GEOLOGIJA. 2005. T. 52. P. 1–10

Geochemija • Geochemistry • Ãåîõèìèÿ

Allothigenous accessory elements in sandy-loamy soil formed in sediments of periglacial zone, Lithuania

Olga Vareikienë

Vareikienë O. Allothigenous accessory elements in sandy-loamy soil formed in sediments of periglacial zone, Lithuania. *Geologija*. Vilnius. 2005. No. 52 P. 1-10. ISSN 1392-110X

The geochemistry of sandy-loamy soil (horizon A_1) of Ašmena Highlands was formed in sediments of periglacial zone studied with reference to allothigenous accessory elements (Zr, Ti, La, Y, Yb, Nb). The distribution of elements among particle-size fractions and light and heavy mineral separates was evaluated. The percentage contribution of different particle-size fractions as well as the contribution of fine-silt-sized heavy minerals to the total content of elements in the whole soil (<2000 mm) were calculated.

Sediments of Ašmena Highlands deposited during Saalian glaciation have been affected during the last 100000 years by weathering processes of Eemian interglacial, Weichselian periglacial and postglacial periods. Weathering and soil-forming processes in the sandy-loamy soil of Ašmena Highlands resulted in the highest content of fine silt and the lowest of clay. In comparison to middle and fine sand, a higher content of heavy minerals was yielded in fine silt.

Ti, Y, Yb, Nb and La were found most intensively accumulated in clay fraction and Zr in fine silt. Because the most significant contribution of all elements, except La, was of the fine silt, the latter was assumed to be the main fraction predetermining the total content of all elements, except La, in the whole soil. Heavy mineral separate of this fraction is characterised by intensive accumulation of allothigenous accessory elements (AAE). It predetermined that heavy minerals account for about 70% of all AAE in fine silt fraction, in spite of the fact that heavy minerals comprise only a very small part of the fraction.

The AAE contribution of fine-silt-sized heavy minerals accounted for more than 90% of Zr and Nb, about 70% of Y, about 50% of Ti and total Yb contents in soil. The significance of heavy minerals for total La content in soil was somewhat less important.

Allothigenous accessory elements are part of the total chemical composition of soil, mainly hosted by weathering-resistant minerals. Therefore, a study of their content and distribution is one of the clues to a better understanding of soil geochemistry and will be useful for further studies of soil as well as of Quaternary sediments in terms of evidence for their weathering since deposition.

Key words: periglacial zone, sandy-loamy soil, geochemistry, allothigenous accessory element, coefficient of accumulation, contribution of particle-size fraction, heavy mineral contribution

Received 02 May 2005, accepted 31 May 2005.

Olga Vareikienë, Institute of Geology and Geography, 2600 Vilnius, Lithuania. E-mail: vareikiene@geo.lt

INTRODUCTION

The redistribution of elements in the surface environment of sediments occurs as a result of physical and chemical weathering. The final products of weathering could be defined as soluble constituents, insoluble secondary minerals, and insoluble residual primary minerals (Kauranne et al., 1992). The latter minerals are the main hosts of allothigenous accessory elements (Zr, Ti, Nb, La, Y, Yb) and therefore are considered to be their main mode of occurrence. Assuming that weathering is greatest towards the surface, and that the rate of weathering exceeds that of translocation, the disintegration of primary minerals should be expressed as an increase of the content of fine-sized primary minerals. Therefore, evidence for weathering since sediment deposition may be recognized as a comminution of primary minerals and their redistribution as well as redistribution of allothigenous accessory elements among the particle-size fractions of sediment.

Sediments of Ašmena Highlands deposited during Saalian glaciation have been affected during the last 100000 years by weathering processes of Eemian interglacial, Weichselian periglacial and postglacial periods. Due to the long duration of weathering processes and especially intensive mechanical disintegration of rock fragments and minerals during Weichselian periglacial, the particle size composition of sediments changed markedly. Changes have caused the uniformity of mineral composition of sediments and formation of a soil distinguished by a homogeneous (mainly sandy-loamy) composition (Basalykas ir kt., 1976). An areal of geochemical anomaly of allothigenous accessory elements was distinguished in this soil (upper horizon A_1) (Kadûnas, 1999). Weathering and soil-forming processes are also very well recorded by the washout of carbonates and iron compounds from the upper part of the soil profile in which the depth of elution mainly depends on the duration of weathering. Carbonates from the soil of Ašmena Highlands were washed out from the upper two meters of the profile (Эйдукявичене, Кудаба, 1977). Due to a complete loss of carbonates, the soil has become slightly acid (pH is about 6.5) (Kadûnas ir kt., 1999). Because mineral stability is fundamentally related to pH, its lower value leads to a more intensive breakdown of minerals and disappearance of mineral species that are less resistant to weathering. In Ašmena Highlands pyrite was not found in some places down to 50 m of the glacial sediment profile, and the weathering of amphiboles and minerals of epidote group was observed (Ðinkûnas, Jurgaitis, 1998).

Sediments of the periglacial zone were studied extensively in different aspects (Basalykas ir kt., 1976; Kozarski, 1993; Vandenberghe and Pissart, 1993; Murton and French, 1994; Christiansen, 1996; French, 1996; Jary, 1996; Gaigalas ir kt., 1998; Issmer, 1999; Kida and Jary, 2001; Švedas, 2001; Jary et al., 2002; Švedas ir kt., 2004). The present paper is a contribution to a better understanding of the geochemistry of soil formed in sediments of areas that at times have been subjected to periglacial conditions. Allothigenous accessory elements (AAE) are part of the total chemical composition of soil, mainly hosted by weathering-resistant minerals. Therefore, studying the AAE content and distribution in soil is one of the clues to a better understanding of soil geochemistry, and it will be useful for further studies of soil as well as of Quaternary sediments in terms of evidence for their weathering since deposition.

The aim of this research was to distinguish the lithological and geochemical features of the sandy-loamy soil formed in sediments of the periglacial zone with reference to allothigenous accessory elements. The main points of study were estimation of AAE distribution among particle-size fractions, evaluation of element contribution of particle-size fractions to the element total content in the whole soil (<2000 µm) and assessment of the contribution of fine-silt-sized heavy minerals to the total content of elements in soil.

METHODS

Sampling, sample preparation and analytical methods. In the sandy-loamy soil of Ašmena Highlands, the area with the highest content of AAE was chosen. The selection was based on the statistical processing of data obtained by chemical analysis of samples from the upper part of soil (0–10 cm) collected during the geochemical mapping of Lithuania and stored in the database of Division of Environmental Geochemistry of Institute of Geology and Geography (Kadûnas ir kt., 1999). For detailed particle-size, chemical and mineralogical analyses, a representative sample (about 80 kg) composed of several subsamples from a 5 m × 5 m square was collected from upper part of soil (A_1 horizon). Preparation of representative soil sample was made at the Research Laboratory of the GSF. The sample was dried at room temperature and sieved to get the fraction <2000 µm. Organic matter was destroyed by hydrogene peroxide (H_2O_2), and after pretreatment the dissolved organic compounds were washed from the residual part using distilled water. The remaining part was dried in the oven at less than 50 °C and comminuted on ceramic plate by hand. Before taking parts of the sample for chemical and mineralogical analyses, homogenization and quartering were carried out. The clay (<5 µm) fraction was sedimentated, fine silt (5–63 µm), coarse silt (63–100 µm), fine sand (100–250 µm), middle sand (250–500 µm), coarse sand (500–1000 µm), and fine gravel (1000–2000 µm) fractions were dry-sieved. To get light and heavy mineral separates, the middle and fine sand fractions were separated using a heavy liquid of d = 3.0 g/cm^3, and for fine silt a heavy liquid of d = 2.78 g/cm^3 was used. The fractions were weighed and the percentage by the mass of each fraction was calculated. Errors of particle-size analysis were minimized by redistributing the remaining weight among fractions depending on their size in the whole soil sample. Primary soil, particle-size fractions, light and heavy mineral separates were analysed by ICP-MS using HF + $HClO_4$ acid dissolution and $LiBO_2$ fusion at the Chemical Laboratory of the GSF.

A polished thin section of fine-silt-sized heavy minerals was made by mounting them in epoxy resin. Evaluation of mineral distribution was performed on the thin section using backscattered electron image (BEI) analysis by an ISM-5900LV scanning microscope equipped with an energy-dispersive X-ray spectrometer (EDS) at the Research Laboratory of the GSF (Vareikienë and Lehtonen, 2004). The result of mineralogical analysis was reported as the percentages of counted heavy minerals. Amphiboles were represented mostly by hornblende, orthopyroxenes by enstatite, clinopyroxenes by diopside, and garnets by almandine.

For evaluation of AAE accumulation intensity in particle-size fractions and light- and heavy mineral separates, the coefficient of accumulation (Ca) was determined by dividing the content of an element in a fraction or a separate by its content in the whole soil sample (<2000 μm).

The weighted content of elements in the particle-size fraction was calculated multiplying the content of element in the fraction by the weight of fraction. The percentage of the weighted content of element in a fraction from the sum of the weighted content of the element in all analysed fractions was used to evaluate the contribution of each fraction to the total content of an element in the whole soil.

For estimation of element contribution of each heavy mineral-carrier, the content of mineral-carrier (%) in the particle-size fraction as well as in the whole soil was estimated. Based on the content of an element in the carrier-mineral (Leibovitz and Smith, 1983) and the content of carrier minerals in the whole soil, the theoretic content of elements in all car-

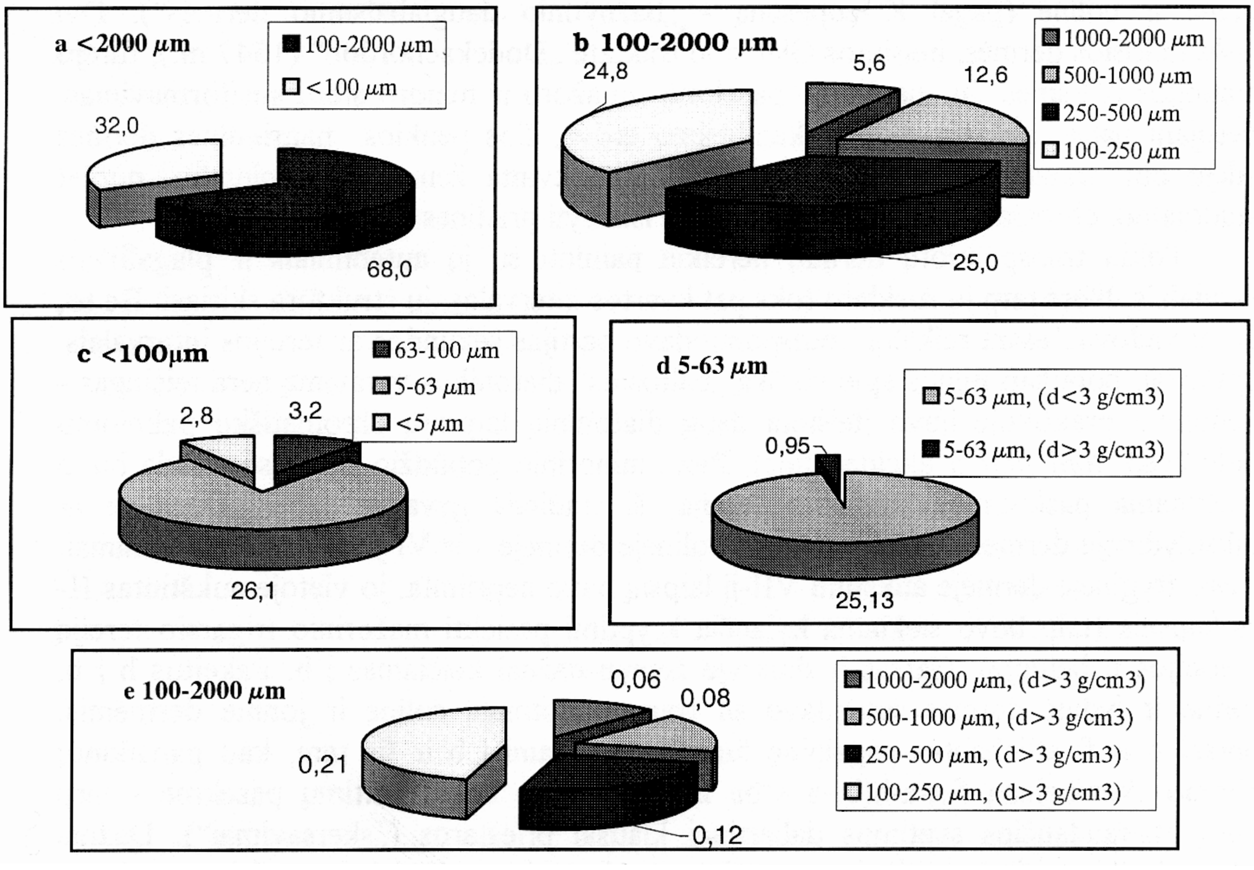

Fig. 1. Particle-size composition (%) of sandy-loamy soil of Ašmena Highlands: *a* – gravel-sand and silt-clay fractions, *b* – gravel-sand-sized fractions, *c* – silt-clay-sized fractions, *d* – content of heavy (d > 3 g/cm^3) and light (d < 3 g/cm^3) minerals in fine silt fraction, and *e* – content of heavy minerals in gravel-sand-sized fractions

1 pav. Aðmenos aukðtumø priesmëlingo dirvoþemio granuliometrinë sudëtis (%): *a* – þvirgþdo-smëlio ir aleurito-molio frakcijos, *b* – þvirgþdo-smëlio frakcijos, *c* – aleurito-molio frakcijos, *d* – sunkiøjø (d > 3 g/cm^3) ir lengvøjø (d < 3 g/cm^3) mineralø kiekis smulkaus aleurito frakcijoje, *e* – sunkiøjø mineralø kiekis þvirgþdo-smëlio frakcijose rier-minerals was calculated. The percentage proportion of an element content of all heavy carrier-minerals from the total content of this element in soil showed the contribution of carrier-minerals to the total content of the element in soil. For recalculation of element contribution of carrier-minerals, only minerals with a density >3 g/cm^3 were chosen.

RESULTS AND DISCUSSION

The particle-size composition of sandy-loamy soil of Ašmena Highlands is detailed in Fig. 1. The most abundant fractions are fine sand (24.8%) and fine silt (26.1%); the clay fraction comprises only a very small part of soil (2.8%) (Fig. 1 b, c). Sandy-loamy soil is usually defined by a more or less equal content of clay, silt and sand (Kadûnas, Gregorauskienë, 1999). Due to weathering and soil-forming processes these proportions could be changed, because part of clay particles could be washed from the upper part of soil down the profile. Clay mineral translocation was proven by X-ray diffraction analysis (XRD) of the light part (d < 2.78 g/cm^3) of soil fine fraction (<100 mm) (Vareikienë et al., 2003) and by geochemical indices characteristic of the soil of Aðmena Highlands (Kadûnas, 2000). According to XRD data, the most abundant minerals in the light fraction include quartz, K-feldspar, plagioclase, dioctahedral mica (mostly illite) and chlorite. Clay minerals of neither the kaoline nor smectite groups were encountered. Most likely such translocation of clay particles was one of the reasons that predetermined the peculiarities of the particle-size composition of sandy-loamy soil in Ašmena Highlands. It caused a relative enrichment of upper soil horizons by weathering-resistant minerals as well as by immobile elements mainly hosted by these minerals. The enrichment of Zr and Ti in the upper horizon of podzol soil with respect to the concentration in the parent till was attributed to the removal of the other more reactive (weatherable) components (Law et al., 1991).

Minerals are one of the main soil parts representing a relatively stable mode of occurrence of trace elements in soil, and their solubility could be a resultant of the influence of several simultaneous factors such as the intensity and nature of weathering and especially the structure and properties of minerals. The resistance order of mineral groups can be generally defined as oxides > silicates > carbonates and sulphides (Kauranne et al., 1992). In a detailed study of the weathering of heavy minerals in acid soil profiles in terms of their relative mineral proportions in the 45–63 μm coarse-silt fraction of soils developed on tills in southwestern Sweden, the following order of stability was found: apatite < titanite < hornblende < garnet < epidote < zircon. Low soil pH conditions are believed to have prevailed since deglaciation, and this relative order of stability has remained the same. Only the weathering intensity of most pH sensitive heavy minerals may have considerably changed during the time of sediment exposure (Lång, 2000). The weathering processes influence the transfer of coarser minerals to finer fractions and their enrichment with heavy minerals hosted before as inclusions in coarser minerals. In the sandy-loamy soil of Ašmena Highlands, the highest content of heavy minerals is yielded in the fine silt fraction in comparison with the middle and fine sand fractions (Fig. 1 d, e). The content of heavy minerals in the silt-sized fraction of soil was reported by M. L. Berrow and R. L. Mitchell (1991). They found that the upper horizon of soil developed on till was rich in silt in comparison to the lower ones, the higher silt content probably reflecting a greater degree of weathering and mineral breakdown.

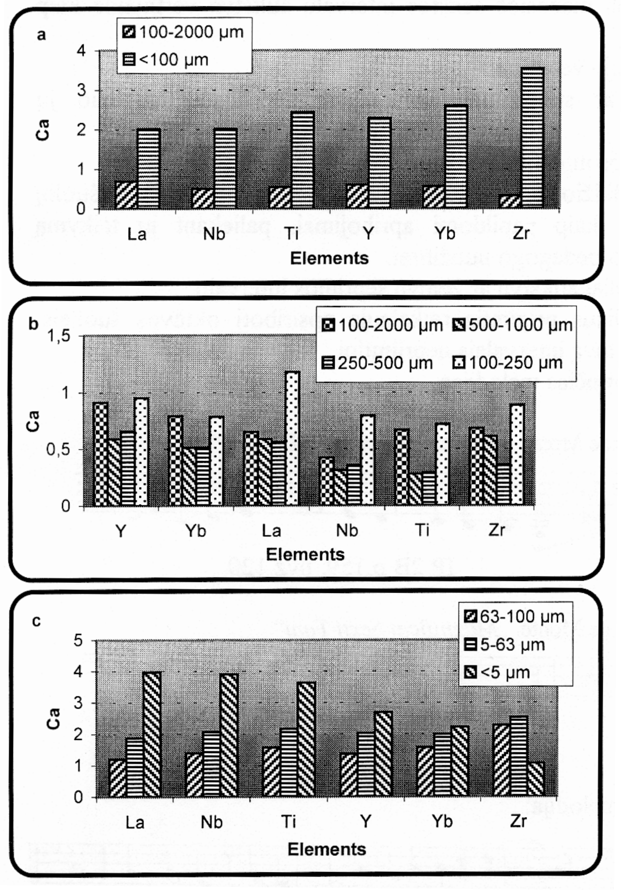

Fig. 2. Accumulation of allothigenous accessory elements in sandy-loamy soil of Ašmena Highlands: *a* – gravel-sand and silt-clay fractions, *b* – separated gravel-sand fractions, *c* – separated silt-clay fractions. Ca – coefficient of accumulation

2 pav. Aðmenos aukðtumø priesmëlingo dirvoþemio alotigeniniø-akcesoriniø mikroelementø kaupimasis: *a* – þvirgþdo-smëlio ir aleurito-molio frakcijose, *b* – atskirose þvirgþdo-smëlio frakcijose, *c* – atskirose aleurito-molio frakcijose. Ca – koncentracijos koeficientas

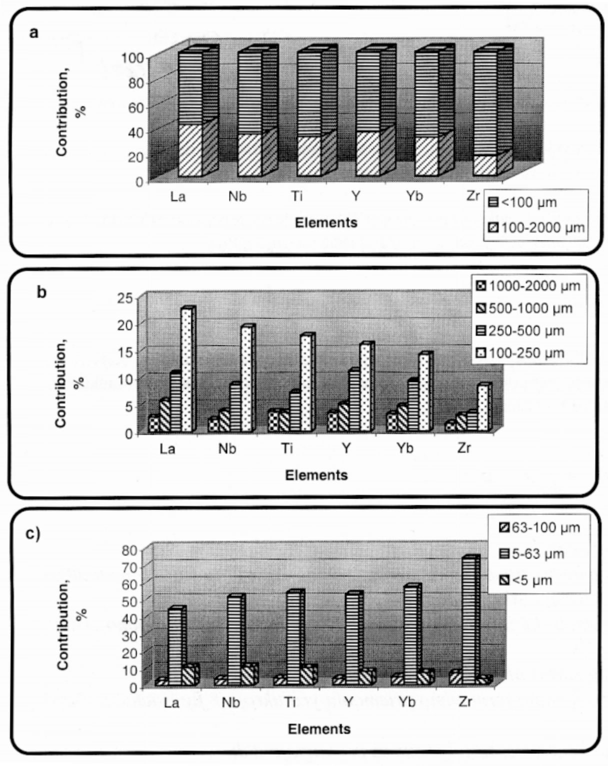

Fig. 3. Contribution of allothigenous accessory elements of differently sized particle fractions to their total content in the whole soil of Ašmena Highlands: *a* – contribution of gravel-sand- and silt-clay-sized fractions, *b* – contribution of separate gravel-sand-sized fractions, *c* – contribution of separate silt-clay-sized fractions

3 pav. Aðmenos aukðtumø priesmëlingo dirvoþemio alotigeniniø akcesoriniø mikroelementø, susijusiø su skirtingomis granuliometrinëmis frakcijomis, ánaðai á bendrà jø kieká visame dirvoþemyje: *a* – ánaðas, susijæs su þvirgþdo-smëlio ir aleurito-molio frakcijomis, *b* – ánaðas, susijæs su atskiromis þvirgþdo-smëlio ir aleurito-molio frakcijomis, *c* – ánaðas, susijæs su atskiromis aleurito-molio frakcijomis

Accumulation of allothigenous accessory elements in particle-size fractions. A previous analysis of sandy soil of Ašmena Highlands showed the content of trace elements mainly to depend on the distribution and chemical composition of their host minerals. The highest content of AAE was found in fine-sand-sized heavy minerals (Vareikienë, 2001). In the sandy-loamy soil of Ašmena Highlands the lowest contents of AAE are typical of the gravel-sand fraction of soil, while the highest contents are found in the silt-clay fraction. Zirconium content in silt-clay fraction is especially high and exceeds the total content of Zr in the whole soil more than 3 times. The coefficients of accumulation of other elements exceed 2 (Fig. 2a). The contrast of accumulation intensity of AAE in the above-mentioned fractions is found to be the highest for Zr (>10). According to the contrast of accumulation intensity, AAE are arranged in the following sequence: $\mathrm{Zr}_{(10,9)}$–$\mathrm{Yb}_{(4,7)}$–$\mathrm{Ti}_{(4,5)}$–$\mathrm{Nb}_{(4,1)}$–$\mathrm{Y}_{(3,8)}$–$\mathrm{La}_{(2,9)}$.

In the fractions >100 µm no accumulation of AAE is observed (Ca<1), indicating that coarse minerals are not enriched by the AAE mineral-carriers. The higher content of AAE is determined in fine gravel and fine sand fractions. Such bimodal distribution of AAE can be related to their different mineral forms in particular particle-size fractions (Fig. 2b). In the fraction <100 µm all AAE, except Zr, are most intensively accumulated in clay fraction (<5 µm). Titanium, La and Nb are distinguished by the highest intensity of accumulation (Ca > 3) (Fig. 2c). According to the intensity of accumulation, AAE form the following sequences: in clay fraction – La > Nb > Ti > Y > Yb > Zr, in fine silt fraction – Zr > Ti > Nb > Y > Yb > La, in coarse silt fraction – Zr > Ti > Yb > Y > Nb > La. Results of this study are consistent with the previous research of the distribution of trace element and grain size effect on trace element concentration in soil of Lithuania (Baltakis, 1993; Kadûnas, Gregorauskienë, 1999).

The contribution of allothigenous accessory element fractions to their total content in the whole soil was of uneven significance and mainly depended on the element content in a fraction and fraction size. Element contribution of the silt-clay fraction to element total contents in the soil of Ašmena Highlands is higher than that of the gravel-sand fraction. For all AAE it comprises more than 50% of their total content in soil. The Zr contribution of silt-clay fraction is especially significant and exceeds more than 5 times the Zr contribution of gravel-sand fraction (Fig. 3a). From all gravel-sand-sized fractions the fine sand fraction is distinguished by the highest contribution of all AAE to their total content in soil. The contribution of fine gravel and coarse sand is less significant (Fig. 3b). Although the accumulation of all AAE is most intensive in the clay fraction, its contribution comprises only a small part of the total AAE content in soil. For all AAE, except La, the contribution of the fine silt fraction which accounts for more than 50% of their total content in soil is most significant (Fig. 3c). **The features of fine silt fraction** were revealed using the results of particle-size and chemical analyses. The content of AAE in light minerals of a fraction is negligible (Fig. 4a). It shows that light minerals of fine silt fractions are not rich in minerals containing high amounts of AAE. An intensive accumulation of AAE is observed in heavy minerals (Fig. 4b). The highest ratio of the AAE concentration coefficients in heavy and light minerals is estimated for Zr. It clearly shows that zircons are mainly distributed in particle size fractions as single grains, while aggregates of zircon with other heavy minerals as well as zircon inclusions in other minerals are rare. The content of AAE in the fine silt fraction is predetermined by the contribution of heavy minerals which accounted for about 70% of AAE total content in this fraction (Fig. 4c).

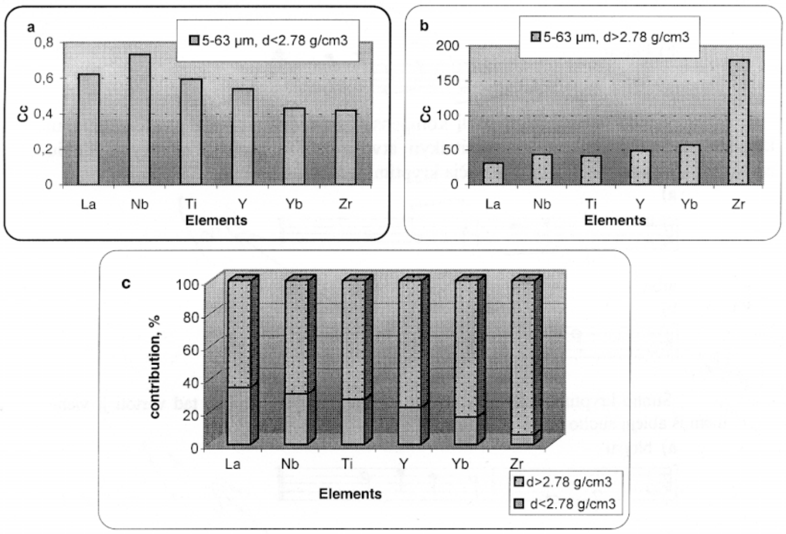

Fig. 4. Accumulation of allothigenous accessory elements in fine-silt-sized light (d < 2.78 g/cm^3) (*a*) and heavy (d > 2.78 g/cm^3) (*b*) minerals of sandy-loamy soil of Ašmena Highlands, *c* – contribution of allothigenous accessory elements of fine-silt-sized light and heavy minerals to their total content in the fine silt fraction of Ašmena Highlands sandy-loamy soil

4 pav. Alotigeniniø akcesoriniø mikroelementø kaupimasis Aðmenos aukðtumø priesmëlingo dirvoþemio smulkaus aleurito frakcijos lengvuosiuose (d < 2,78 g/cm^3) (*a*) ir sunkiuosiuose (d > 2,78 g/cm^3) (*b*) mineraluose, *c* – Aðmenos aukðtumø priesmëlingo dirvoþemio smulkaus aleurito frakcijos lengvøjø ir sunkiøjø mineralø reikðmë alotigeniniø akcesoriniø mikroelementø kiekiui smulkaus aleurito frakcijoje

Allothigenous accessory elements contribution of heavy minerals. To elucidate the mineralogical composition of the soil, the distribution of heavy minerals in fine silt fraction was examined by SEM-EDS. The predominant minerals include amphiboles, epidote, ilmenite (>10%), meanwhile garnets, rutile, clinopyroxenes, hematite, zircon, and titanite are less abundant (10–3%). Turmaline, staurolite, apatite, orthopyroxenes and monacite are subordinate species in the fraction (<3%). Xenotime and chromite are found to be present only in traces (<0.5%) (Fig. 5). It is worth mentioning that heavy minerals of the fine silt fraction are mostly represented by single mineral grains (Vareikienë, 2005).

The results of the present study show that although heavy minerals of the fine silt fraction comprise only a very small part of soil, they are important for the total content of AAE in soil. The content of Zr in soil is mainly predetermined by the contribution of zircon. This mineral can be ascribed to the main source of Zr in soil, although smaller amounts of Zr could also be found in other minerals. Zirconium can substitute Fe and Mg in the structure of silicates. Its content in amphiboles ranges from 47 to 800 ppm, in pyroxenes from 130 to 2870 ppm and in mica from 88 to 378 ppm (Иванов, 1997). In the anomalous soil of Ašmena Highlands, Zr contribution from fine-silt-sized heavy minerals comprises more than 90% of the total Zr content in soil, the contribution of other minerals being not important (Fig. 6).

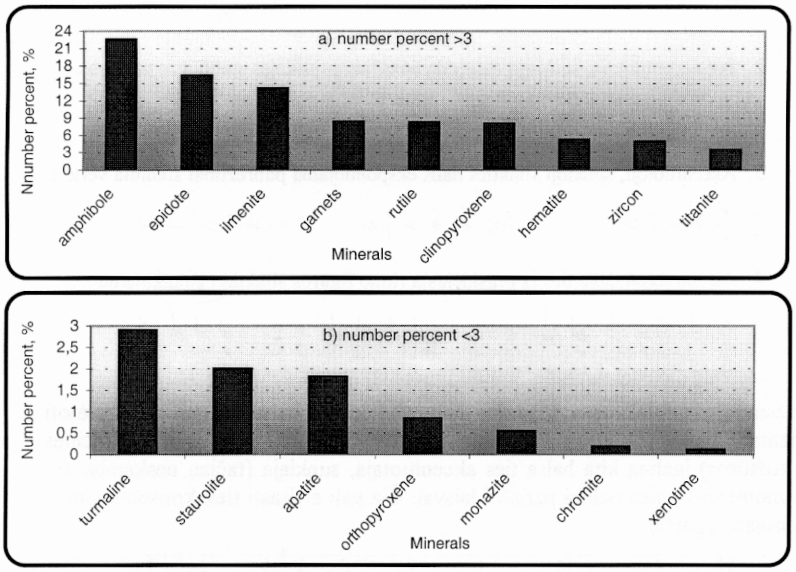

Fig. 5. Distribution of heavy minerals (d > 3 g/cm^3) in the fine silt fraction of soil of Ašmena Highlands. The number of analysed mineral grains is 1650

5 pav. Aðmenos aukðtumø dirvoþemio smulkaus aleurito frakcijos sunkiøjø mineralø (d > 3 g/cm^3) pasiskirstymas (iðanalizuota 1650 mineralø grûdeliø)

The main heavy mineral-carriers of Ti and Nb are the same. The only difference is that titanium has been found in these minerals as the main component and Nb as an isomorphous substitute. In spite of this difference, niobium contribution from rutile is more than 60%, while Ti contribution of the same mineral is found to comprise only about 24% of its total content in soil. Xenotime is the main Y-bearing mineral. Although in soil this mineral is usually found only in traces, Y contribution from this mineral comprised more than 30% of total Y content in soil. Yttrium contribution from zircon is more than 30%, the contribution of titanite is much lower and the contribution of other minerals is about several per cent. Xenotime and monazite are the main carrier-minerals of Yb. The highest content of La has been determined in monazite; less amounts of La could be found in other minerals (in titanite about 1.36%

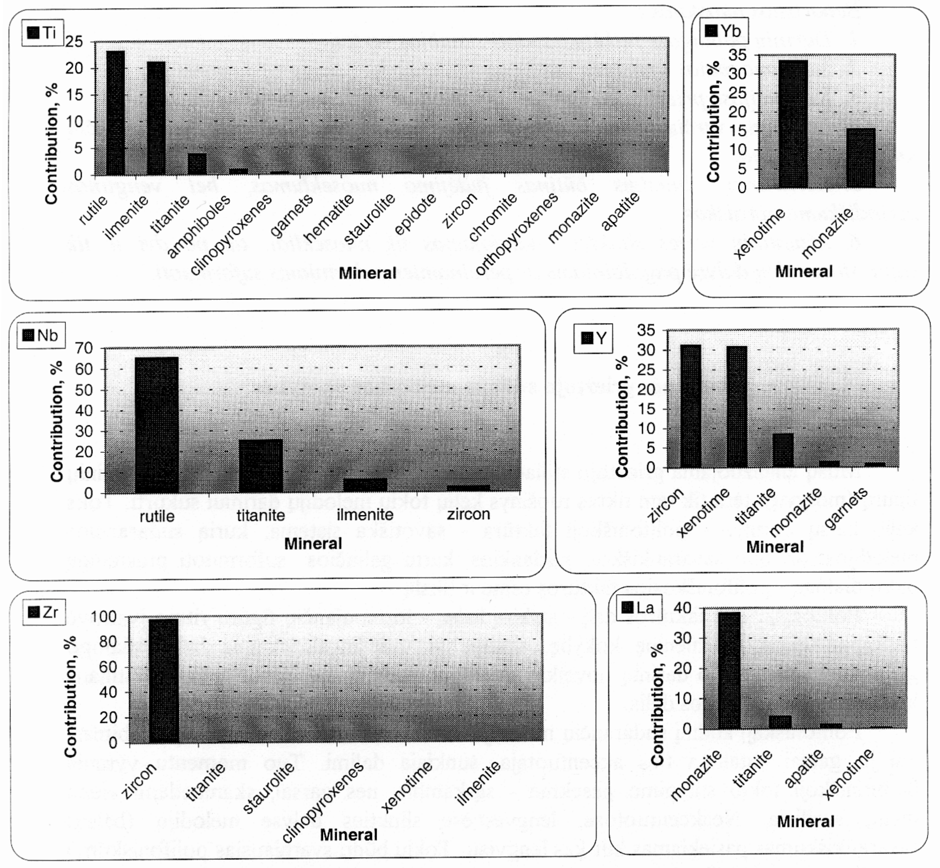

Fig. 6. Contribution of allothigenous accessory elements of fine-silt-sized heavy minerals (d > 3 g/cm^3) to the their total content in the whole soil of Ašmena Highlands

6 pav. Aðmenos aukðtumø priesmëlingo dirvoþemio smulkaus aleurito frakcijos sunkiøjø mineralø (d > 3 g/cm^3) reikðmë alotigeniniø akcesoriniø mikroelementø bendram kiekiui dirvoþemyje

of La, in epidote about 1.47%). Lantanium contribution from monacite is about 40% of its total content in soil, the contribution of other minerals being insignificant (Fig. 6).

The contribution of allothigenous accessory elements of fine-silt-sized heavy minerals accounted for more than 90% of Zr and Nb, about 70% of Y, and about 50% of Ti and Yb total contents in soil (Fig. 7).

CONCLUSIONS

The features of allothigenous accessory element distribution in sandy-loamy soil of Ašmena Highlands, formed in sediments of the periglacial zone, were predetermined by the intensive and long-lasting weathering and soil-forming processes. A high content of fine silt fraction and a very small content of clay fraction is characteristic of this soil. The weathering processes have influenced the washdown of carbonates from the upper part of the soil profile, the disappearance of less resistant mineral species, and the disintegration of coarser minerals to finer ones. Disintegration also led to enrichment of finer fractions with heavy minerals, hosted before as inclusions in coarser minerals. Therefore, the general feature of the sandy-loamy soil of Ašmena Highland is defined as an increased content of heavy minerals in the fine silt fraction in comparison with the coarser fractions.

Analysis of the distribution of AAE in the sandy-loamy soil of Ašmena Highlands showed its distinct dependence on the particle-size composition. It was ascertained that Ti, Y, Yb, Nb and La were most intensively accumulated in clay fraction and Zr in fine silt fraction. Such dependence was predetermined by peculiarities of mineral distribution in particle-size fractions as well as by different forms of occurrence of allothigenous accessory elements in a particular fraction.

Allothigenous accessory element contribution of fractions to the total content of an element in the whole soil was of uneven significance and mostly depended on the content of element in a fraction and the size of a fraction. The contribution of all AAE, except La, of the fine silt fraction, which accounted for more than 50% of element total content in soil, was most significant. So, fine silt was assumed to be the main fraction predetermining the total content of all AAE, except La, in the whole soil. The main feature of this fraction was intensive accumulation of AAE in the heavy mineral separate. It predetermined the importance of heavy mineral contribution, accounting for about 70% of the total content of all AAE in the fine silt fraction, in spite of the fact that heavy minerals comprise only a very small part of the fraction.

In the fine silt fraction, La contribution was predetermined by the contribution of monazite, Nb contribution – by rutile, titanite, and ilmenite, Ti contribution – by rutile, ilmenite and titanite, Y contribution – by xenotime, zircon and titanite, Yb – by xenotime and monazite, and Zr contribution – by zircon.

The contribution of allothigenous accessory elements of fine-silt-sized heavy minerals accounted for

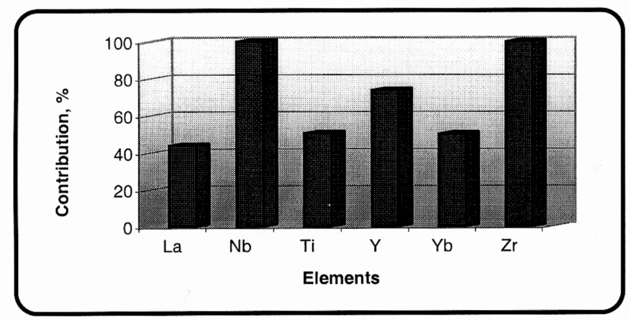

Fig. 7. Total contribution of allothigenous accessory elements of fine-silt-sized heavy minerals (d > 3 g/cm^3) to their content in the sandy-loamy soil of Ašmena Highlands
7 pav. Alotigeniniø akcesoriniø mikroelementø bendras ánaðas ið smulkaus aleurito frakcijos sunkiøjø mineralø (d > 3 g/cm^3) á visà jø kieká Aðmenos aukðtumø priesmëlingame dirvoþemyje

more than 90% of Zr and Nb, about 70% of Y, about 50% of Ti and Yb total contents in soil. The significance of heavy minerals for the total La content in soil was somewhat less important. The results of this study have shown that the total content of allothigenous accessory elements in the soil of Ašmena Highlands is predetermined by the AAE contribution of fine-silt-sized heavy minerals.

ACKNOWLEDGEMENTS

The author gratefully acknowledges financial support provided by the Geological Survey of Finland to this research. Dr. V. Kadûnas is thanked for professional advice during this study, and Dr. P. Ðinkûnas and Dr. D. Kaminskas are thanked for a review of the manuscript and valuable comments.

References

Berrow M. L., Mitchell R. L. 1991. Location of trace elements in soil profiles: total contents of particle-size separates. *Transactions of the Royal Society of Edinburg: Earth Sciences*. ***82***. 195–209.

Christiansen H. 1996. Periglacial sediments in an Eemian–Weichselian succession at Emmerlev Klev, soutwestern Jutland, Denmark. *Palaeogeography, Palaeoclimatology, Palaeoecology*. ***138***. 245–258.

French H. M. 1996. *The Periglacial Environment*. Longman: Harlow. 341 pp.

Issmer K. 1999. Vistulian loess deposits of the Dalkow Hills. *Geological Quaterly*. ***43***(*1*). 113–120.

Jary Z. 1996. Chronostratygrafia oraz warunki sedymentacji lessów Polski poùudniowo-zachodniej na przykùadzie Plaskowyýu Glubczyckiego i Wzgórz Trzebnickich. *Acta Universitatis Wratislaviensis*. 1766. *Studia Geograficzne*. ***63***. Wrocùaw.

Jary Z., Kida J., Snihur M. 2002. *Lessy i osady lessopochodne w poludniowo-zachodniej Polsce*. Inst. Geogr. Uniw. Wrocùaw.

Kauranne K., Salminen R. and Eriksson K. 1992. Regolith exploration geochemistry in arctic and temperate terrains. *Handbook of Exploration Geochemistry*. ***5***. Amsterdam: Elsevier. 443 p.

Kida J., Jary Z. 2001. Liessy i utwory lessopodobne w poùudniowo-zachodniej Polsce. Wrocùaw, Inst. Geogr. Uniw.

Kozarski S. 1993. Late Plenivistulion deglaciation and the expansion of the periglacial zone in NW Poland. *Geol. En Mijnbouw*. ***72***. 143–157.

Lång Lars-Ove. 2000. Heavy mineral weathering under acidic soil conditions. *Appl. Geochemistry*. ***15***. 415–423.

Law K. R., Nesbitt H. W., Longstaffe F.J. 1991. Weathering of granitic tills and the genesis of a podzol. *Amer. J. Sci*. ***291***. 940–976.

Leibovitz D. P., Smith D. G. W. 1983. Commercial computer program "MinIdent-P version 1.00".

Murton I., French H. M. 1994. *Cryostructures in Permafrost. Tuktoyaktuk Coastlands. Western Arctic Canada*. 737–747.

Vandenberghe J., Pissart A. 1993. Permafrost changes in Europe during the last glacial. *Permafrost and Periglacial Processes*. ***4***. 121–135.

Baltakis V. 1993. Foniniai mikroelementø pasiskirstymai ir jø tarpusavio ryðiai Lietuvos dirvoþemiuose. *Geologija*. ***15***. 32–42.

Basalykas A., Jurgaitis A., Mikalauskas A., Švedas K. 1976. Periglacialiniø dengiamøjø dariniø struktûra Medininkø aukðtumoje ir Eiðiðkiø plynaukðtëje. *Geografija ir geologija*. ***12***. 33–50.

Gaigalas A., Dvareckas V., Meleðytë M. 1998. Pietø Lietuvos pavirðiaus denudacija. *Geografija*. ***34***(*2*). 5–12.

Kadûnas V. 1999. Gamtinës geocheminës anomalijos Lietuvos dirvoþemiuose. *Geologija*. ***26***. 27–37.

Kadûnas V., Gregorauskienë V. 1999. Mikroelementai dirvoþemio granuliometrinëse frakcijose Lietuvoje. *Geologija*. ***28***. 15–22.

Kadûnas V. 2000. Lietuvos skirtingo amþiaus glacigeniniø nuogulø dirvoþemiø mikroelementinës sudëties ypatumai. *Geologija*. ***30***. 5–13.

Kadûnas V., Budavièius R., Gregorauskienë V., Katinas V., Kliaugienë E., Radzevièius A., Taraðkevièius R. 1999. *Lietuvos geocheminis atlasas*. Ats. red. J. Satkûnas. Vilnius: Lietuvos geologijos tarnyba, Geologijos institutas. 90 p.

Šinkunas P., Jurgaitis A. 1998. *Ledyniniø nuogulø litologija ir sedimentacija*. Vilnius: Academia. 71 p.

Ðvedas K. 2001. Medininkø aukðtumos paleogeografinë raida vëlyvajame Pleistocene. *Geografijos metraštis*. ***34***(*1*). 95–105.

Ðvedas K., Baltrûnas V., Pukelytë V. 2004. Paleogeography of South Lithuania in Nemunas (Weichselian) Glaciation of Late Pleistocene. *Geologija*. ***45***. 6–15.

Vareikienë O. 2001. Genesis of anomaly in soil formed on deposits of Medininkai glaciation. *Geologija*. ***35***. 1–7.

Vareikienë O., Marmo J., Kadûnas V., Lindqvist K. 2003. Mineral mode of occurence of selected elements in the fine fraction of soil (horizon A_1) of Ašmena Highlands, Lithuania. *Geologija*. ***42***. 9–18.

Vareikienë O., Lehtonen M. 2004. Heavy minerals in the study of soil: applied techniques, their limitations and advantages. *Geologija*. ***46***. 1–7.

Vareikienë O. 2005. Lietuvos dirvoþemiø alotigeniniø akcesoriniø mikroelementø gamtiniø geocheminiø anomalijø ypatumai. Daktaro disertacija. Vilnius. 93 p.

Эйдукявичене М., Кудаба Ч. 1976. Глубина вымывания карбонатов как критерий выделения разновозрастных гляцигенных комплексов на территории Литвы. *География и геология*. ***13***. 31–35.

Иванов В. 1997. Экологическая геохимия элементов. Справочник. Под ред. Э. К. Буренкова. Москва: Недра.

Olga Vareikienë

ALOTIGENINIAI AKCESORINIAI MIKROELEMENTAI (AAM) PRIESMËLINGUOSE LIETUVOS DIRVOÞEMIUOSE, SUSIFORMAVUSIUOSE PERIGLACIALINËS ZONOS NUOSËDOSE

Santrauka

Alotigeniniø akcesoriniø mikroelementø (Zr, Ti, La, Y, Yb, Nb) pasiskirstymo priesmëlinguose Aðmenos aukðtumos dirvoþemiuose, susiformavusiuose periglacialinës zonos nuosëdose, geocheminiai ypatumai buvo nustatyti ávertinus mikroelementø kiekio pasiskirstymà granuliometrinëse ir mineralø tankio frakcijose, taip pat mikroelementø, susijusiø su minëtomis frakcijomis, ánaðo á jø bendrà kieká dirvoþemyje reikðmingumà. Jungtinës granuliometrinës, cheminës, mineraloginës analiziø metodikos taikymas dirvoþemio tyrimui leido apskaièiuoti ir alotigeniniø akcesoriniø mikroelementø (AAM), susijusiø su sunkiaisiais mineralais (d>3 g/cm^3), ánaðà á bendrà jø kieká.

Aðmenos aukðtumos glacigeninës nuosëdos, suklostytos Medininkø apledëjimo metu, per pastaruosius 100000 metø buvo veikiamos dûlëjimo Merkinës tarpledynmeèiu, Nemuno periglacialo ir poledynmeèio laikotarpiais. Ilgai trukæs dûlëjimas ir ypaè intensyvus nuosëdø mechaninis performavimas veikiant periglacialiniams procesams, vienodino jø mineralinæ sudëtá – formavosi homogeniðkos, daugiausia priesmëlingos-aleuritingos, nuosëdos. Mechaninës dirvoþemio sudëties ypatumus nulëmë ir dirvodaros procesai, sukëlæ molingø daleliø iðplovimà ir dirvoþemio virðutiniø horizontø santykiná praturtinimà sunkiaisiais mineralais. Minëti procesai turëjo átakos alotigeniniø akcesoriniø mikroelementø geocheminës anomalijos susiformavimui Aðmenos aukðtumos dirvoþemio pavirðiniame sluoksnyje.

Dël dûlëjimo procesø buvo iðplauti karbonatai ið virðutinës dirvoþemio profilio dalies, iðnyko maþiau dûlëjimui atsparûs mineralai, ávyko stambesniø mineralø dezintegracija. Tiek dël stambesniø mineralø dezintegracijos, tiek ir dël stambesniuose mineraluose aptinkamø sunkiøjø mineralø intarpø iðlaisvinimo dirvoþemis praturtëjo smulkesniais mineralais. Aðmenos aukðtumos priesmëlingame dirvoþemyje didþiausias sunkiøjø mineralø kiekis aptiktas smulkaus aleurito frakcijoje, lyginant su vidutinio ir smulkaus smëlio frakcijomis.

Alotigeniniø akcesoriniø mikroelementø kiekio pasiskirstymas priesmëlinguose Aðmenos aukðtumø dirvoþemiuose labai priklauso nuo granuliometriniø frakcijø. Nustatyta, kad Ti, Y, Yb, Nb ir La intensyviausiai kaupiasi pelitinëje, o Zr – smulkaus aleurito frakcijoje. Tokià priklausomybæ nulëmë mineralø pasiskirstymo frakcijose ypatumai ir skirtingos ðiø mikroelementø bûvio formos atskirose frakcijose.

Atskirø granuliometriniø frakcijø reikðmingumas bendram mikroelementø kiekiui dirvoþemyje yra nevienodas ir daugiausia priklauso nuo mikroelementø kiekio frakcijose bei frakcijø kiekio. Didþiausias AAM ánaðas, sudarantis daugiau nei 50% jø bendro kiekio dirvoþemyje, yra susijæs su smulkaus aleurito frakcija, tad ji gali bûti apibûdinta kaip frakcija, formuojanti ir lemianti AAM bendrà kieká dirvoþemyje. Pagrindinis smulkaus aleurito frakcijos ypatumas, iðryðkëjæs granuliometrinës ir cheminës analiziø metu, yra intensyvus AAM kaupimasis frakcijos sunkiuosiuose mineraluose. Tai nulëmë ir AAM, susijusiø su smulkaus aleurito frakcijos sunkiaisiais mineralais, pagrindinæ reikðmæ jø bendram kiekiui visoje frakcijoje. Mineralogine smulkaus aleurito frakcijos sunkiøjø mineralø analize skenuojanèiu mikroskopu nustatyta, kad daugiausia mineralø aptikta savarankiðkos formos. Tyrimo metu iðanalizuota 1650 mineralø grûdeliø. Labiausiai paplitæ amfibolai, epidotas, ilmenitas (>10%), maþiau – granatai, rutilas, klinopiroksenai, hematitas, cirkonas ir titanitas (10–3%). Turmalino, staurolito, apatito, ortopiroksenø ir monacito grûdeliø kiekis sudaro maþiau nei 3%. Chromito ir ksenotimo paplitimas labai ribotas (<0,5%). Nors sunkieji mineralai sudaro tik nedidelæ dalá viso dirvoþemio, jie yra reikðmingi bendram AAM kiekiui dirvoþemyje. Aðmenos aukðtumos priesmëlingame dirvoþemyje Zr ánaðas, susijæs su smulkaus aleurito dydþio cirkonu, sudaro daugiau nei 90% jo bendro kiekio dirvoþemyje. Pagrindiniai Ti ir Nb kilmës mineralai – ilmenitas, rutilas ir titanitas. Ksenotimas – pagrindinis Y kilmës mineralas. Nepaisant labai reto ðio mineralo paplitimo, su juo susijæs Y ánaðas sudaro apie 30% jo bendro kiekio dirvoþemyje. Tokio pat dydþio Y ánaðas yra susijæs ir su cirkonu, ánaðas ið titanito daug maþesnis. Ksenotimas ir monacitas – pagrindiniai Yb kilmës mineralai, kuriø ánaðai á Yb bendrà kieká dirvoþemyje yra reikðmingi (atitinkamai 34 ir 15%). Didþiausias La kiekis nustatytas monacite (13,5%), tai lëmë ir La, susijusio su monacitu, pagrindinæ reikðmæ jo kiekiui dirvoþemyje.

Alotigeniniø akcesoriniø mikroelementø ánaðas, susijæs su jø kilmës sunkiaisiais mineralais, sudaro daugiau nei 90% Zr ir Nb, apie 70% Y, apie 50% Ti ir Yb bendro kiekio dirvoþemyje. Maþesnë jø reikðmë La kiekiui (apie 44%).

Oëüãà Âàðåéêåíå

ÀËËÎÒÈÃÅÍÍÛÅ ÀÊÖÅÑÑÎÐÍÛÅ ÝËÅÌÅÍÒÛ Â ÑÓÏÅÑ×ÀÍÛÕ ÏÎ×ÂÀÕ ËÈÒÂÛ, ÐÀÇÂÈÒÛÕ ÍÀ ÎÒËÎÆÅÍÈßÕ ÏÅÐÈÃËßÖÈÀËÜÍÎÉ ÇÎÍÛ

Ðåçþìå

Îñîáåííîñòè ðàñïðåäåëåíèÿ àëëîòèãåííûõ àêöåññîðíûõ ýëåìåíòîâ (Zr, Ti, La, Y, Yb, Nb) â

ñóïåñ÷àíûõ ïî÷âàõ Àøìÿíñêîé âîçâûøåííîñòè, ðàçâèòûõ íà îòëîæåíèÿõ ïåðèãëÿöèàëüíîé çîíû, âûÿâëåíû ñëåäóþùèì îáðàçîì: óñòàíàâëèâàëîñü ðàñïðåäåëåíèå ìèêðîýëåìåíòîâ â ãðàíóëîìåòðè÷åñêèõ è ìèíåðàëüíûõ ôðàêöèÿõ, çàòåì îïðåäåëÿëàñü êîëè÷åñòâåííàÿ äîëÿ ñâÿçàííûõ ñ ýòèìè ôðàêöèÿìè ìèêðîýëåìåíòîâ â èõ îáùåì ñîäåðæàíèè â ïî÷âå. Ïðèìåíåíèå îáúåäèíåííîé ìåòîäèêè ãðàíóëîìåòðè÷åñêîãî, õèìè÷åñêîãî, ìèíåðàëîãè÷åñêîãî àíàëèçîâ ïîçâîëèëî îïðåäåëèòü è äîëþ ìèêðîýëåìåíòîâ, ñâÿçàííûõ ñ òÿæåëûìè ìèíåðàëàìè (d > 3 ã/ñì^3) ìåëêîàëåâðèòîâîé ôðàêöèè, â èõ îáùåì ñîäåðæàíèè â ïî÷âå.

Äëÿ ñóïåñ÷àíûõ ïî÷â Àøìÿíñêîé âîçâûøåííîñòè õàðàêòåðíî íàèáîëüøåå êîëè÷åñòâî ìåëêîàëåâðèòîâîé ôðàêöèè è íàèìåíüøåå – ïåëèòîâîé. Îñîáåííîñòè ãðàíóëîìåòðè÷åñêîãî ñîñòàâà ïî÷â ïðåäîïðåäåëåíû äëèòåëüíîñòüþ âûâåòðèâàíèÿ ïî÷âîîáðàçóþùèõ îòëîæåíèé, êîòîðûå ïîäâåðãàëèñü è âîçäåéñòâèþ ïåðèãëÿöèàëüíûõ ïðîöåññîâ. Ïî÷âîîáðàçîâàòåëüíûå ïðîöåññû îáóñëîâèëè âûíîñ ãëèíèñòûõ ÷àñòèö èç âåðõíåé ÷àñòè ïî÷âåííîãî ïðîôèëÿ è åãî îòíîñèòåëüíîå îáîãàùåíèå òÿæåëûìè ìèíåðàëàìè. Ïðîöåññû âûâåòðèâàíèÿ ñïîñîáñòâîâàëè ðàñòâîðåíèþ è âûíîñó êàðáîíàòîâ, èñ÷åçíîâåíèþ ìåíåå óñòîé÷èâûõ ê âûâåòðèâàíèþ ìèíåðàëîâ è äåçèíòåãðàöèè áîëåå êðóïíûõ ìèíåðàëîâ. Â ðåçóëüòàòå ïî÷âà áûëà îáîãàùåíà áîëåå ìåëêèìè ìèíåðàëàìè êàê èç-çà ïðîèñõîäÿùåé äåçèíòåãðàöèè ìèíåðàëîâ, òàê è èç-çà âûñâîáîæäåíèÿ èíêëþçèâíûõ âêëþ÷åíèé òÿæåëûõ ìèíåðàëîâ èç áîëåå êðóïíûõ ìèíåðàëîâ. Â ñóïåñ÷àíûõ ïî÷âàõ Àøìÿíñêîé âîçâûøåííîñòè íàèáîëüøåå ñîäåðæàíèå òÿæåëûõ ìèíåðàëîâ âûÿâëåíî âî ôðàêöèè ìåëêîãî àëåâðèòà (ïî ñðàâíåíèþ ñ ôðàêöèÿìè ñðåäíåçåðíèñòîãî è ìåëêîãî ïåñêà).

Ðàñïðåäåëåíèå àëëîòèãåííûõ àêöåññîðíûõ ìèêðîýëåìåíòîâ (ÀÀÌ) â ñóïåñ÷àíûõ ïî÷âàõ Àøìÿíñêîé âîçâûøåííîñòè çàâèñèò îò ãðàíóëîìåòðè÷åñêèõ ôðàêöèé. Óñòàíîâëåíî, ÷òî Ti, Y, Yb, Nb è La áîëåå èíòåíñèâíî íàêàïëèâàþòñÿ â ïåëèòîâîé, à Zr – âî ôðàêöèè ìåëêîãî àëåâðèòà. Òàêàÿ çàâèñèìîñòü îáóñëîâëåíà îñîáåííîñòÿìè ðàñïðåäåëåíèÿ ìèíåðàëîâ è íàëè÷èåì ðàçëè÷íûõ ôîðì ñîñòîÿíèÿ ýòèõ ýëåìåíòîâ â îòäåëüíûõ ôðàêöèÿõ.

Ðîëü âíîñà ÀÀÌ èç îòäåëüíûõ ãðàíóëîìåòðè÷åñêèõ ôðàêöèé â èõ îáùåå ñîäåðæàíèå â ïî÷âå ðàçëè÷íà è â îñíîâíîì çàâèñèò îò êîëè÷åñòâà ìèêðîýëåìåíòà âî ôðàêöèè è îò ñîäåðæàíèÿ ñàìîé ôðàêöèè. Íàèáîëåå çíà÷èòåëüíûé âêëàä ÀÀÌ – áîëåå 50% èõ îáùåãî ñîäåðæàíèÿ â ïî÷âå – ñâÿçàí ñ ôðàêöèåé ìåëêîãî àëåâðèòà. Ïîýòîìó ýòà ôðàêöèÿ ìîæåò áûòü îïðåäåëåíà êàê ãëàâíàÿ, ôîðìèðóþùàÿ îáùåå ñîäåðæàíèå ÀÀÌ â ïî÷âå. Ãëàâíàÿ îñîáåííîñòü ôðàêöèè ìåëêîãî àëåâðèòà, âûÿâëåííàÿ â ðåçóëüòàòå ãðàíóëîìåòðè÷åñêîãî è õèìè÷åñêîãî àíàëèçîâ, – èíòåíñèâíîå íàêîïëåíèå ÀÀÌ â ñîñòàâëÿþùèõ óêàçàííóþ ôðàêöèþ òÿæåëûõ ìèíåðàëàõ. Ýòî ïðåäîïðåäåëèëî è äîëþ ÀÀÌ, ñâÿçàííûõ ñ òÿæåëûìè ìèíåðàëàìè, â ôîðìèðîâàíèå îáùåãî ñîäåðæàíèÿ ÀÀÌ âî ôðàêöèè ìåëêîãî àëåâðèòà.

Ìèíåðàëîãè÷åñêèé àíàëèç òÿæåëûõ ìèíåðàëîâ ôðàêöèè ìåëêîãî àëåâðèòà, ïðîâåäåííûé ñ ïîìîùüþ ýëåêòðîííîãî ñêàíèðóþùåãî ìèêðîñêîïà, ïîêàçàë, ÷òî â îñíîâíîì ìèíåðàëàì ñâîéñòâåííà ìîíîìèíåðàëüíàÿ ôîðìà. Îñóùåñòâëåí àíàëèç 1650 ìèíåðàëîâ. Íàèáîëåå ðàñïðîñòðàíåíû àìôèáîëû, ýïèäîò, èëüìåíèò (>10%); ãðàíàòû, ðóòèë, êëèíîïèðîêñåíû, ãåìàòèò, öèðêîí è òèòàíèò – ìåíåå (10–3%). Êîëè÷åñòâî òóðìàëèíà, ñòàâðîëèòà, àïàòèòà, îðòîïèðîêñåíà è ìîíàöèòà ñîñòàâëÿåò ìåíåå 3%, à õðîìèòà è êñåíîòèìà – ìåíåå 0,5%.

Õîòÿ òÿæåëûå ìèíåðàëû ñîñòàâëÿþò òîëüêî íåçíà÷èòåëüíóþ ÷àñòü âñåé ïî÷âû, îíè ìîãóò ïðåäîïðåäåëÿòü îáùåå ñîäåðæàíèå ÀÀÌ â ïî÷âàõ. Â ñóïåñ÷àíûõ ïî÷âàõ Àøìÿíñêîé âîçâûøåííîñòè âíîñ Zr èç öèðêîíà, íàõîäÿùåãîñÿ âî ôðàêöèè ìåëêîãî àëåâðèòà, ñîñòàâëÿåò áîëåå 90% îò åãî îáùåãî ñîäåðæàíèÿ â ïî÷âå. Îñíîâíûå íîñèòåëè Ti è Nb – èëüìåíèò, ðóòèë è òèòàíèò, à Y – êñåíîòèì. Íåñìîòðÿ íà ðåäêóþ âñòðå÷àåìîñòü êñåíîòèìà, ñâÿçàííûé ñ íèì âíîñ Y ñîñòàâëÿåò áîëåå 30% îò îáùåãî ñîäåðæàíèÿ Y â ïî÷âå. Òàêîé æå âíîñ Y ñâÿçàí è ñ öèðêîíîì, âíîñ èç òèòàíèòà çíà÷èòåëüíî ìåíüøå. Êñåíîòèì è ìîíàöèò – îñíîâíûå ìèíåðàëû-íîñèòåëè Yb, ñâÿçàííûé ñ íèìè âíîñ Yb â åãî îáùåå ñîäåðæàíèå â ïî÷âå ÿâëÿåòñÿ çíà÷èòåëüíûì (ñîîòâåòñòâåííî 34 è 15%). Ñàìîå âûñîêîå ñîäåðæàíèå La óñòàíîâëåíî â ìîíàöèòå (13,5%), ýòî îáóñëîâèëî è âàæíîñòü ñâÿçàííîãî ñ ýòèì ìèíåðàëîì âíîñà La â åãî îáùåå ñîäåðæàíèå â ïî÷âå.

Ñóììàðíûé âíîñ ÀÀÌ, ñâÿçàííûõ ñ èõ òÿæåëûìè ìèíåðàëàìè-íîñèòåëÿìè ìåëêîàëåâðèòîâîãî ðàçìåðà, ñîñòàâëÿåò áîëüøå 90% îò îáùåãî ñîäåðæàíèÿ Zr è Nb â ïî÷âå, îêîëî 70% Y è îêîëî 50% Ti è Yb. Ðîëü òÿæåëûõ ìèíåðàëîâ-íîñèòåëåé â ôîðìèðîâàíèè îáùåãî ñîäåðæàíèÿ La â ïî÷âå íåñêîëüêî ìåíüøå (ñâÿçàííûé ñ íèìè âíîñ ñîñòàâëÿåò îêîëî 44%).