

Mineral mode of occurrence of selected elements in the fine fraction of soil (horizon A₁) of Ašmena Highlands, Lithuania

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The mineralogical study of the fine fraction (<0.1 mm) allows us to conclude that according to the contribution of certain elements from carrier heavy minerals to the fine fraction (<0.1 mm), the elements studied could be subdivided into three groups: 1 – elements least dependent on the content of heavy minerals: P, Al, Zn (contribution from the host minerals is <10%), 2 – elements moderately dependent: Ti, V, Fe and Ni (contribution is 10–50%), 3 – elements strongly dependent: Zr, Nb, Y, La, Mn, Co (contribution > 50%).

In spite of the low content of heavy minerals in the sample studied, absolute accumulation of Zr and Nb, as well as strong accumulation of Y, La, Mn, and Co in the fine fraction could be explained by the high concentration of the elements in their carrier heavy minerals. Low contributions of other elements from their host heavy minerals indicate their preferred accumulation in other modes of occurrence, such as in the lattice of light minerals, in secondary minerals formed during weathering or in adsorbed forms.

Keywords: mineral mode of occurrence, carrier-mineral, host mineral, coefficient of accumulation

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INTRODUCTION

A high total concentration of certain elements in the fine fraction (<0.1 mm) of soil samples compared to the fraction <2 mm of the whole sample has been reported by several authors (*e. g.*, Baltakis, 1993; Gregorauskienė and Kadūnas, 1999). Elements in the inorganic part of a soil are accumulated according to the original mineral distribution in various grain-size fractions, and elemental concentrations depend on the abundance of primary mine-

rals, clay particles and different types of secondary oxides/hydroxides. The aim of this work, employing a more or less theoretical approach, was to determine and quantify the host minerals for selected elements analysed by chemical methods in the fine fraction (<0.1 mm) based on investigation of the primary heavy minerals in the same fraction. The soil sample was chosen so as to represent the oldest soil of Lithuania. This study has been supported by CIMO, the Geological Survey of Finland (GTK) and the Institute of Geology, Lithuania (GI).

MATERIAL AND METHODS

All mineralogical studies were conducted at the Research Laboratory of GTK. The soil sample studied was taken from the A₁ horizon (depth 5–15 cm). The uppermost part of the soil rich in organic matter was removed before sampling; roots and other coarse organic particles were removed during the sampling. In order to facilitate mineralogical analysis, pre-treatment of the soil was carried out by removing organic matter using hydrogen peroxide at gradually increasing concentrations (from 3 to 30%). A strong oxidizing solution could also cause partial extraction of Fe oxides, dissolution of carbonates and weak alteration of chlorite and mica (Tiessier et al., 1979). Manganese oxides / hydroxides as well as different sulphides could be dissolved during this treatment (Chao, 1972). After pre-treatment, inorganic matter was dry-sieved into two fractions: coarse (2–0.1 mm) and fine (<0.1 mm). The fine fraction was separated into two fractions using a heavy liquid (D 2.78, slightly diluted bromoform). By evaluating XRD studies on both fractions, the heavy fraction was chosen for further mineralogical analysis. A polished thin section of heavy minerals was made from the heavy fraction and about 1000 mineral grains were identified using a Jeol 5600-LV scanning electron microscope. Mineral identification was made by comparing the obtained EDS spectra of grains to an EDS data base of known mineral species at the Research Laboratory.

For chemical analysis, the fine fraction was dry-sieved into two fractions, <0.063 mm and >0.063 mm. Further particle-size separation of the fraction <0.063 mm into fractions <0.005 and >0.005 mm was conducted according to Stokes's law. All fractions including the primary inorganic sample were analysed at the GTK Geolaboratory by ICP-AES and ICP-MS methods for main and trace elements.

For evaluation of the accumulation of elements in the fine fraction (<0.1 mm), the coefficient of accumulation (Cac) was determined by dividing the content of the element in the fine fraction by its content in the fraction <2 mm of a pre-treated inorganic soil sample. Correspondingly, for evaluation of the accumulation and distribution of elements in the different grain size separates of the fine fraction, the Cac was calculated by dividing the content of an element in each grain-size separate by its content in the fraction <2 mm of a pre-treated inorganic soil sample. The estimation of the distribution of an element among the possible carrier minerals in the fine fraction was based on the content of the carrier phase (%) in the heavy mineral fraction, average content of the element in the carriers (cf. Lei-

bovitz et al., 1983) and the relative proportion of the heavy fraction in the fine fraction. We agreed to designate as the carrier phase of an element a mineral containing that particular element as the main constituent.

SOIL OF AŠMENA HIGHLANDS

The soil of Ašmena Highlands formed from glacial till of the Medininkai (Wartian / Upper Saalian) of the Middle Pleistocene glaciation. The till was subjected to post-depositional weathering and soil-forming processes for 100000 years longer than the other Lithuanian glacial sediments formed during the Nemunas (Weichselian) glaciation of the Upper Pleistocene. This caused more intensive chemical and physical disintegration of detrital minerals and leaching of certain elements, as well as migration of fine and especially clay particles downwards within the soil profile. This resulted in a relative enrichment of resistant minerals in the upper soil horizon and in a relative depletion of elements present in clay minerals. Consequently, a natural geochemical anomaly was generated in the soil (Kadūnas, 1999). For the purpose of explaining the origin of this type of anomaly, the inorganic soil sample (<2 mm) was primarily dry-sieved into a coarser (2–0.1 mm) and a finer (<0.1 mm) fractions. Later both of them were further separated into finer fractions for chemical and mineralogical analysis. Analysis of the fine fraction was included as part of the anomaly investigation.

RESULTS AND DISCUSSION

Compared to the pre-treated inorganic sample (<2 mm), the elements chemically analysed (for list of elements see Fig. 1) were found to be enriched in the fine fraction (<0.1 mm). According to the calculated Cac, all elements studied could be divided into 3 groups: (1) intensively accumulated ones with Cac > 3 (Zr, Ag, Cr), (2) moderately accumulated with Cac = 2–3 (Yb, Ti, P, V, Y, Zn, Sc, Th, U, Cu, Co, Nb, La), and (3) slightly accumulated with Cac < 2 (all other elements). The major elements (Fe, Mn, Al) belong to the group of slightly accumulated elements (Fig. 1).

Almost all the elements studied accumulate more intensively in the clay-sized separate (<0.005 mm) of the fine fraction. The clay-sized separate shows a pronounced accumulation of P (Cac > 11) and strong accumulation of Cu, Zn, Ni, Co, Cr, V, Sn, Fe, Mn (Cac > 5). Moderate accumulation (Cac > 3) was shown by Sc, Ga, La, Nb, Ti, Th, Al, Rb, U. Other elements accumulate slightly. It is noteworthy that Zr ascribed to the group of elements intensively accumu-

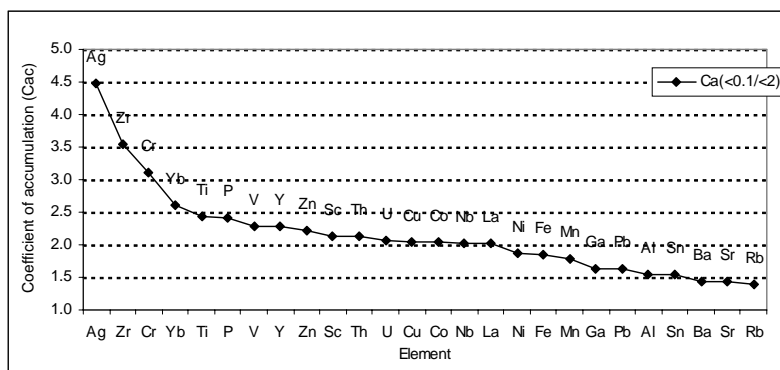


Fig. 1. Accumulation of elements in the fine fraction (<0.1 mm) of soil (A_1 horizon)

1 pav. Cheminių elementų kaupimasis Ašmenos aukštumų dirvožemio A_1 horizonto smulkiojoje frakcijoje ($<0,1$ mm)

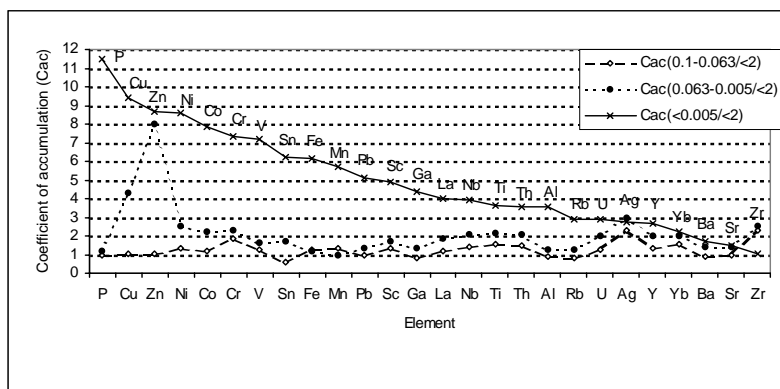


Fig. 2. Accumulation of elements in separated subfractions of the fine fraction (<0.1 mm) of soil (A_1 horizon) of Ašmena Highlands, Lithuania

2 pav. Cheminių elementų kaupimasis Ašmenos aukštumų dirvožemio A_1 horizonto aleuritinėje ir pelitinėje frakcijoje

lating in the fine fraction shows a pronounced accumulation in the aleuritic part (0.063–0.005 mm) of the fine fraction and not in the clay. Ag was more evenly distributed within all separates of the fine fraction (Fig. 2).

Zr, Nb, Yb, Ti, Y and La, which are rendered to be immobile or only slightly mobile during soil forming processes, are characteristically hosted by the most resistant heavy minerals. Previous investigations of the total chemical composition of grain-size fractions of soil from Ašmena Highlands showed the highest content of Ti, Zr, Y, Yb, Ag and Mn in the heavy fraction of the fine sand fraction (Vareikienė, 2001). This allowed

us to suggest that the carrier minerals could, by analogy, explain an increased content of these elements in the fine fraction. The other elements studied usually occur only partly in primary heavy minerals and obviously they have other modes of occurrence.

To test this hypothesis, XRD analyses of the fine fraction were performed. According to the 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 group nor the smectite group were encountered (Fig. 3). A decreased adsorption capacity of the fine fraction followed, and thus the elements were almost exclusively hosted by the primary minerals and secondary Fe–Mn oxides / hydroxides that remained after the pre-treatment.

Electron optical imaging and spectral analysis of the heavy fraction showed that the predominant minerals include amphibole (mostly hornblende), epidote, garnet, ilmenite, rutile, clinopyroxene (mostly diopside) and zircon. Because of structural changes which occurred both during primary weathering and after pre-treatment of the sample, the mica minerals with their alteration products up to chlorite and a minor amount of other minerals, such as weathered amphibole, pyroxene and epidote, are included in the group of unrecognised minerals. For the purpose of theoretical cal-

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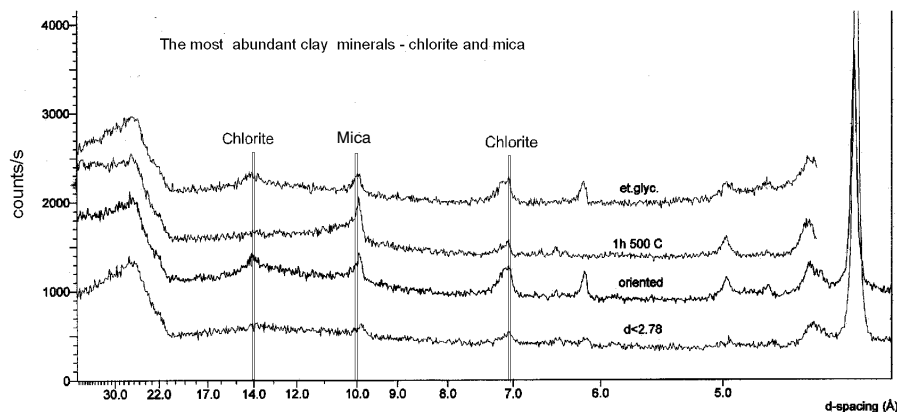


Fig. 3. XRD analysis of clay minerals in the fine fraction (< 0.1 mm) of Ašmena Highlands, Lithuania

3 pav. Ašmenos aukštumų dirvožemio A_1 horizonto molio mineralai (rentgenograma)

culations, biotite was chosen as the mica mineral in the calculation of the contribution of elements to the fine fraction.

Tourmaline, sphene, apatite, monazite and hematite were subordinate heavy mineral species in the fraction. Xenotime and chromite were found to be present but in traces (Fig. 4). This distribution of heavy minerals resulted from their primary origin in the bedrock of the provenance, their physical properties and the initial grain size. The major part of the most abundant minerals, mostly amphibole, pyroxene and garnet, was inherited from rocks of the Fenoscandian Shield and eroded, transported and deposited by glaciogenic processes during the Medininkai (Wartian / Upper Saalian) glaciation of the Middle Pleistocene. The most resistant minerals, such as rutile, zircon, tourmaline, ilmenite and possibly some other minerals were recycled from various types of pre-Quaternary sedimentary rocks which underwent several prolonged periods of intense chemical weathering. An extraordinary high content of ilmenite (more than half of the heavy fraction) is characteristic of the aleuritic fraction of pre-Quaternary deposits (Иозапавичус, 1974).

Although heavy minerals account for only 1.67% of the fine fraction, they could be important carriers of many elements in soil. The elements of the above-mentioned major groups are found as main and trace elements in a variety of minerals, but the contribution of Fe and Al to the fine fraction from the corresponding host minerals is low (about 12% for Fe and <3% for Al), while the contribution of Mn amounts to 60% (Fig. 5). Calculations based on the mineral chemistry of the carrier minerals in the heavy fraction show that ilmenite, amphibole, hematite, biotite and epidote are the main mineral sources of Fe in the fine fraction. In spite of the high average content of Fe in hematite, ilmenite and amphibole are the main contributors due to their high abundance (Fig. 6a). Spessartine (with a contribution exceeding 30%) seems to be the main source of Mn, ilmenite and almandine are less important (with a contribution in the range 6–10%), while other Mn-containing minerals only insignificantly influence the total amount of Mn

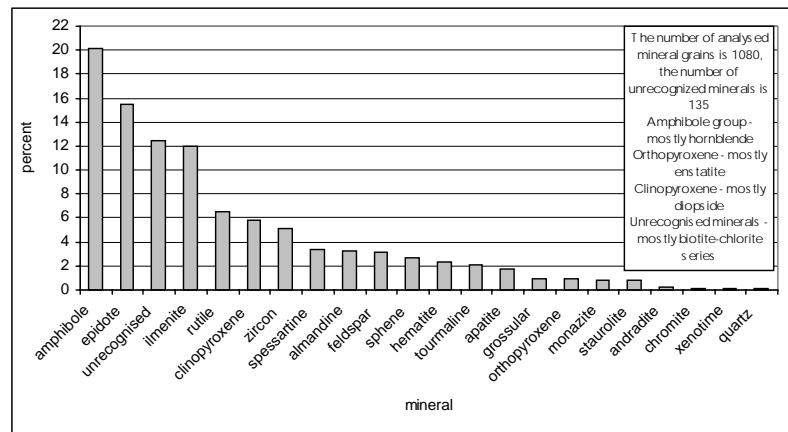


Fig. 4. Distribution of heavy minerals in the fine fraction (<0.1 mm) of soil (A₁ horizon) of Ašmena Highlands, Lithuania
4 pav. Sunkiųjų mineralų pasiskirstymas Ašmenos aukštumų dirvožemio A₁ horizonto smulkiojoje frakcijoje (<0,1 mm)

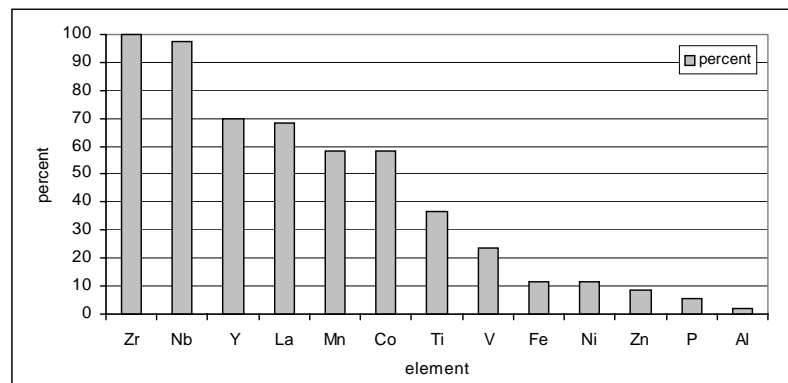
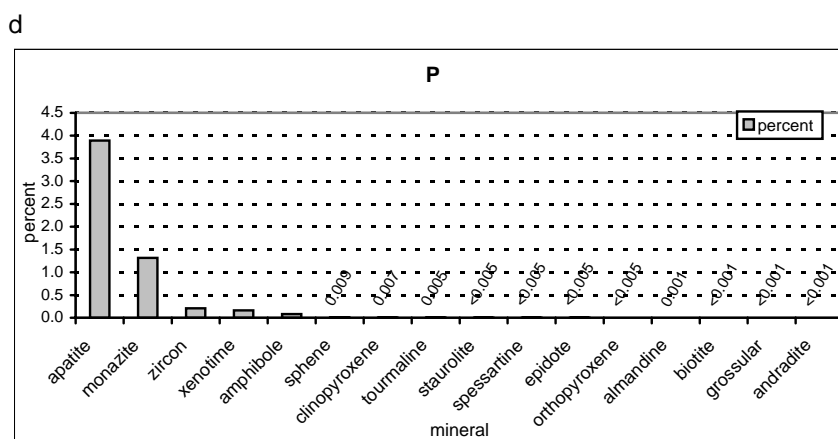
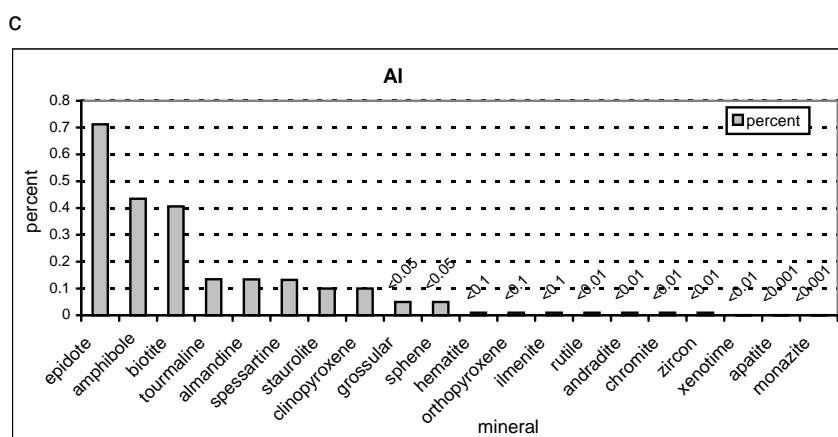
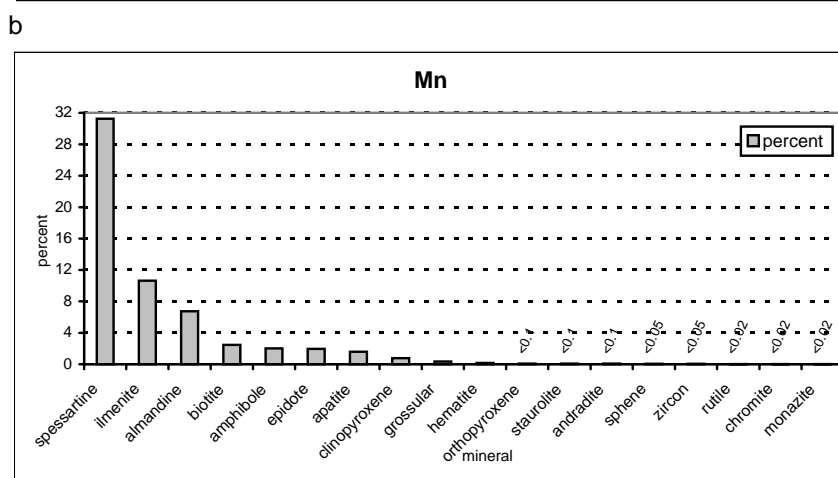
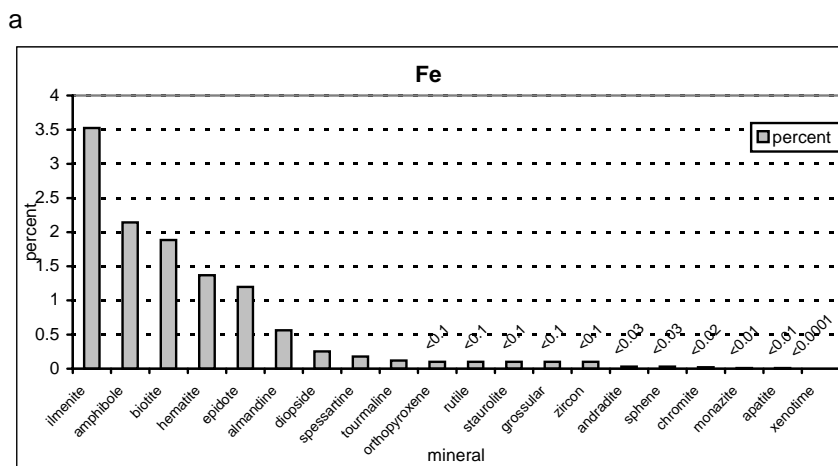


Fig. 5. Total contribution of selected elements from their carriers (heavy minerals) in their total amount in the fine fraction (<0.1 mm) of soil (A₁ horizon) of Ašmena Highlands, Lithuania
5 pav. Atskirų elementų įnašas iš sunkiųjų mineralų-nešėjų į bendrą Ašmenos aukštumų dirvožemio (A₁ horizontas) smulkiosios frakcijos (< 0,1 mm) sudėtį

in the fine fraction (Fig. 6b). The contribution of Al from the host heavy minerals is less than 3%, the main mineral sources of Al are epidote, amphibole and a wide group of other minerals (*e. g.*, staurolite, clinopyroxene, grossular, xenotime, sphene) that contain Al only in traces (Fig. 6c).

The highest contents of P, which is moderately accumulated in the fine fraction and most intensively accumulated in the clay-sized separate, are usually found in apatite and monazite. However, the contribution to the total amount of P from these carriers is low, reaching about 4% from apatite and less than 1.5% from monazite (Fig. 6d). The total contribution of P from host heavy minerals is low and makes up only about 6% (Fig. 5). The direct determination of all phosphate minerals in soils is difficult due to the complex chemistry and transfor-

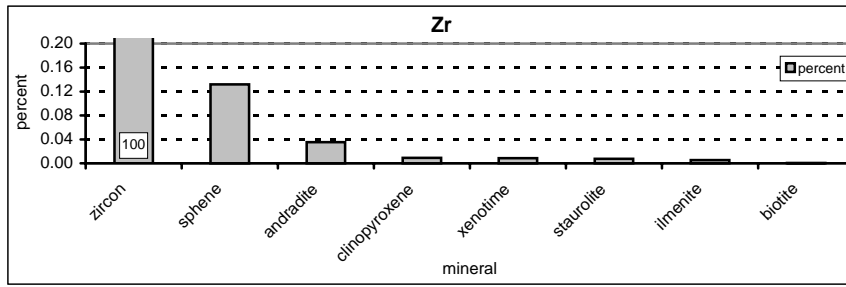


mation processes in soil phosphates. Detrital phosphate minerals comprise only a small part of the total inorganic matrix of soil. Approximately 30 phosphate minerals have been reported in soils, but a considerable fraction of P is present in organic forms or as adsorbed P (Dixon J. B., 1977).

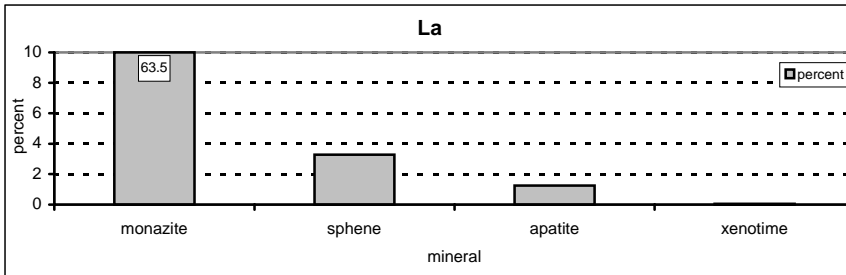
The contents of Zr, Ti, Y, Yb, La, which were attributed to the groups of intensively (Zr) and moderately (Ti, Y, Yb, La) accumulated elements in the fine fraction (Fig. 1), are almost exclusively dependent on the contents of their host heavy minerals. Here they form the major constituents, for example, Zr in zircon and Ti in rutile and ilmenite. In some minerals, a particular element is present in traces, *e. g.* Y in zircon, Zr in xenotime and staurolite, and Nb in rutile and sphene. Consequently, a high contribution of Zr, Y, Nb, La, Ti in the heavy mineral fraction may be expected.

Quantitative distribution of Zr and Nb is predicted by the abundance of the corresponding main carrier minerals, namely zircon for Zr and rutile, sphene and to a less extent ilmenite for Nb (see Fig. 6 e, g). The content of zirconium in the most resistant and abundant Zr-mineral, zircon, is on average about 45%. In natural compounds, Zr is isomorphic with Ti, Nb, Th, rare-earths, Ca, etc. Isovalent isomorphism with Ti is revealed in zirconium in titanium minerals, in ilmenite Zr may replace iron. The presence of Zr in sphene could be understood through the following mechanism: $\text{Ca}^{2+} + \text{Ti}^{4+} \leftarrow \leftarrow \text{Zr}^{4+} + (\text{Mg}, \text{Fe})^{2+}$. The same scheme of isomorphism is assumed for titaniferous garnets. In other minerals Zr occurs in very small amounts. Nb is dispersed mostly as an isomorphic inclusion in titanium,

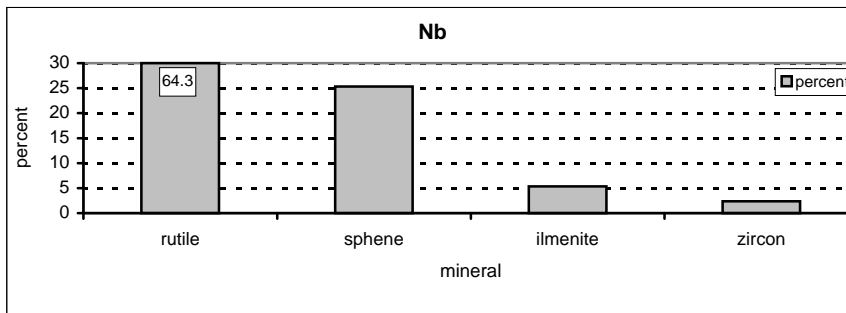
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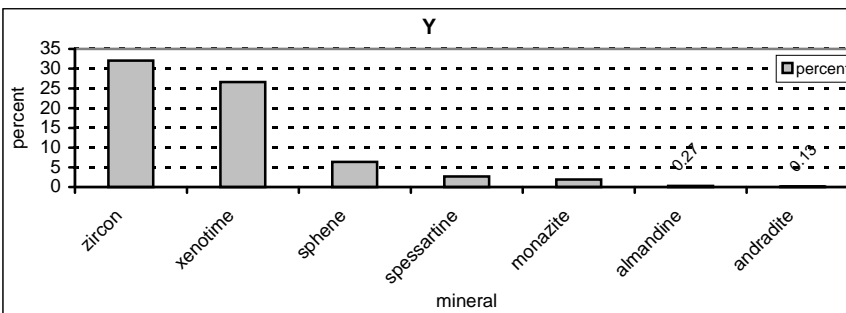
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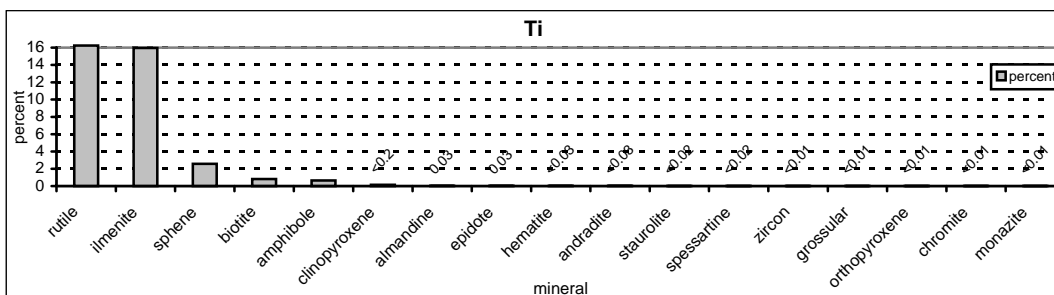
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zirconium and iron minerals. The heterovalent isomorphism of Nb is very pronounced, it is usually subdivided into two classes: 1) Nb (V) replaces certain tetravalent cations (Ti, Zr, Sn), and 2) Nb (V) replaces trivalent cations (Fe, REE). The first type of heterovalent isomorphism, characterized by the substitution of Nb for Ti and Zr, is most common (Vlasov K. A., 1966). The particularly close geochemical relationship between Nb and Ti explains the high Nb contribution from the main carrier minerals to the fine fraction: rutile (about 64%), sphene (up to 25%), ilmenite (about 5%) (Fig. 6g). The total average contributions of Zr and Nb from respective host heavy minerals amount to 100% (Fig. 5). Yttrium contribution to the fine fraction is found to be highest from zircon, xenotime and sphene. Monazite and sphene account for La contribution. Total contributions of Y and La from host minerals are more than 50%. The contribution of Ti from host minerals reaches up to 40% and results mainly from such carrier minerals as rutile, ilmenite and to some extent from sphene. Clay-sized anatase crystals are usually formed in the soil environment during the weathering processes (Dixon J. B., 1977) and they could be the main carriers of Ti in clay-sized separates.

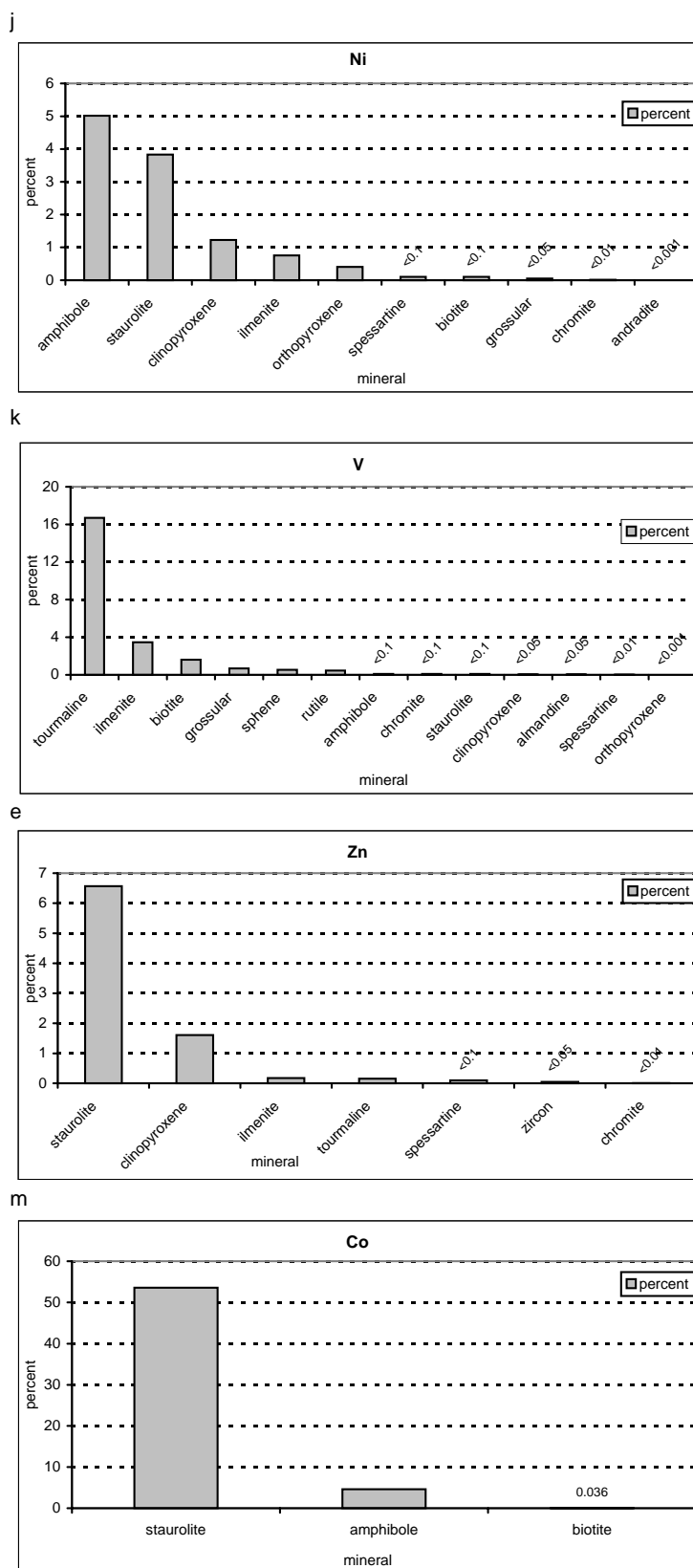


Fig. 6. Estimation of the contribution of the elements from carrier heavy minerals to their total amount in the fine fraction (<0.1 mm) of soil (A_1 horizon) of Ašmena Highlands, Lithuania
6 pav. Elementų įnašas iš sunkiųjų mineralų-nešėjų į bendrą elementų kiekį Ašmenos aukštumų dirvožemio A_1 horizonto smulkiojoje frakcijoje ($< 0,1$ mm)

It has been noted that out of the elements predominantly accumulated in the clay-sized separate, only the contribution of Co from host minerals is high ($>50\%$), while the contributions of Zn, Ni and V are low and do not exceed 30% (Fig. 5). This indicates a preferable accumulation in other modes of occurrence, such as in the lattice of light minerals and other minerals formed during weathering, or adsorbed as ions on the surface of weathered minerals and covered and protected by subsequent precipitation of secondary oxides / hydroxides. Since their coefficients of accumulation are very high in the clay-sized separate, is suggested that the increase can be attributed to the presence of very low levels (mostly <0.002 mm) of secondary Fe and Mn oxides / hydroxides, which mostly precipitated on the surface of detrital crystals and remained after the pre-treatment of the sample.

The explanation of the origin of the increased content of Ag, Cr, Ba, Sr and some other elements analysed requires additional studies of the chemical composition of both the light and the heavy fractions as well as identification of the light minerals of the fine fraction.

CONCLUSIONS

The current study allows to conclude that according to the contribution of certain elements from carrier heavy minerals to the fine fraction (<0.1 mm), the elements studied could be subdivided into 3 groups:

- 1 – elements least dependent on the content of heavy minerals: P, Al, Zn (contribution from the host minerals is $<10\%$),
- 2 – elements moderately dependent: Ti, V, Fe and Ni (contribution is 10–50%),
- 3 – elements strongly dependent: Zr, Nb, Y, La, Mn, Co (contribution $> 50\%$).

In spite of the low content of heavy minerals in the sample studied, absolute accumulation of Zr and Nb, as well as strong accumulation of Y, La, Mn and Co in the fine fraction could be explained by a high concentration of the elements in their carrier heavy minerals. Low contributions of other elements from their host heavy minerals indicate their preferred accumulation in other modes of occurrence, such as in the lattice of light minerals, in secondary minerals formed during weathering or in adsorbed forms.

The approach used in this attempt to quantify the contribution of various mineral species to the chemical composition of the sample proved to be feasible; the results achieved were reasonable, despite the fact that sources of potential errors were not determined. These errors include: (1) separation of lighter and heavier minerals during sample preparation, (2) large grain size distribution in the fractions studied, (3) lack of density and areal distribution corrections, (4) statistical errors caused by the use of an average chemical composition of minerals from a data base, which was not created from the minerals of the study material, and 5) calculation of elemental contribution from a group of unrecognized minerals only as from one mineral (biotite). The ongoing research will focus on improving the accuracy of the results through an appropriate estimation of the sources of errors.

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KAI KURIŲ ELEMENTŲ MINERALINĖS BŪVIO FORMOS AŠMENOS AUKŠTUMŲ DIRVOŽEMIO (A₁ HORIZONTAS) SMULKIOJOJE FRAKCIJOJE (< 0,1 mm)

S a n t r a u k a

Mikroelementų kiekis dirvožemyje labai priklauso nuo jų kiekio smulkiojoje frakcijoje (< 0,01 mm). Elementai šioje

dirvožemio dalyje pasiskirsto priklausomai nuo pirminių mineralų sudėties, molio dalelių ir įvairių antrinių oksidų bei hidroksidų gausos. Šio darbo tikslas buvo nustatyti pasirinktų elementų mineralus-nešėjus seniausiam Lietuvos dirvožemyje, susidariusiam priešpaskutiniojo ledynmečio (Medininkų) nuogulose.

Dirvožemio mėginys paimtas iš A₁ horizonto (5–15 cm gylio). Organinė medžiaga ardyta panaudojus laipsniškai didėjančias H₂O₂ koncentracijas (nuo 3 iki 30%). Likusi mineralinė mėginio dalis sietais padalyta į stambiają (2–0,1 mm) ir smulkiąją (< 0,1 mm) frakciją. Paskutinioji frakcija praskiestu bromoformu (d-2,78) padalyta į lengvąją ir sunkiąją frakciją, kurios pirminiam mineralų pasiskirstymui įvertinti buvo analizuojamos XRD metodu. Apie 1000 sunkiųjų mineralų grūdelių identifiukuota skenuojančiu elektroniniu mikroskopu. Visos frakcijos, kaip ir pirminis mėginys, analizuotos ICP-AES ir ICP-MS metodais, nustatant makro- ir mikroelementų kiekius. Elementų įnašas apskaičiuotas panaudojant procentinį atskirų mineralų pasiskirstymą sunkiojoje frakcijoje, vidurkinis elementų kiekius mineraluose-nešėjuose ir santykinį sunkiosios frakcijos kiekį visame analizuojamame smulkiosios frakcijos mėginyje.

Visų cheminių elementų kiekiai smulkiojoje dirvožemio frakcijoje, palyginus su kiekiu visame dirvožemyje, yra didesni. Pagal koncentracijos koeficientus visi elementai gali būti suskirstyti į tris grupes: intensyviai (Kk >3; Ag, Cr ir Zr), vidutiniškai (Kk 2–3; P, V, Zn, Ti, Y, Sc, Th, U) ir mažai besikaupiantys (Kk 1–2; visi kiti tirti elementai) (1 pav.).

Smulkioje dirvožemio frakcijoje dauguma cheminių elementų koncentruojasi jos pelitinėje dalyje (2 pav.). Lyginant su kiekiu visoje smulkiojoje frakcijoje, pelitinėje jos dalyje, labiausiai kaupiasi (Kk >5) P, Mn, Fe, Co, Cr, Cu, Ni, V, Sn ir Zn. Pažymėtina, kad smulkiojoje frakcijoje intensyviausiai besikaupiantis Zr yra susijęs ne su pelitine, o aleuritine dirvožemio dalimi, o Ag pasiskirstęs tolygiai po visas frakcijas.

XRD analizė parodė, kad lengvojoje frakcijoje labiausiai paplitę kvarcas, K-lauko špatas, plagioklazas, dioktaedrinis žerutis bei chloritas. Beveik neaptikta smektitio bei kaolino grupių molio mineralų (3 pav.). Tai reiškia sumažėjusį dirvožemio sorbcinio komplekso imlumą, todėl pagrindiniai elementų nešėjai smulkiojoje frakcijoje – pirminiai mineralai ir antriniai oksidai / hidroksidai, išlikę mėginį apdorojus H₂O₂.

Elektroninė spektrinė sunkiosios frakcijos analizė parodė, kad labiausiai paplitę amfibolai (daugiausia raginukė), epidotas, granatai, ilmenitas, rutilas, piroksenai (daugiausia diopsidas) ir cirkonas. Biotito–chlorito serijos mineralai bei maža grupė kitų mineralų (amfibolai, piroksenai, epidotas it kt.) dėl identifikavimo sunkumų, susijusių su mineralų struktūriniais pakitimais dūlėjimo bei mėginio apdoravimo metu, priskirti nenustatytų mineralų grupei. Turmalinas, sfenas, apatitas, monacitas ir hematitas paplitęs vidutiniškai. Ksenotimo ir chromito buvo aptikti tik mikrokiekiai (4 pav.).

Nors sunkieji mineralai sudaro tik 1,67% visos smulkiosios frakcijos, dirvožemyje jie gali būti svarbiais elementų nešėjais. Pagal apskaičiavimus, pagrįstus sunkiosios frakcijos mineralų chemine sudėtimi, ilmenitas, amfibolai, biotitas, hematitas, epidotas – pagrindiniai Fe mineralai-nešėjai smulkiojoje frakcijoje, nors jų bendras įnašas ne didesnis kaip 12% (5 pav.). Nepaisant aukšto vidurkinio Fe kiekio hematite, ilmenitas ir amfibolai dėl jų gausumo gali būti

pagrindiniai Fe šaltiniai (6 pav., a). Spesartinas yra pagrindinis Mn nešėjas, tuo tarpu kitų mineralų-nešėjų įtaka bendram Mn kiekiui smulkiojoje frakcijoje menka (6 pav., b). Al įnašas iš mineralų-nešėjų mažesnis nei 3%, pagrindiniai Al šaltiniai – epidotas, amfibolai (6 pav., c). Daugiausia P paprastai yra apatite ir monacite, bendras P įnašas iš sunkiųjų mineralų nedidelis (5 pav.).

Zr ir Nb kiekiai visiškai priklauso nuo jų mineralų-nešėjų kiekio, pagrindinis Zr mineralas-nešėjas – cirkonas, Nb – rutilas, sfenas, mažiau ilmenitas (6 pav., e, g). Zr kiekis cirkone sudaro vidutiniškai apie 45%. Kituose mineraluose Zr kiekiai labai maži ir jų įtaka bendram Zr kiekiui smulkiojoje frakcijoje nedidelė. Nb daugiausia pasiskirsto kaip izomorfinė priemaiša Ti, Zr ir Fe mineraluose. Labai artimas geocheminis Nb ir Ti ryšys nulėmė Nb paplitimą pagrindiniuose mineraluose-nešėjuose: rutilas (apie 64%), sfene (iki 25%), ilmenite (apie 5%) (6 pav., g). Bendras Zr ir Nb mineralų-nešėjų įnašas į jų kiekius smulkiojoje frakcijoje siekia 100% (5 pav.). Didžiausias Y įnašas yra iš cirkono, ksenotimo ir sfeno, La – monacito ir sfeno. Šių elementų bendri įnašai iš mineralų-nešėjų sudaro daugiau nei 50%. Ti įnašas iš mineralų-nešėjų į jo bendrą kiekį smulkiojoje frakcijoje sudaro apie 40% (5 pav.) ir yra didžiausias rutilas, ilmenite, mažesnis – sfene (6 pav., i).

Pažymėtina, kad iš elementų, intensyviai besikaupiančių pelitinėje frakcijoje, tikrai Co įnašas iš jo sunkiųjų mineralų-nešėjų yra aukštas (> 50%), tuo tarpu Zn, Ni bei V neviršija 30% (5 pav.). Tai rodo jų kaupimąsi kitose formose: lengvuose mineraluose, sorbuotos formos antriniuose mineraluose, susiformavusių dūlėjimo procesų metu.

Pagal atskirų elementų įnašą iš sunkiųjų mineralų-nešėjų į bendrą jų kiekį Ašmenos aukštumų dirvožemio (A_1 horizontas) smulkiojoje frakcijoje (< 0,1 mm), analizuojami elementai gali būti suskirstyti į 3 grupes: 1) elementai, kurių kiekiai mažai priklauso nuo sunkiųjų mineralų kiekio – P, Al, Zn (įnašas < 10%), 2) elementai, kurių kiekis vidutiniškai priklauso nuo sunkiųjų mineralų kiekio – Ti, V, Fe ir Ni (įnašas 10–50%), 3) elementai, kurių kiekis labai priklauso nuo šių mineralų kiekio – Zr, Nb, Y, La, Mn, Co (įnašas > 50%). Bendras Zr ir Nb kiekis, taip pat didžioji dalis Y, La, Mn ir Co bendro kiekio smulkiojoje frakcijoje gali būti paaiškinta jų kiekio priklausomybe nuo sunkiųjų mineralų kiekio, nors šie mineralai sudaro nedidelę smulkiosios frakcijos dalį. Šie su akcesoriniais mineralais susiję cheminiai elementai smulkiojoje dirvožemio frakcijoje daugiausia aptinkami kaip pagrindiniai mineralų elementai ir kaip izomorfinės priemaišos. Kitų cheminių elementų kiekiai daugiau priklauso nuo lengvųjų pirminių ir antrinių mineralų kiekio bei nuo sorbuotos jų formos.

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МИНЕРАЛЬНЫЕ ФОРМЫ НЕКОТОРЫХ ЭЛЕМЕНТОВ В МЕЛКОЙ ФРАКЦИИ (<0,1 мм) ПОЧВ (ГОРИЗОНТ A_1) АШМЯНСКОЙ ВОЗВЫШЕННОСТИ

Резюме

Содержания элементов в почвах в основном зависят от их содержания в мелкой фракции (<0,1 мм), в которой элементы распределены в зависимости от состава первичных минералов, глинистых частиц, а

также различных вторичных оксидов и гидроксидов. Главная задача этой работы состояла в определении минералов-носителей отдельных (некоторых) элементов в старейшей почве, сформировавшейся в ледниковых отложениях предпоследнего Мядининкского оледенения Литвы.

Образец почв взят из горизонта A_1 (глубина 5–15 см). Разложение органического вещества произведено используя H_2O_2 , оставшаяся минеральная часть сетовым методом разделена на крупную (2–0,1 мм) и мелкую (<0,1 мм) фракции. Используя частично разбавленный бромформ (D – 2,78), последняя фракция разделена на легкую и тяжелую фракции, которые были анализированы рентгено-дифракционным методом (РДМ). Около 1000 отдельных минералов идентифицированы с помощью сканирующего электронного микроскопа (СЭМ). Для определения макро- и микроэлементного состава все фракции были анализированы ИСП-АЭС и ИСП-МС методами. Для определения вноса элементов из отдельных минералов были использованы: процентное распределение минералов в тяжелой фракции, средние содержания элементов в минерал-носителях и процентное содержание тяжелой фракции в мелкой фракции.

Содержания всех анализируемых элементов выше в мелкой фракции по сравнению с их количеством в первичном образце. По коэффициентам концентрации элементы подразделены на три группы: 1 – интенсивно накапливающиеся ($K_k > 3$) – Ag, Cr и Zr, 2 – средне накапливающиеся ($K_k 2–3$) – P, V, Zn, Ti, Y, Sc, Th, U и 3 – мало накапливающиеся ($K_k 1–2$) – все остальные элементы (рис. 1).

В мелкой фракции большинство элементов накапливаются в ее пелитовой части (рис. 2), в которой определены наибольшие количества P, Mn, Fe, Co, Cr, Cu, Ni, V, Sn и Zn ($K_k > 5$). Нужно отметить, что интенсивно накапливающийся в мелкой фракции Zr связан не с ее пелитовой, а с алевритовой частью, в то время как содержание Ag равномерно распределено по всем фракциям.

По результатам РДМ, в легкой фракции наиболее распространены кварц, K-полевые шпаты, плагиоклазы, диоктаэдрические слюды и хлорит. Глинистые минералы из групп смектита и каолина не определены (рис. 3). Это предуславливает уменьшенную сорбционную емкость почв, а также накопление элементов в основном в первичных минералах и вторичных оксидах и гидроксидах.

По данным анализа с помощью СЭМ, в тяжелой фракции наиболее распространены амфиболы, эпидот, гранаты, ильменит, пироксены и циркон. Минералы биотитовой-хлоритовой серии, как и небольшая часть первично выветрелых других минералов, включены в группу неопределенных минералов из-за трудностей их идентификации, связанной со структурными изменениями как в процессе выветривания, так и во время обработки с H_2O_2 . Определены небольшие количества турмалина, sfena, апатита, монацита, гематита и очень малые – ксенотима и хромита (рис. 4).

Хотя тяжелые минералы составляют очень малую процентную часть всей мелкой фракции, они могут быть основными носителями отдельных элементов. Подсчеты на основе химического состава минералов тяжелой фракции показали, что основными минералами-носителями Fe являются ильменит, амфиболы, биотит, гематит, эпидот, хотя общий внос Fe из минералов составляет не больше 12% (рис. 5). Несмотря на высокое среднее содержание Fe в гематите, ильменит и амфиболы являются его основными источниками – носителями (рис. 6а). Спессартин – основной носитель Mn, остальные минералы в малой степени влияют на его содержание в мелкой фракции (рис. 6б). Основные минералы-носители Al – эпидот и амфиболы (рис. 6с). Общий внос Al из минералов <3% (рис. 5). Общий внос P из минералов небольшой (рис. 5), основные минералы-носители – апатит и монацит (рис. 6д).

Содержания Zr и Nb полностью зависят от количества их минералов-носителей, основной минерал-носитель Zr – циркон, в других минералах его количество небольшое и не влияет на его содержание в мелкой фракции (рис. 6е). Основные минералы-носители Nb – рутил (внос 64%), сфен (внос около 25%), в меньшей степени ильменит (внос около 5%) (рис. 6г). Общий внос Zr и Nb из их

минералов-носителей в их содержание в мелкой фракции составляет 100% (рис. 5). Циркон, ксенотим и сфен являются основными носителями Y (рис. 6h), а монацит и сфен – La (рис. 6f). Общий внос этих элементов из их минералов-носителей составляет <50%. Внос Ti наибольший из рутила, ильменита, в меньшей степени из сфена (рис. 6i), общий внос Ti из его минералов-носителей составляет около 40% (рис. 5).

Из элементов, интенсивно накапливающихся в пелитовой фракции, только внос Co из его минералов-носителей высокий (>50%), в то время как общий внос Zn, Ni и V не превышает 30% (рис. 5). Это указывает на другие их формы накопления: легкие минералы, вторичные минералы, сорбированные формы.

Отдельные элементы мелкой фракции (<0,1 мм) почв (горизонт A₁) Ашмянской возвышенности по их вносу из минералов-носителей могут быть подразделены на 3 группы: 1 – элементы, накопление которых слабо зависит от содержания минералов-носителей: P, Al, Zn (внос <10%), 2 – элементы, накопление которых средне зависит от содержания минералов-носителей: Ti, V, Fe и Ni (внос 10–50%), 3 – элементы, накопление которых сильно зависит от содержания минералов-носителей: Zr, Nb, Y, La, Mn, Co (внос >50%).