fraction with a density of 2.8–3.3 g/cm^3 is low (Fig. 3). The concentration of zircon in pelite fraction is slightly lower than in the fractionally undifferentiated sample. It also contains mineral zircon, but part of Zr in pelite fraction may be present in the form of sorbed ions (Berrow, Mitchell, 1991).

Table 3. **Mineral composition of high part (density >2.8 g/cm3) of sand and coarse-grained silt fraction in the soil of the Kaunas–Kaišiadorys glaciolacustrine basin**
3 lentelė. **Kauno–Kaišiadorių limnoglacialinio baseino dirvožemio smėlio-stambaus aleurito frakcijos sunkiosios dalies mineralinė sudėtis**

Minerals	Sandy loam		Loam	
	g	%	g	%
Quartz	0.03	8.0	0.023	4.5
Feldspars of potassium	0.002	0.5	0.011	2.2
Ilmenite	0.13	34.6	0.026	5.1
Garnets	0.05	13.3	0.13	25.7
Zircon	0.02	5.3	0.04	7.9
Hematite	0.07	18.7	0.026	5.1
Limonite	0.01	2.7	0.001	0.2
Pyrite	0.004	1.1	0.004	0.8
Rutile	0.0012	0.3	0.004	0.8
Tourmaline	0.006	1.6	0.007	1.4
Magnetite	0	0.0	0.012	2.4
Galenite	0	0.0	0.002	0.4
Epidote	0.001	0.3	0.02	4.0
Hornblende	0	0.0	0.08	15.8
Actinolite	0	0.0	0.031	6.1
Sericite, chlorite	0	0.0	0.012	2.4
Intergrowths of different minerals	0.051	13.6	0.077	15.2
Total	0.3752	100	0.506	100

Table 4. **Content of chemical elements in accessory minerals (Иванов, 1997)**
4 lentelė. **Cheminių elementų kiekiai akcesoriniuose mineraluose (Иванов, 1997)**

Minerals	Content, %						
	Ti	Zr	Nb	Y	Yb	La	Hf
Ilmenite	31.6	0.34	0.02				0.004
Rutile	60	0.5	0.09	0.35–0.48			
Zircon	1.5–1.7	49.5	0.02–0.05	0.3–0.35	0.024–0.03		to some %
Magnetite	to some %	0.045	0.005–0.21	0.015			0.004
Apatite		0.15		0.11	0.0017	0.018–0.032	
Monazite		to some %		to 1%		to some tens %	
Tourmaline				0.005–0.011			
Garnets	0.5–0.6			0.13	0.007		0.0005–0.0014
Biotite	to some %		0.02	0.013		0.014	
Hornblende	to some %						
Hematite	to some %						
Epidote					0.02		

Niobium and ***ytterbium*** anomalies are associated with increased contents of heavy minerals. The most contrasting anomaly of Nb has been determined in the sandy loam formed on the Merkys valley silt (Kk = 1.9). Anomalies of Yb are characteristic of the soils of glaciolacustrine basins (Kk up to 2.5). Its highest values have also been found in the silt fraction of soil, but their difference from the values found in pelite fraction is smaller than that of Zr values (1.2–1.3 times) (Fig. 2). The soil contained no minerals with Nb as the main constituent. The varying concentrations of Nb depend on the content of zircon, rutile, ilmenite, magnetite and biotite in the soil (Table 4). These minerals have been also detected in the pelite fraction of soil. Zircon and garnets are the main minerals predetermining the concentration of Yb in the soil. Their portion among heavy minerals of sand-clay fraction in the soil of the Kaunas–Kaišiadorys glaciolacustrine basin makes from 13 to 26% (Table 3). The ytterbium anomaly may be related to increased contents of apatite (Baltrūnas, 1995).

A high concentration of hafnium (up to 0.07% in dense minerals >3.3 g/cm^3) has been observed in the same portion of heavy minerals, where the concentrations of mineral zircon are high. Increased concentrations of cerium and neodymium (Ce up to 146, Nd up to 48 ppm) have been found in the pelite fraction of soils of the Kaunas–Kaišiadorys glaciolacustrine basin. This implies a high diversity of isomorphous impurities of accessory minerals.

Heavy accessory minerals are also responsible for higher concentrations of other rare-earth elements in the soil (***yttrium*** and ***lanthanum***). Their most contrasting anomalies have also been found in soils of the glaciolacustrine basin (Y concentration coefficient up to 2.5, La up to 2.3). Yttrium and lanthanum most readily accumulate in silt and pelite fractions (Fig. 2). They are isomorphous impurities in heavy minerals. An unidentified mineral phase (monazite?) of La has been observed in the pelite fraction of loam in the Kaunas–Kaišiadorys glaciolacustrine basin. Part of the ions of these elements – mobile in water containing hydrocarbonate ions and organic matter – can be sorbed by minerals of pelite fraction, carbonates and hydromicas in the first place (Иванов, 1997). Part of Y and La ions in pelite fraction may be anthropogenic in origin, *i.e.* come with phosphorus fertilizers, where the concentration of these components is several times higher than in the soil (Сает, 1990). Therefore, some anomalies of these elements may be associated with the use of the mentioned fertilizers (Vareikienė, 1998).

CONCLUSIONS

Anomalous concentrations of titanium, zirconium, niobium and rare-earth elements (Y, Yb, La, Ce, Nd) in Lithuanian soils mostly depend on the content of accessory heavy minerals. Increased contents of these minerals are associated with the genesis of soil parent material: deposition of glaciolacustrine or alluvial sediments or a long-term weathering process when the content of resistant minerals relatively increases in a weathered horizon. The trace elements studied are the main elements in accessory heavy minerals (Ti in rutile and ilmenite, Zr in zircon), or important isomorphous impurities (Ti in magnetite and biotite, Zr in rutile, ilmenite and magnetite, Nb in rutile, zircon and magnetite, Y and Yb in zircon and garnets, La in apatite, monazite and biotite). Resistant heavy minerals accumulate in fine-grained silt and pelite fraction as individual minerals, as micro-insertions in low density minerals (amphiboles, micas, garnets, feldspars, etc.), or form aggregate intergrowths with other light main soil minerals (clay minerals, potassium feldspars, plagioclases, micas). This explains a comparatively high concentration of elements of accessory association in light mineral fractions. In pelite fraction, which is often responsible for anomalous concentrations of elements in the whole soil, they may exist not only in mineral form but also in the form of sorbed ions. The latter form is especially important for the elements of the association that are mobile in water (Y, La). Part of these ions may be of anthropogenic origin, *i. e.* related to the use of phosphorous fertilizers.

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Ti, Zr, Nb IR RETŲJŲ ŽEMIŲ ELEMENTŲ GAMTINIŲ ANOMALIJŲ GENEZĖ LIETUVOS DIRVOŽEMIUOSE

S a n t r a u k a

Lietuvos dirvožemyje kai kuriose vietovėse yra padidėjęs Ti, Zr, Nb ir retųjų žemių elementų (Y, Yb, La, Ce) kiekis (1 pav.). Šie mikroelementai pasižymi glaudžiais tarpusavio koreliaciniais ryšiais ir yra susiję su atspariais dūlėjimui alotigeniniais akcesoriniais mineralais, todėl paviršiaus nuosėdose išskiriami į paragenetinę akcesorinę asociaciją. Nors šių mikroelementų kiekis dirvožemyje yra mažas (išskyrus Ti ir Zr), tačiau jie dalyvauja biogeocheminiuose procesuose ir turi įtakos gamtinės aplinkos kokybei.

Dirvožemio A horizonto mėginiai buvo tirti panaudojus įvairius metodus: granuliometrinį, skirstymą sunkiuose skysčiuose išskiriant mineralų grupes pagal tankį, optinės emisinės spektrinės, rentgenostruktūrinės, rentgenofazinės analizės ir inercinį-dinaminį.

Intensyviausios šių elementų anomalijos aptiktos dirvožemiuose, susiformavusiuose Nemuno ledynmečio limnoglacialinių baseinų nuogulose (1 lentelė). Pagal koncentracijos koeficientus išrūšiuotoje šių elementų kaupimosi eilėje prie labiausiai besikaupiančių elementų priskiriami Zr, Y, Yb ir Ti. Medininkų aukštumos dirvožemiuose, susiformavusiuose priešpaskutinio ledynmečio glacigeninėse nuogulose, taip pat nustatyti anomalūs šių elementų kiekiai. Juose labiausiai besikaupiantys elementai yra Zr, Yb ir Y (2 lentelė). Šių elementų anomalijos taip pat nustatytos dirvožemiuose, susiformavusiuose aliuvinėse nuosėdose (Merkio ir Grūdos upių slėniuose). Jų anomaliniai kiekiai daugiausia priklauso nuo akcesorinių sunkiųjų mineralų kiekio (3 lentelė). Šių mineralų pagausėjimas kai kuriose Lietuvos vietovėse yra susijęs su dirvodarinių uolienų geneze – nuosėdų frakcionavimo procesais klostantis limnoglacialinėms ar aliuvinėms nuosėdoms arba ilgai trukusiu dūlėjimo procesu, kai išdūlėjusiame horizonte santykinai pagausėja atsparių dūlėjimui mineralų kiekis. Akcesoriniuose sunkiuosiuose mineraluose šie mikroelementai yra pagrindiniai elementai (Ti – rutile ir ilmenite, Zr – cirkone) arba reikšmingos izomorfinės priemaišos (Ti – magnetite ir biotite, Zr – rutile, ilmenite ir monacite, Nb – rutile, cirkone ir magnetite, Y ir Yb – cirkone ir granatuose, La – apatite, monacite ir biotite) (4 lentelė). Šie atsparūs dūlėjimui sunkieji mineralai kaupiasi smulkaus aleurito ir pelitinėje frakcijose, todėl jose akcesorinės asociacijos mikroelementų kiekis yra didžiausias (2 pav.). Šie mineralai kaip mikromineralai-įtarpai kituose mažesnio tankio mineraluose (amfiboluose, žėrutyje, granatuose, feldšpatuose ir kt.) būna savarankiški individai arba sudaro agregatinius suaugimus su kitais lengvais pagrindiniais dirvožemio mineralais (molio mineralais, kalio feldšpatais, plagioklazais, žėručiu). Tuo paaiškinamas palyginti didelis šios asociacijos elementų kiekis ne tik pačioje sunkiausioje dirvožemio frakcijoje (3 pav.). Pelitinėje frakcijoje, nuo kurios kiekio dažniausiai priklauso anomalus šios asociacijos elementų kiekis visame dirvožemyje, jie, be mineralinės, būna ir sorbuotų jonų formos. Pastaroji ypač svarbi tiems šios asociacijos elementams, kurie yra judrūs vandenyje (Y, La). Dalis tokių jonų, daugiausia susijusi su fosforo trąšų naudojimu, gali būti technogeninės kilmės.

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ГЕНЕЗИС АНОМАЛИЙ Ti, Zr, Nb И РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В ПОЧВАХ ЛИТВЫ

Р е з ю м е

На территории Литвы в некоторых местах в почве установлены повышенные содержания Ti, Zr, Nb и редкоземельных элементов (Y, Yb, La, Ce) (рис. 1). В почве эти микроэлементы связаны между собой сильными корреляционными связями, а их носителями в основном являются устойчивые к выветриванию акцессорные минералы, поэтому микроэлементы выделяются в парагенетическую акцессорную ассоциацию. Содержание упомянутых микроэлементов в почвах обычно невелико (за исключением Ti, Zr), однако они участвуют в биогеохимических процессах и влияют на качество окружающей среды.

Образцы почв были отобраны с горизонта A_1 и исследованы с помощью различных методов: гранулометрического, разделения в тяжелых жидкостях, инерционно-динамического, эмиссионно-спектрального, рентгено-структурного и рентгено-фазового.

Наиболее интенсивные аномалии этих элементов установлены в почвах, образовавшихся на отложениях лимногляциальных бассейнов Нямунского (Валдайского) оледенения (таблица 1). Наиболее высокими коэффициентами концентрации (Кк) выделяются Zr, Y, Yb и Ti. В почвах Мядининкской возвышенности, образовавшихся на отложениях Мядининкского (Московского) оледенения, также установлены аномальные концентрации этих элементов. В них по высоким Кк выделяются Zr, Yb и Y (таблица 2). Аномальные содержания этих элементов установлены также в почвах, образовавшихся на аллювиальных отложениях (в долинах рек Мяркис и Груда). Содержания этих элементов в почвах в основном зависят от содержания акцессорных тяжелых минералов (таблица 3). Увеличение содержания этих минералов в отложениях в основном зависит от генезиса материнских пород, от процессов естественного фракционирования осадков по плотности при образовании лимногляциальных или аллювиальных отложений, а также от длительного процесса выветривания, из-за которого в почвах увеличивается количество устойчивых к выветриванию минералов. В

акцессорных минералах эти микроэлементы могут быть основными (Ti – в рутиле и ильмените, Zr – в рутиле, ильмените и монаците, Nb – в рутиле, цирконе и магнетите, Y и Yb – в цирконе и гранатах, La – в апатите, монаците и биотите) (таблица 4). Устойчивые к выветриванию минералы накапливаются в пелитовой и мелкоалевритовой фракциях, поэтому в них установлены наиболее высокие концентрации микроэлементов этой ассоциации (рис. 2). Минералы выступают как самостоятельные индивиды, как составные части других более легких минералов (микроминералов), а также образуют агрегатные сростки с иными легкими основными минералами почв (фельдшпатами, слюдами, глинистыми минералами). Этим объясняется наличие аномальных содержаний названных элементов не только в самой тяжелой минеральной фракции почв (рис. 3). В пелитовой фракции, от содержания которой в почвах в основном и зависят аномальные содержания этих микроэлементов в целом, им, кроме минеральной, присуща и сорбционная форма, особенно более подвижных в водной среде элементов (Y, La). Часть сорбированных ионов этих элементов имеет техногенную природу и попадает в почву с фосфорными удобрениями.