GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA XX. 2 — BRATISLAVA, DEZEMBER 1969

JOZEF FORGÁČ*

GEOCHEMISTRY OF ANDESITES WEATHERING

(Figs. 1—21)

Abstract: The mostly wide spread alteration in areas formed by neovolcanic rocks in Slovakia is weathering. I performed the study of this process on the example of two profiles of gradual transition from fresh andesite to completely leached and weathered one and on one profile of mining works below the surface, where I traced the process of weathering of chloritized andesite. In the work I present the succession of weathering of these rocks and geochemical dependences between macroelements and microelements in weathering process.

Introduction

The process of weathering of andesites is one of the mostly wide spread processes in the region of Slovakian neovolcanites, in the course of which gradually complete decomposition of rocks is reached and in this way also great geochemical changes in the composition of original rock take place. I studied this process on three continuous profiles in the succession from fresh andesite to completely weathered one at the localities of Fieberg and Breziny on the surface, where fresh andesites underwent weathering and in Banská Štiavnica below the surface in the cross adit of the Maxmilian Pit, where weathering of chloritized andesite with slight impregnation of sporadic clusters of pyrite was taking place. I studied changes in representation of principal rock-forming elements and trace elements and their mutual relations in weathering process with increasing intensity of rock alteration. In this study the overburden of eluvial loams at the first two localities was not included. Geochemical changes are directly connected with alteration of original minerals in the rock. In the characterization of individual profiles I therefore also mention the changes in mineralogical composition of rock with the succession of weathering.

Course of Weathering at the Locality of Fieberg

A distinct profile of weathering is exposed in the quarry of Fieberg, about 1 km northwest of Krupina in pyroxenic andesite with distinct prismatic jointing. High alteration of andesite was taking place in northern and north-western part of the quarry, where andesite is altered from the surface to the depth of 6 to 11 m below humic greyishbrown loam, resting on andesite 40 cm to 1 m thick. On the wall of the quarry there is a gradual transition from completely altered andesite to fresh andesite in the lower part of the quarry (fig. 1).

Fresh andesite is of dark colour, porphyric texture. The groundmass is vitrophyric-cryptocrystalline with finely dispersed ore pigment. From the minerals are mostly represented in the rock plagioklases in the form of tables and laths, which correspond in basicity to andesine-labradorite ($Ab_{60}An_{40}$ to $Ab_{42}An_{58}$). From dark-coloured minerals the rock contains augite and hypersthene. Representation of chemical elements is in table 2, no. 1. Towards the surface gradually precipitation of Fe oxides takes place on joints and the rock is getting grey and later greyishbrown o light-greyishbrown colour.

---

* RNDr. J. Forgáč, CSc., Dionýz Štúr Institute of Geology, Bratislava, Mlynská dol. 1.

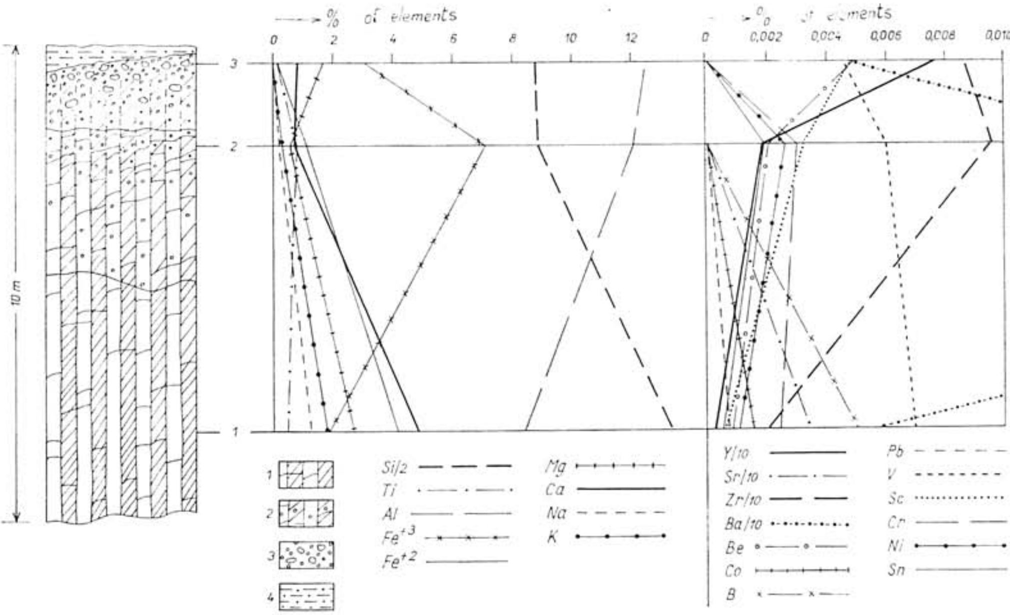

Fig. 1. Profile of weathering of pyroxenic andesite in the quarry of Fieberg. 1 — Dark coloured pyroxenic andesite. 2 — Grey to lightgrey, slightly coherent, partly disintegrating pyroxenic andesite. 3 — Completely weathered and disintegrated pyroxenic andesite. 4 — Greishbrown humous loam.

At the edges it is peeling off in the form of concave crusts 1 to 6 m thick from almost fresh rock. In higher parts of the wall of the quarry the rock is of light greyishbrownish colour. the alteration pervades all the rock. which becomes little coherent and starts to break up into small shreds. mainly at the edges of prismatic jointing. Original prismatic jointing becomes less distinct than in the lower part of the quarry. With alteration of the rock plagioclases loose their cluster and break from the periphery along fissures into a light coloured gelous mass with slight indications of polarization. Gradually complete disintegration of plagioclases proceeds. A submicroscopic aggregate of prevailingly light colour gradually crystallizes from the mass. In places after the plagioklases sometimes colloform structures are forming or the spaces after plagioklases are penetrated with Fe oxides.

On the first stage of alteration from pyroxenes Fe starts to exerete in the form of coatings and clusters formed by Fe oxides and in further stage serpentinization is manifesting in them by formation of chrysotile and antigorite, which break up into a gelous mass of prevailingly brownish colour in higher stage of alteration and submicroscopic aggregate crystallizes from it. In this alteration selective alteration of minerals was manifested. in which plagioklases started to break up earlier and more intensely than pyroxenes.

The groundmass of the rocks is getting slight brownish colour. which is formed by submicroscopic aggregate, nearer undeterminable. In rock alteration montmorillonite and kaolinite originated according to DTA and X-ray analyses. In this stage of alteration original porphyritic texture is still evident in the rock.

Table 1. Weight Per Cent of Chemical Analyses

	Fieberg			Breziny				Banská Štiavnica			
	1	2	3	1a	2a	3a	4a	1b	2b	3b	4b
SiO_2	57,73	38,07	37,80	57,79	56,66	53,76	53,82	55,80	57,56	53,12	54,45
TiO_2	0,93	1,50	0,40	0,93	0,93	0,93	1,32	0,57	0,65	0,58	0,77
Al_2O_3	15,84	21,05	21,50	17,85	17,40	17,09	16,06	18,63	20,00	19,52	16,49
Fe_2O_3	2,75	10,18	4,47	2,90	4,79	7,82	8,51	1,15	1,88	1,68	7,31
FeO	5,61	1,43	0,28	5,03	2,87	0,80	0,38	4,10	2,34	6.01	0,42
MnO	0,12	0,07	0,18	0,13	0,15	0,24	0,15	0,08	0,09	0,23	0,09
MgO	4,55	1,05	2,97	3,40	2,55	2,12	2,01	3,09	1,66	2,08	1,09
CaO	6.84	1,26	1,20	7,00	5,25	2,38	2,38	4,29	3,57	1,35	2,17
Na_2O	1,92	0,20	0,04	1,92	1,86	1,12	1,04	1,25	1,20	0,45	0,27
K_2O	2,20	0,22	0,06	1,52	1,52	1,40	1,44	2,65	2,25	2,90	3,08
P_2O_5	0,08	0,06	0,03	0,06	0,24	0,21	0,11	0,12	0,13	0,12	0,12
SO_3	—	—	—	—	—	—	—	0,46	0,39	1,09	4,82
H_2O (110)	0,17	12,82	23.38	0,57	3,17	7,02	7,20	0,68	1,48	1,80	3,07
H_2O (900)	0,94	10,45	8,21	2,37	2,59	5,59	5,95	6,91	7.34	9,34	6,74
The sum	99,68	98,40	100,44	101,47	99,98	100,54	100,37	99,78	100,54	100.27	100,89

Analysed by J. Dvonč, Dionýz Štúr Institute of Geology, Bratislava.

Distinct petrographic changes were also reflected in chemical composition of the rock (tab. 2, no. 2). Ca, Mg, Na, K, Si, Pb, Co, Sr, B, V were intensely leached from the rock. In this stage of alteration Al, Be, Sn, Ga, Y, Zr, Ba and Fe were manifested as little mobile to immobile elements. At Fe intense oxidation of Fe^{+2} to Fe^{+3} was taking place, the latter element was not carried away from the rock. As a consequence of small mobility of the mentioned elements a relative increase in their representation in altered rock compared to fresh rock takes place or their relative representation in the rock almost does not change.

In upper parts of the wall of the quarry under a thin humous cover andesite is completely weathered or disintegrated (in moist state it is rubbing between the fingers), indications of original prismatic and porphyritic texture of the rock are disappearing. In the uppermost parts the rock is completely decomposed and incoherent, formed by soft parts of altered andesite rounded by weathering. To the depth the amount of completely altered but slightly coherent andesite gradually increases and slight indications of the original prismatic jointing start to appear. In the upper parts of the quarry with alteration of andesite larger amount of montmorillonite and less of kaolinite originated. Chemical composition of the rock shows continuing carrying away of Na and K from the rock, however, with diminishing intensity of leaching (tab. 2, no. 3). Intensely leached from the rock are Fe^{+3}, Sn, Ni, Cr, Ba, which in deeper parts are manifesting as immobile elements. Little mobility show Ga, Zr, Ca, Si, Al, which do not show essential changes in their relative representation in rock compared to foregoing degree of alteration with intensive rock alteration. As immobile were manifested Mg, Y, Be, V, Sc, the content of which relatively increases in completely altered rock.

Table 2. Representation of Elements in % in the Profile of Weathering of Pyroxenic Andesite at the Locality of Fieberg

	1	2	3
Si^{+4}	26,97	17,78	17,66
Ti^{-4}	0,55	0,89	0,23
Al^{+3}	8,38	12,11	12,55
Fe^{+3}	1,92	7,12	3,12
Fe^{+2}	4,27	1,11	0,21
Mn^{+2}	0,09	0,05	0,13
Mg^{+2}	2,74	0,63	1,79
Ca^{+2}	4,88	0,90	0,85
Na^{+}	1,37	0,14	0,02
K^{+}	1,82	0,18	0,04
P^{+5}	0,03	0,07	0,01
Ga^{+3}	0,0010	0,0020	0,0020
Be^{+2}	0,0006	0,0020	0,0050
V^{+3}	0,0070	0,0060	0,0046
Y^{+3}	0,0039	0,0195	0,0777
Sc^{+3}	0,0007	0,0032	0,0048
Zr^{+4}	0,0209	0,0978	0,0871
Ba^{+2}	0,0589	0,3810	0,0479
Sr^{+2}	0,0347	—	—
B^{+3}	0,0050	—	—
Sn^{+4}	0,0005	0,0020	—
Pb^{+2}	0,0006	—	—
Ni^{+2}	0,0010	0,0026	—
Co^{+2}	0,0015	—	—
Cr^{+3}	0,0024	0,0031	—

The largest migration of elements was generally taking place with disintegration of the rock in the stage of breaking up of primary silicates, when the prevailing part of rock-forming elements and Pb. Co. Sr. V from trace elements passed over into solutions, whereby pH increased in percolating solutions. This stage of alteration is characterized by high leaching coefficient — 2.22 (calculated according to I. I. Ginzburg 1963), high oxidation of Fe^{+2} to Fe^{+3} was taking place, wherein Fe^{+3}, Al, Ti, Y, Zr, Ba, Sn, Be, Sc, Ni, Ga, Cr are little mobile to immobile as a consequence of what their ration in the rock relatively increases. On the basis of the mobility of elements in dependence on pH of solutions that of percolating solutions may be supposed to vary in the limits between 5 and 6. At this value of pH $Fe(OH)_3$ and $Al(OH)_3$ as well as a series of other elements are little mobile and Si in the sense of I. I. Ginzburg (1960) shows relatively small tendency to precipitation from the solutions in the form of colloids, it was intensely leached out from the rock together with other elements.

After leaching a larger amount of Na, K, Mg, Ca, Si, V and carrying away of Pb, Co, B, Sr their passing into solutions essentially diminished as formation of clay minerals, mainly of montmorillonite and less of kaolinite took place, wherein a part of the elements remained bound in their structural lattice or they were entrapped in products of disintegration of andesite as sorbents so that they did not pass into the solutions. As a consequence of that no greater change of pH of solutions was evident, which percolated from the surface through the humous overburden into the rock and pH value probably varied between 4 and 5. The elements which appeared as immobile at the beginning of the process of alteration were intensely carried away from the rock, they are mainly Fe^{+3}, Sn, Ni, Cr, Ba, the elements Y, Zr, Sc, Be, V, Ga, Mg, Al are entrapped in the rock, by what their ratio relatively increased. As a consequence of that also the coefficient of leaching decreased from 2,22 to 1,42 and the coefficient of hydratation from 0,04 to 0,03. In the course of time the zone of increased leaching of elements from the rock is shifting to deeper parts of the andesite body after breaking up of primary silicates.

The Course of Weathering at the Locality of Breziny

Another profile of weathering I have studied in the quarry on the eastern side of the Neresnícka Valley, 3.5 km northeast of the community of Breziny. The quarry is opened in pyroxenic andesite, altered and decomposed in the upper part and covered by a thin layer of humous forest loam, 10 to 40 cm thick. The thickness of weathered andesite is changing. In the southern part of the quarry it is 40 cm to 1 m while in its northwestern part it attains 3 to 6 metres. In this part of the quarry I studied continuous transition from completely altered andesite under the humous loam to fresh andesite in the lower part of the quarry (fig. 2).

Fresh andesite is of dark to dark-grey colour, with porphyritic texture. Among the minerals plagioclase of hypidiomorphic to allotriomorphic delimitation with the basicity of andesine-labradorite ($Ab_{62}An_{38}$ to $Ab_{43}An_{57}$) is mostly represented. From dark-coloured minerals hypersthene is mostly represented, sporadically augite and brown amphibole with opacite rim is present. The groundmass is of hyalopilitic character with small microlites of the mentioned minerals and small clusters of magnetite. Representation of elements is given in tab. 2, no. 1a.

In the first stages of weathering the rock is getting grey colour with yellowishbrown facets irregularly distributed. As a consequence of the colour change of the groundmass phenocrysts are stressed. Plagioclases are prevailingly fresh, to a small degree they

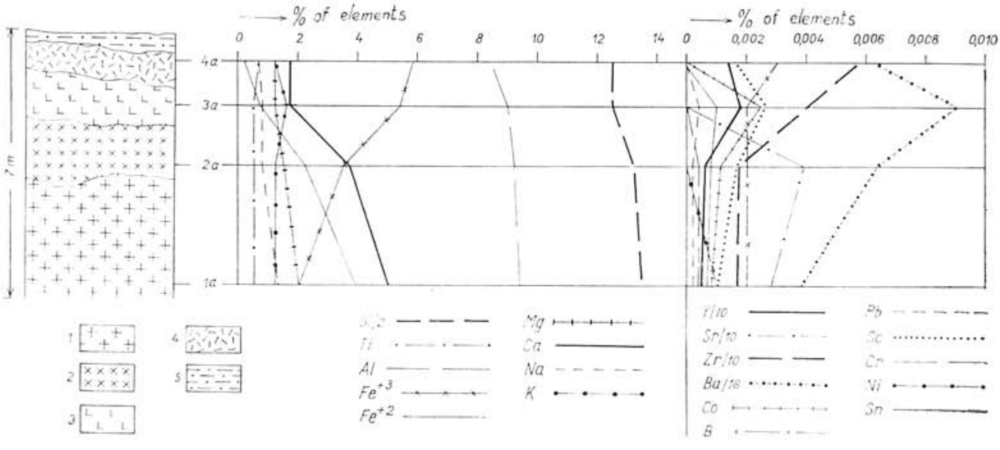

Fig. 2. Profile of andesite weathering in the quarry northwest of the community of Breziny. 1 — Dark-coloured pyroxenic andesite with amphibole. 2 — Greyishbrownish andesite. 3 — Greyishbrownish slightly coherent andesite (getting soft in moist state). 4 — Light-brownish completely altered andesite, friable in dry state. 5 — Greyishbrown stony humous loam.

start to change to an almost sheer isotropic mass. In dark-coloured minerals excretion of Fe oxides is proceeding and the minerals are altering from the periphery and along the fissures into yellowishbrown ones of scaled and fibrous character with slight pleochroism, straight extinction, index of refraction lower than that of Canada balsam. According to optical qualities they belong to chrysotile and antigorite. Small clusters of magnetite as well as opacite rims on amphibole begin gradually to change into Fe oxides. In chemical composition of the rock (tab. 3, no. 2a) changes took place as a consequence of leaching of Ca, Mg, Ni and partly Cr. At iron Fe^{+2} oxidized to Fe^{+3} and the latter appears to be an immobile element together with Be, Co, Y and their content in the rock consequently has increased. Representation of the prevailing part of elements remains almost without changes. With higher alteration the rock is getting greyishbrownish colour, is little coherent.

Plagioclases break up completely into a light-coloured submicroscopic aggregate with the content of slightly polarizing fine light-coloured scales with straight extinction, which crystallize from isotropic gelous mass in spaces after the plagioclases. Chrysotile and antigorite in spaces after pyroxenes and amphibole gradually break up into an almost isotropic mass of brownish colour with the content of slightly polarizing submicroscopic aggregate. In this breaking Fe-oxides get released in the form of fine coatings. In alteration of the rock montmorillonite formed (according to DTA and X-ray analysis).

Table 3. Representation of Elements in % in the Profile of Weathering of Pyroxenic Andesite at the Locality of Breziny

	1b	2a	3a	4a
Si^{+4}	26,99	26,45	25,11	25,14
Ti^{+4}	0,55	0,55	0,55	0,78
Al^{+3}	9,44	9,20	9,03	8,48
Fe^{+3}	2,02	3,35	5,47	5,95
Fe^{+2}	3,90	2,22	0,68	0,29
Mn^{+2}	0,10	0,11	0,18	0,11
Mg^{+2}	2,05	1,53	1,27	1,21
Ca^{+2}	5,00	3,75	1,70	1,70
Na^{+}	1,37	1,45	0,83	0,76
K^{+}	1,26	1,26	1,66	1,19
P^{+5}	0,02	0,10	0,09	0,04
Ga^{+3}	0,0010	0,0010	0,0010	0,0010
Be^{+2}	0,0004	0,0006	0,0012	0,0012
V^{+3}	0,0020	0,0020	0,0020	0,0030
Y^{+3}	0,0046	0,0051	0,0126	0,0056
Sc^{+3}	0,0053	0,0060	0,0182	0,0139
Zr^{+4}	0,0010	0,0017	0,0026	0,0016
Ba^{+2}	0,0174	0,0187	0,0408	0,0589
Sr^{+2}	0,0399	0,0646	0,0934	0,0617
B^{+3}	0,0286	0,0399	—	—
Sn^{+4}	0,0007	0,0008	0,0010	—
Pb^{+2}	0,0003	0,0003	0,0005	—
Ni^{+2}	0,0009	—	—	—
Co^{+2}	0,0008	0,0011	0,0026	—
Cr^{+3}	0,0005	0,0004	—	—

In chemical composition of the rock (tab. 3. no. 3a) intense leaching of Ca, Sr, Cr and to a smaller extent also of Na, Mg, Si, Al is proceeding. Fe^{+3}, Be, V, Y, Zr, Ba, Co, Sn, Pb, K appear to be immobile and their relative representation in the rock relatively increases regarding to the foregoing stage of alteration. The rock is most intensely altered in the uppermost part of the wall of the quarry under the humous cover, where is of light-brownish colour, friable in dry state and rubbing in the fingers in moist state. In crumbled fragments of the rock there are still indications of original porphyric texture. The spaces after dark-coloured minerals are prevailingly empty and only at places relics of Fe-oxides are in them. In plagioclases their original delimitation is partly preserved but they are completely altered into light-coloured to light-brownish gelous mass with slightly polarizing submicroscopic aggregate. The groundmass is of light-brownish colour and in the proximity of fine joints it sometimes acquires even dark-brownish colour. It is altered similarly as the phenocrysts. According to DTA and X-ray analysis montmorillonite and to a smaller degree also kaolinite formed in the rock. Clay minerals formed to a larger extent than in the foregoing stage of alteration. Migration of some principal rock-forming elements is getting slower and only slight indications of leaching are manifesting, mainly of Al, K (tab. 3. no. 4a). Fe^{+2} bound in relics of magnetite resting from the foregoing stage is oxidized to Fe^{+3} that starts to show slight indications of solubility but its content in the rock increases regarding to oxidation of Fe^{+2}. Representation of Si, Mg, Na, Be and Ga almost does not change and they probably enter the structural lattice of clay minerals together with Al. Pb, Sn, Co, V and Ba become mobile elements and are leached out from the rock compared to foregoing stage of alteration.

Similarly as at the foregoing locality also here most intense leaching of elements was taking place in the stage of breaking up of primary silicates. First Ca, Mg were leached and Fe^{+2} intensely oxidized to Fe^{+3}. Leaching of natrium followed intense carrying away of Ca. Pb, Cr and Sr were also intensely leached. Al and K show only slight indications of carrying away. The predominant part of trace elements shows relatively increased content, mainly Y, V, Ba, Sc, Be, which are probably sorbed to gelous products of rock disintegration. In the upper part of the outcrop, below humous loam, i. e. in places of intense formation of clay minerals a part of the elements enters their structure lattice as consequence of what their leaching out of the rock diminishes. From the principal rock-forming elements the content of Al and K diminishes and Fe^{+2} is almost entirely oxidized to Fe^{+3}. From the trace elements Pb, Sn, Co are intensely carried away. To a smaller extent V, Ba and Sc are carried away. In the rock representation of Fe^{+3}, Ti, B, Zr relatively increases.

In the whole profile diminishing of hydratation coefficient from 0.51 to 0.22 and increase in leaching coefficient from 2.04 to 3.41 may be observed towards the upper parts of the outcrop. In the whole profile Fe^{+3}, Y, Zr, B, Ba are almost immobile elements. Relatively small mobility display also Si, Al, K, Mn, Ga. As it may be concluded from that, pH of solution has only little changed with percolation through the rock and its alteration. In the uppermost parts of the outcroup pH of percolating solutions was probably 4 to 5 and increased to 5 in the lower parts, at which value the mentioned elements appear to be immobile according to I. I. Ginzburg 1960.

The Course of Weathering at the Deposit in Banská Štiavnica

The third profile of andesite weathering I have studied in Banská Štiavnica in the Vth horizon of the Maximilian Pit in the principal cross adit, 80 m above the Terézia

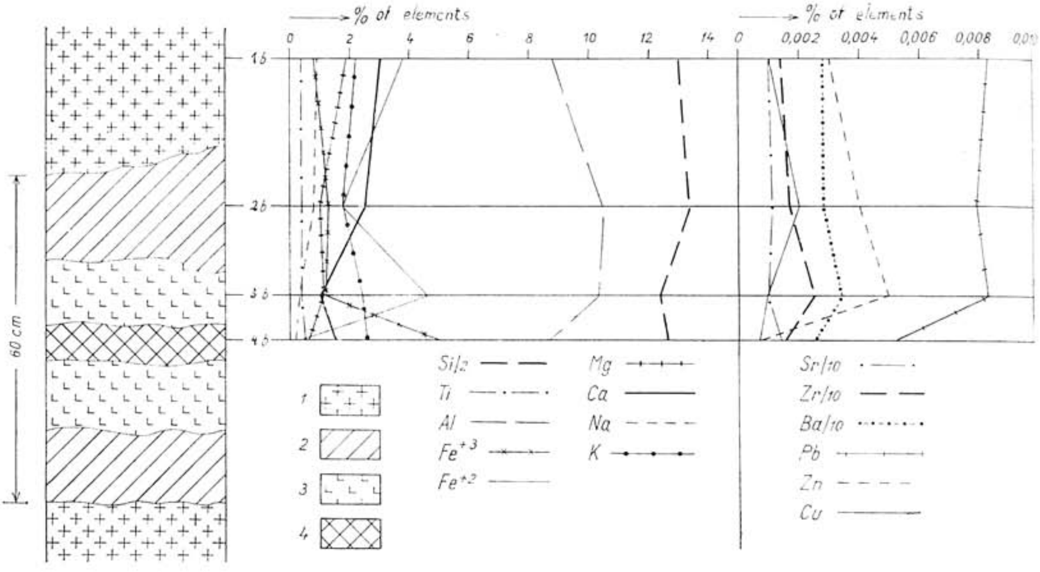

Fig. 3. Profile of weathering in Banská Štiavnica in the Vth horizon of the Maxmilian Pit in the principal cross adit, 80 m above the Terézia Vein. 1 — Chloritized pyroxenic andesite of dark-greyishgreenish colour. 2 — Greyishbrownish andesite penetrated with dense network of nerve-like diverging joints. 3 — Light-grey, slightly coherent andesite with slight brownish shade, starting to get soft in moist state. 4 — Completely weathered and disintegrated andesite of light-brownish colour.

Vein. The cross adit is in this place situated in chloritized pyroxenic andesite completely altered on a steeply dipping joint, along which water percolated and gradual transition to solid andesite of dark-greyishgreenish colour may be studied at a distance of 30 to 60 centimetres (fig.3).

Andesite near the altered zone is solid, of dark-greyishgreenish colour, with compact groundmass, porphyritic texture. In the rock in small amounts pyrite is finely dispersed. The original dark-coloured minerals (pyroxenes) are altered into chlorite and sporadical clusters of carbonate. Plagioclases are only to an insignificant extent substituted by sericite and carbonate. The mentioned alteration corresponds to the stage of post-volcanic alterations that preceded weathering (J. Forgáč 1966). Chemical composition of the rock is shown in tab. 4, no. 1b.

In the first stages of weathering the rock is getting greybrownish colour, penetrated with a dense network of nerve-like diverging joints, along which the rocks breaks up after a slight hit of the hammer. On the joints thin coatings of Fe-oxides are precipitated. Chlorites are gradually getting brown colour in the direction from the periphery as a consequence of oxidation of Fe^{+2} to Fe^{+3} and decomposition of carbonates is proceeding. Plagioclases do not show any essential change. Finely dispersed pyrite as well as sporadic small clusters of magnetite are changing into Fe-oxides.

In chemical composition of the rock (tab. 4, no. 2b) Fe^{+2} changes to Fe^{+3} and Fe^{+3}. Mg, Ca and K are leached out from the rock. Immobile elements appear to be Al and Si, the content of which in the rock is relatively slightly increasing. Trace elements did not show any essential changes in their representation. With higher alteration the

Table 4. Representation of Elements in % in the Profile of Weathering of Chloritized Pyroxenic Andesite at the Locality of Banská Štiavnica

	1a	2b	3b	4b
Si^{+4}	26,06	26,89	24,81	25,43
Ti^{-4}	0,35	0,38	0,35	0,47
Al^{+3}	9,85	10,58	10,32	8,72
Fe^{+3}	0,80	1,31	1,17	5,11
Fe^{+2}	3,18	1,81	4,66	0,32
Mn^{+2}	0,06	0,06	0,19	0,06
Mg^{+2}	1,86	1,00	1,25	0,65
Ca^{+2}	3,06	2,55	0,96	1,54
Na^{+}	0,92	0,89	0,33	0,20
K^{+}	2,19	1,86	2,40	2,55
P^{+5}	0,05	0,05	0,05	0,05
S^{+4}	0,18	0,15	0,43	1,93
Ga^{+3}	0,0014	0,0018	0,0025	0,0019
V^{+3}	0,0105	0,0118	0,0112	0,0115
Zr^{+4}	0,0145	0,0174	0,0251	0,0148
Ba^{+2}	0,0282	0,0288	0,0339	0,0251
Sr^{+2}	0,0010	0,0010	0,0010	0,0010
Pb^{+2}	0,0083	0,0079	0,0083	0,0052
Zn^{+2}	0,0030	0,0040	0,0050	0,0007
Cu^{+2}	0,0010	0,0020	0,0010	0,0007
Ni^{+2}	0,0010	0,0010	0,0015	0,0010
Co^{+2}	0,0010	0,0010	0,0013	0,0010
Cr^{+3}	0,0010	0,0020	0,0022	0,0022

rock is gradually getting light-gray to light colour with brownish shade, is slightly coherent and starts to get soft in moist state. Chlorites and plagioclases break up into light-coloured to brownish, slightly polarizing submicroscopic aggregate, clusters of carbonates are preserved sporadically only. DTA and X-ray analyses found out kaolinite and montmorillonite to have formed in the rock. Changes in mineralogical composition of the rock were evident by intense leaching out of Ca, Na and relatively small decrease in the content of Si (tab. 4. no. 3b). Slight indications of leaching are also evident at Cu. Immobile elements in this stage of alteration are Al, K, Mg, Ga, Zr, Ni, Cr, Ba, Zn, of which a part is sorbed to the products of disintegration of rock or enters the structure lattice of secondary minerals and a part probably forms insoluble sols.

In the terminal stage of alteration the rock is disintegrating, looses the porphyritic texture, is of light-brown colour, greasy in moist state and lumpy in dry state. In the rock formation of montmorillonite, kaolinite an jarosite took place (according to DTA and X-ray analyses). Intense leaching out of Mg, Al, Cu, Zn, Pb also proceeded in the rock (tab. 4. no. 4b). Lesser mobility was evident at Na, Ga, Zr, Ba, V, Ni, Co, Cr, Sn, their representation decreases to a small extent only or does not change. Immobile elements are Fe^{+3}, Ca, Si, K, Sr and their content increases with changing ratio compared to the foregoing stage of alteration.

At the preceding localities with percolation of the solutions through the rocks increase in their pH took place. At this locality a reverse process may be supposed. The solutions which percolated into the rock evoked disintegration of rock-forming minerals as well as of pyrite that had been scattered in small clusters in them. With disintegration of pyrite SO_4 formed and by the influence of inner tension jointing of rock proceeded according to a nerve-like network of small dense joints (J. Forgáč

1968). Percolating solutions were enriched in SO_4, getting more acid in this way. This process is indicated by leaching of iron in the first stage of alteration. With intense alteration of the rock ions of SO_4 entered the structure lattice of jarosite, whereby pH of the solutions increased and consequently Fe^{+3} became immobile and its representation in rock got higher. In this stage of alteration there was also the greatest mobility of trace elements, mainly of Cu, Pb, Zn. In the process of weathering in Banská Štiavnica migration of elements was the highest with intense stage of alteration as the coefficient of leaching indicates, the value of which gradually increases from 1,31 to 2.60 while the coefficient of hydration attains the highest values in the first stages of rock alteration.

Relative Representation of Elements

Weathering of andesites is characterized by breaking up of primary minerals and formation of secondary ones, accompanied by change of mutual ratio of chemical elements in the rock. From the principal rock-forming elements uni- and bivalent as well as three- and fourvalent ones are more intensely leached out from the rock with weathering and their ratio increases from 2,4 to 12,5 with higher alteration (fig. 4). Great differences are evident also in mutual ratio of the individual elements. Aluminium generally manifests as relatively little mobile element, its ratio to some elements increases in direct proportion or remains almost unchanged. The mutual ratio of Si : Al continuously decreases from 3,21 to 1,33 with increase in representation of Al (fig. 5). With increasing representation of Al also relative representation of Ca, Mg and alkalii (Na—K) changes, their relative representation decreases in direct proportion (fig. 6, 7, 8). The ratio of potassium and aluminium is also different, remaining almost unchanged with the decrease in the content of aluminium and varying prevailingly in the limits of 0.133 to 0.29 (fig. 9). Potassium is prevailingly sorbed to gelous constituents with andesite weathering or is partly bound to structure lattices of secondary minerals and its mobility almost equals to that of aluminium while natrium is carried away from

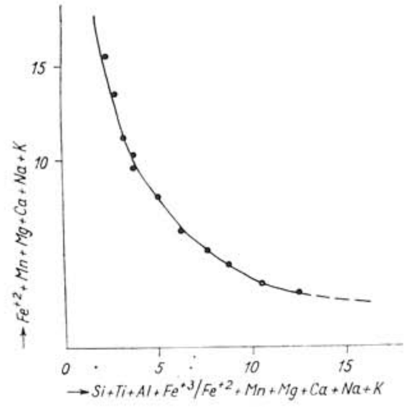

Fig. 4. Relative representation of univalent and bivalent to three- and fourvalent elements.

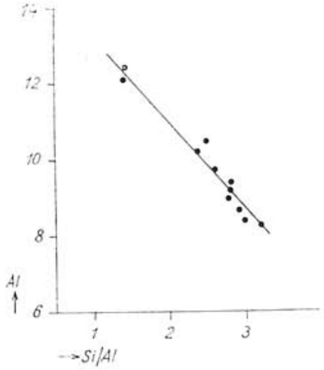

Fig. 5. Relative representation of silicon and aluminium.

the rock. The ratio of titanium and aluminium shows only slight indications of relative increase with diminishing of representation of Al (fig. 10). Gallium and aluminium did not show mutual relation in representation but their ratio is changing with weathering (tab. 5). Relation of aluminium to other elements was not manifested distinctly.

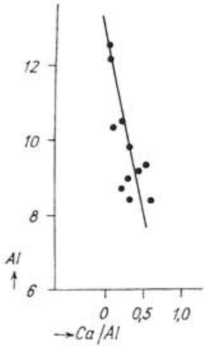

Fig. 6. Relative representation of calcium and aluminium.

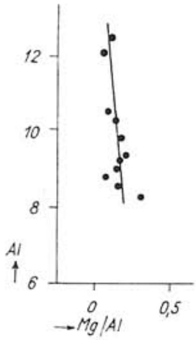

Fig. 7. Relative representation of magnesium and aluminium.

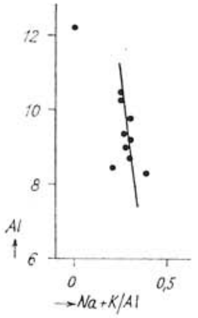

Fig. 8. Relative representation of alkalii and aluminium.

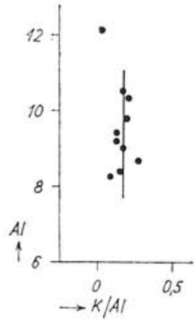

Fig. 9. Relative representation of potassium and aluminium.

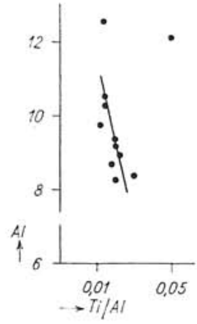

Fig. 10. Relative representation of titanium and aluminium.

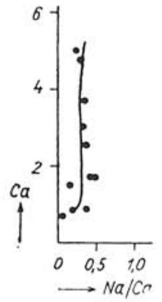

Fig. 11. Relative representation of natrium and calcium.

Natrium and calcium are almost equably leached out from the rock as also indicated by their mutual relation. With decreasing calcium their mutual ratio remains almost constant (fig. 11). Alkalii generally (Na—K) behave differently in dependence on the content of calcium. In the first stages of leaching of calcium their mutual ratio almost continuously increases and after carrying away of a larger part of calcium from the rock the ratio of calcium and alkalii rapidly increases as a consequence of the sorption of potassium in the products of disintegration, whereby ist mobility considerably diminishes compared to natrium and calcium (fig. 12). The mobility of Mg and Ca is from the beginning of weathering almost equal and after carrying away of prevailing part of Ca from the rock their ratio rapidly increases since Mg remains bound to the

Table 5. Mutual Ratio of Elements

	Fieberg			Breziny				Banská Štiavnica			
	1	2	3	1a	2a	3a	4a	1b	2b	3b	4b
V. 1000/Fe^{+3}	3,64	0,84	1.49	2,27	1,53	1,39	0,66	13.12	9,00	9,57	2,25
V. 1000/Mg	2,55	9,52	2,56	2,24	3,33	9.91	4,62	5,64	11,80	8,96	17,67
Sc. 1000/Fe^{+2}	0,16	2.88	22.85	0,25	0.76	3,82	5,51	—	—	—	—
Y. 1000/Fe^{+2}	0,91	17.56	370,00	1,35	2,70	26,76	47,93	—	—	—	—
Ba. 100/K	3,23	221,66	119,75	3,16	5,12	5,62	5,13	1,28	1,54	1,41	0,98
Ba. 100/Ca	1,20	42,33	5,63	0,79	1,72	5,49	3,62	0,92	1,12	3,55	1,62
Si/Al	3,19	1,45	1,40	2,85	2,87	2,78	2,96	2,64	2,54	2,40	2,90
Ti/Al	0,02	0,05	0,01	0,02	0,02	0,02	0,03	0,01	0,01	0,01	0,01
Ca/Al	0,58	0,07	0,06	0,52	0,40	0,18	0,20	0,31	0,24	0,09	0,17
K/Al	0,21	0,01	—	0,13	0,13	0,18	0,14	0,22	0,17	0,23	0,29
Mg/Al	0,32	0,05	0,13	0,21	0,16	0,14	0,14	0,18	0,09	0,12	0,07
Mg/Fe^{+2}	0,64	0,56	8,52	0,52	0,68	1,86	4,17	0,58	0,55	0,26	0,03
Mg/Ca	0,56	0,70	2,41	0,41	0,40	0,74	0,71	0,60	0,39	1,30	0,42
Na/Ca	0,28	0,15	0,02	0,27	0,38	0,48	0,44	0,30	0,34	0,34	0,12
Na+K/Al	0,38	0,02	—	0,27	0,29	0,27	0,22	0,31	0,25	0,26	0,31
Na+K/Ca	0,65	0,35	0,07	0,52	0,72	1,46	1,14	1,01	1,07	2,84	1,78
Fe^{+3}/Fe^{+2}	0,44	6,41	14,85	0,51	1,50	8,04	20,51	0,25	0,72	0,22	15,96

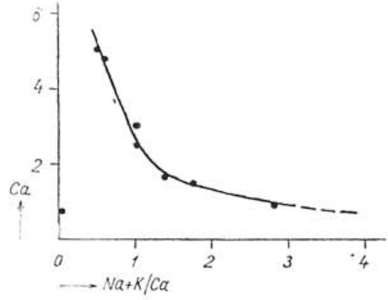

Fig. 12. Relative representation of alkalii and calcium.

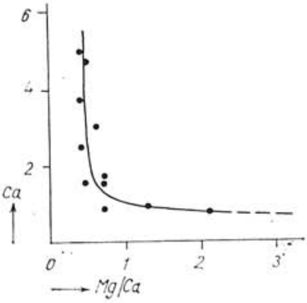

Fig. 13. Relative representation of magnesium and calcium.

structure lattice of montmorillonite and consequently becomes immobile (fig. 13). The ratio of calcium and barium is also similar, almost constant at the beginning of alteration by weathering and after carrying away of larger part of Ca from the rock it starts to increasse rapidly, probably as a consequence of formation of little soluble bicarbonates of barium in weathered andesite (fig. 14). Relation of barium and potassium is a little different as their mutual ratio increases in direct proportion with the decrease in the content of potassium as a consequence of lesser mobility of barium (fig. 15). Direct dependence is manifested at two- and three-valent iron in the first stages of rock alteration only, when as a consequence of oxidation Fe^{+2} to Fe^{+3} their ratio increases nearly in direct proportion and with intense stage of alteration this ratio

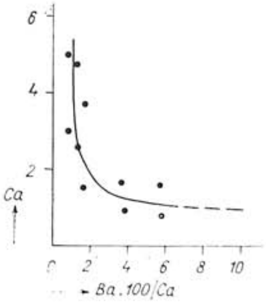

Fig. 14. Relative representation of barium and calcium.

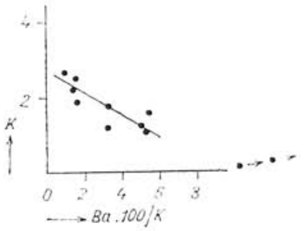

Fig. 15. Relative representation of barium and potassium.

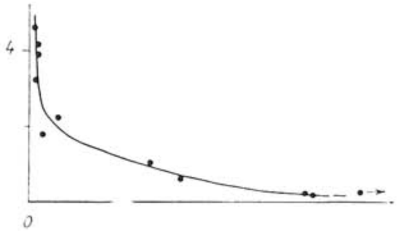

Fig. 16. Relative representation of bivalent and three-valent iron.

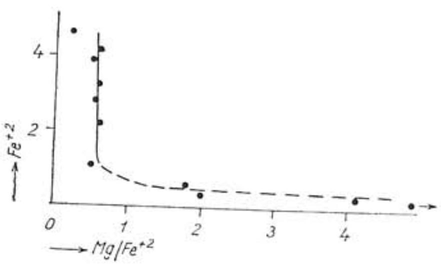

Fig. 17. Relative representation of bivalent iron and magnesium.

rapidly increases as a consequence of predominating change of Fe^{+2} to Fe^{+3} (in the foregoing stage of alteration) and of partial carrying away of Fe^{+3} from the rock (fig. 16). Relation of Fe^{+2} and Fe^{+3} in the first stage of alteration is different in the rock overlying the Terézia Vein in Banská Štiavnica, where carrying away of Fe^{+3} is taking place at the same time with oxidation of iron. Very different is relative representation of Fe^{+2} and Mg in the commencing and terminal stage of alteration. Fe^{+2} and Mg participate in the structure of dark-coloured minerals in original rock. With breaking up of dark-coloured minerals representation of Fe^{+2} and Mg in the rock gradually decreases in almost equal ratio (fig. 17). In the terminal stages of alteration Mg enters the structure lattice of clay minerals, whereby it becomes an immobile element and oxidation of Fe^{+2} continues although to a smaller extent than in the first stage of alteration and in this way their mutual ratio increases (fig. 17). A dependence of indirect proportion is also evident between Fe^{+2} and rare earths, of which yttrium and scandium were studied at the localities of Ficberg and Brezina. Representation of Y and Sc relatively increases with the process of andesite weathering while Fe^{+2} decreases there. This fact causes an increase in their mutual ratio with the intensity of rock weathering due to high sorption qualities of Sc and Y. On the basis of relative increase in the content of both the elements one may conclude that in weathering products of andesite yttrium has better sorption qualities than scandium as also indicated by their relative representation and Fe^{+2} (fig. 18, 19). Indirect relation was also evident between vanadium and magnesium, their mutual ratio increases with diminishing of Mg content in the rock as a consequence of more intense leaching out of Mg than of V (fig. 20). The ratio between V and Fe^{+3} is also similar as a consequence of a large increase in the content of Fe^{+3}, mainly by oxidation of Fe^{+2} to Fe^{+3} (fig. 21) their mutual ratio decreases with the increase in Fe^{+3}.

Strontium and barium which are predominantly bound to plagioclases with Ca and K get apart with weathering. After breaking up of plagioclases Sr ist almost completely carried away from the rock while Ba is almost immobile in the first stages of alteration, whereby its content relatively increases as a consequence of the origin of little soluble bicarbonates of Ba and it shows indications of leaching out in the terminal stages of rock alteration only. The content of Ba and Sr is almost unchanged in the profile in Banská Štiavnica, where except bicarbonates probably also insoluble sulphates of Sr and Ba are formed. Pb, Ni, Co, Cr, Sn are very little mobile at the localities of Ficberg and Breziny and after breaking up of primary silicates, in the structure lattice of which they were bound, they are carried away from the rock and in completely altered

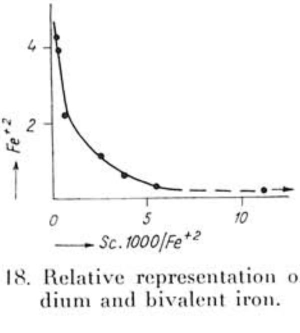

Fig. 18. Relative representation of scandium and bivalent iron.

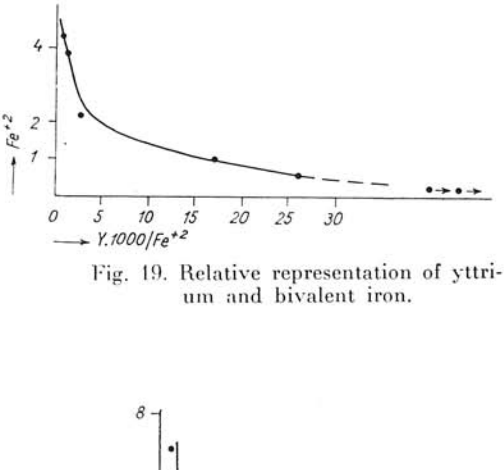

Fig. 19. Relative representation of yttrium and bivalent iron.

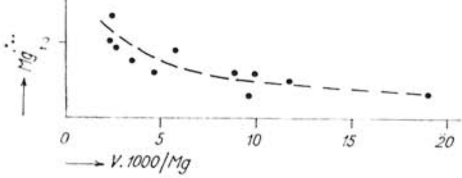

Fig. 20. Relative representation of vanadium and magnesium.

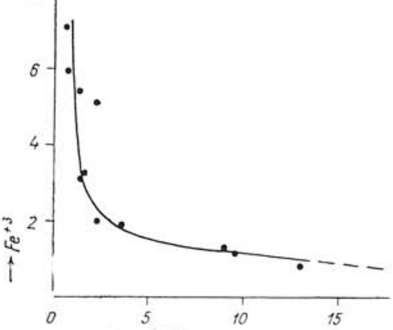

Fig. 21. Relative representation of vanadium and three-valent iron.

andesites under the humus cover their presence has not been proved. This fact hinders tracing of their relation to other elements in whole profiles of andesite weathering. At the locality of Banská Štiavnica the content of Ni, Co and Sn does not change, they probably remain scattered in weathering products and are sorbed into secondary minerals. Cr is immobile and its content increases twice. Pb and Cu are leached out from the rock with intense alteration. In weathering of rocks at the mentioned localities solutions with predominating content of ions of HCO_3 were acting and in Banská Štiavnica they were also carrying SO_4 as it is evident on the basis of the intensity of leaching out of elements and of their relative representation in the process of weathering.

Translated by J. Pevný.

REFERENCES

Ahrens L. H., 1963: Lognormal-type distribution in igneous rocks Geochim, et Cosmochim. Acta 27. — Ahrens L. H., 1963a: Element distribution in igneous rocks. IV. Negative skewness of SiO_2 and K. Geochim. et Cosmochim. Acta 27. — Butler I. R., 1953: The geochemistry and mineralogy of rock weathering. The Lizard area, Cornwall. Geochim. et Cosmochim. Acta 4. — Forgáč J., 1966: Petrografia a geochémia premenených hornín v štiavnicko-hodrušskom rudnom obvode. Zborn. geol. vied, Západné Karpaty 5, Bratislava. — Forgáč J., 1967: Die Entfärbung der Gesteine und deren Zerfall in Erzrevier von Banská Štiavnica. Geol. práce, Zprávy 42, Bratislava. — Forgáč J., Dvonč V., Gerthofferová H., 1968: Vybielovanie a rozpad andezitov v laboratórnych podmienkach. Geol. práce, Zprávy 46, Bratislava. — Ginzburg I. I., Kabanova E. E., 1960: Soderženie kremnezema v prirodnych vodach i formy ego prisutstvija. Kora vyvetrivanija 3, Moskva. — Ginzburg I. I., 1963: Tipy drevnich kor vyvetrivania, formy ich projavlenia i klassifikacia. Kora vyvetrivanija 6, Moskva. — Perelman A. I., Batulin S. G., 1962: Migracionnije rjady elementov v kore vyvetrivanija. Kora vyvetrivanija 4, Moskva. — Vinogradov A. P., 1957: Geochimija redkých i rassejannych chimičeskich elementov v počvach. Moskva.

Review by B. Cambel.