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BASALT WEATHERING IN THE AREA OF THE CEROVÁ VRCHOVINA HIGHLANDS — GEOCHEMICAL ASPECTS

(Figs. 17, Tabs. 4)

Abstract: The authors deal with the problem of basalt weathering the Cerová vrchovina highlands (S Slovakia). On the basis of detailed mineralogical, morfological, micromorfological and chemical studies of basalts and their weathering products they have suggested a geochemical weathering model according which all components are mobile (were added or extracted). The following order of decreasing mobility of chemical elements was found: Na > Ca > > Mg > K > Si > Fe (Mn) > Al, Ti.
The extraction of trace elements is controlled by the mobility of the main components and their ability to enter secondary mineral phases or sorption complex of secondary colloid components.

Резюме: Авторы в статье занимаются проблемой выветривания базальтов в районе Церовой возвышенности. На основе детального морфологического, микроморфологического, минералогического и химического исследования базальтов и продуктов их выветривания они предложили геохимическую модель выветривания базальтов изучаемого района, по которой все компоненты мобильными (они были принесены или отнесены). Тенденция относа элементов как следует: Na > Ca > Mg > K > Si > Fe (Mn) > Al, Ti. Относ редких элементов контролирует мобильность главных компонентов и способность входа этих элементов во вторичные минеральные фазы или в сорпционный комплекс вторичных коллоидных компонентов.

In literature there are many ways of the evaluation of geochemical changes during weathering. By their comparison one can ascertain that in spite of similar trend, the succesion an intensity of the extraction of individual elements is different. These differences are controlled mainly by the character of parent rocks, degree and character of weathering, solubility and mobility of elements bind in different phases and to an important extent by the ability of elements to form secondary mineral phases in weathering systems.

The weathering systems are open, i. e. there are substance exchanges between them and surrounding systems. No element of this system can be regarded as immobile. Relative accumulation of elements in relation to the original parent rock is controlled by complex changes associated with the history of the weathering crust formation in which vertical structural and chemical differentiation is conected not only with the extraction of elements but also with vertical and/or lateral translocation of secondary weathering products.

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Any comparison of the chemical composition of individual weathering products and their parent rocks results in overlooking numerous particularities ot development changes. As is stated by Chesworth et al., (1981) this approach results in the integration of all changes over time (since the beginning of weathering till the moment of the weathering product study). Complications occur especially if the weathering takes place in different weathering regimes (climatic changes).

In order to intercept some development changes the authors, based on micromorphological and mineralogical studies, try to put new light into the inside of the processes an think on the possibility of a geochemical model application in real weathering conditions. They give the results of the study of chemical composition changes during weathering and their geochemical evaluation. Because of the relatively young age of the basalts (Pliocene — Pleistocene) their kaolinic character is surprising and probably reflects fading out of intensive weathering in the regime existing at the time when the Poltár Formation originated in the end of the Neogene (Kraus, 1968; Vass — Kraus, 1985). These considerations depends, of course, on validity data about the basalt age. The alkaline character of the basalts probably contributed to the final result, too. Because of high mobility of basic cations, the basalts were more quickly dealkalized and gradually desilicified.

Geology of the area and rock character

The study of the basalt weathering products covers the Cerová vrchovina highlands (southern Slovakia). The basalts build top parts of the ranges and form several separate lava flows or sheets (Karolus et al., 1959, 1965). Their distribution is schematically shown in a map (Fig. 1).

Radiometric dating of the basalts provided ages 2.75 to 1.35 m. y. (Balogh et al., 1981; Kantor — Wiegrová, 1981) corresponding with the Late Pliocene to Pleistocene. The basalts are designated as the Cerovo Basalt Formation and according to earlier works (Karolus et al., 1959, 1965) the basalt flows filled former valleys. Later erosional processes led to relief inversion and consequently they form elevations in the present relief. Their fairly high altitude relative to present valleys (100—200 m) and the young age of the basalts gives the idea about erosion rate in this area. The erosion and gradual emergence of the basalts with better drainage might have accelerated the weathering process. Some basalt flows are desintegrated ("Sonnenbrand") to considerable depths (up to 20 m).

Petrographic study of the basalts of the area concerned has been performed by Fiala (1936), Šimová (1965) and mainly Mihálikova (1966) and geochemical study has been carried out by Forgáč (1970). Despite some variability in chemical composition they belong among alkali basalts, of which three groups are present: basanitoids, amygdaloidal limburgitoid rocks and most abundant nephelinic basanites (Mihálikova, 1966).

On the latter rocks we have studied relict weathering crusts in localities Veľké Dravce, Trebeľovce and Šiatorošská Bukovinka with a type profile shown in Fig. 2. Relict and fossil weathering crusts of conspicuous rusty-brown colour are of a larger regional distribution. The nephelinic basanites have holocrystalline-porphyric texture with doleritic development of the groundmass. The groundmass consists of plagioclase microliths, isometric olivine grains, pyroxenes and Ti-magnetite (Fig. 3). Very fine apatite needles are abundant (Fig. 4). Olivine (partly or completely altered to iddingsite), pyroxenes (augite) and tabular plagioclases (labradorite) form porphyric phenocrysts. Besides the basalts of the Cerová vrchovina highlands, also those of the Podrečany Basalt Formation occur in the vicinity (SW and NW parts of the Lučenecká kotlina basin). The latter are older (6–7 m. y.) of Pontian age. Kaolinic weathering crusts have been found on them, too (W a s s — K r a u s, 1985).

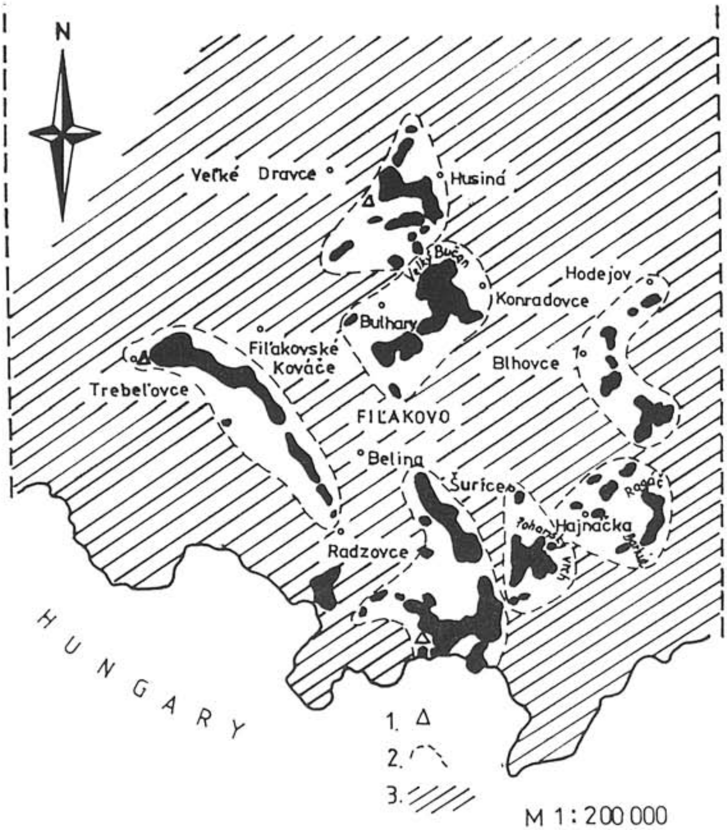


Fig. 1. Generalised geology and basalt occurrences in the Cerová vrchovina highlands.
Explanations: 1 —location of sampling, 2 — individual lava flows, 3 — surrounding Neogene sedimentary rocks.

Morphological characteristics of the representative profile

Basalt weathering crusts of the Cerová vrchovina highlands are of conspicuous red-brown colour and various thickness. Accumulated redeposited wea-

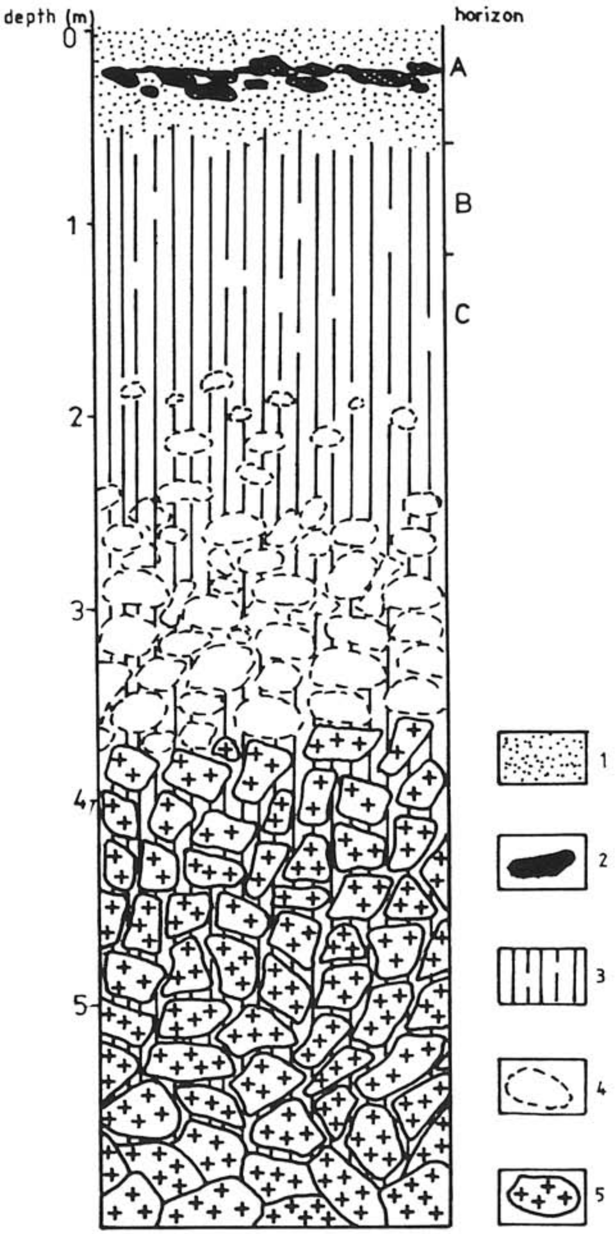


Fig. 2. Weathered profile at Šiatorošská Bukovinka.
Explanations: 1 — humus horizon — recent soil, 2 — fractured blocks of Fe-crust, 3 — clay residue, 4 — entirely disintegrated basalt, 5 — slightly weathered to unweathered basalt.

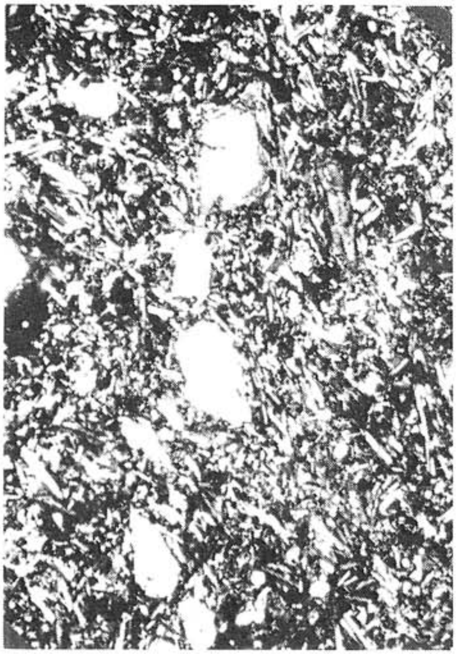


Fig. 3. Texture of unweathered nephelinic basalt (doleritic matrix). Magn. 17x, +N. Photographed by L. O s w a l d.

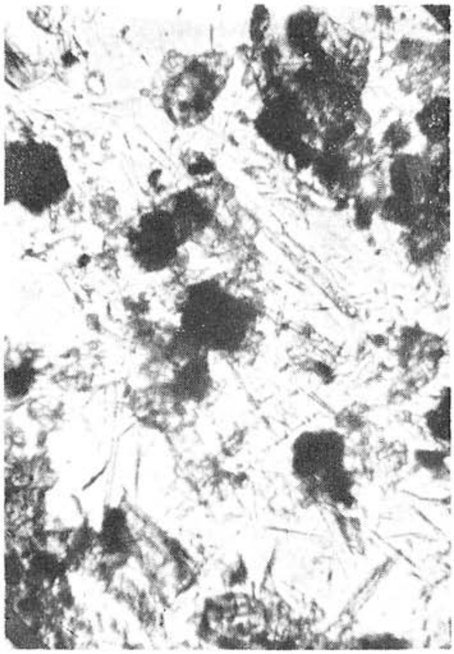


Fig. 4. Tiny apatite needles in matrix. Magn. 430x, /N. Photographed by L. O s w a l d.

thering products or weathering crusts affected by erosion are often present. In places they are of fossil character, covered with variable thicknesses of Quaternary deposits.

The most completely preserved profile without any signs of redeposition has been found in a quarry, about 1 km SE of the village Šiatorošská Bukovinka, in close vicinity of the Czechoslovak/Hungarian border.

Its morphological characteristics are following (Fig. 2).:

0—20 cm A — humus-nowadyas soil horizon of the fine-cloded texture, loamy with abundant iron nodules.

20—32 cm B — sesquioxidic horizon of relict character represented by an iron (limonitized) crust, fractured and partly leached by recent pedogenetic processes.

32—98 cm B_1t — horizon of rusty-brown colour with an iron nodule content, of prismatic texture, loamy-clayey, Mn-coatings, only slightly affected by recent pedogenetic processes, with rare roots.

98—162 cm B_2t markedly illuviated relict subhorizon with abundant illuviated clay in fissures and locally preserved totally disintegrated basalt rolls of tuffogenous appearance. The clayey substance is brown to red-brown and gradually passes into the underlying horizon. The disintegrated basalt is gray.

162—330 cm C_I — horizon — disintegrated basalt of tuffogenous character, gray, locally with less weathered basalt blocks (regoliths), with illuviated clay in fissures.

330—520 cm disintegrated basalt ("Sonnenbrand") with irregularly distributed macroscopically unweathered but highly fractured blocks. Less clay coatings along fissures.

below 520 cm disintegrating basalt with abundant fissures of block jointing, with illuviated colloid coatings along fissures.

The basalt desintegration (in earlier works referred to as "Sonnenbrand") can be observed at depths of up to 10—20 m and minor clay coatings of gel character along fissures at depths of up 30—40 m in the quarry faces.

The iron crust is discontinuous. In other places there occur small iron nodules and concretions or even fairly thick zones (80—100 cm at Trebeľovce) with disintegrating concretions. They are of relict character and their origin evidently is not related to recent pedogenesis. The illuviated gel coatings are of double character: brown-red (originally Fe-Al gels?) and white (Si gels?). Calcite is locally present in deeper fissures but we have not studied especially its relation to the process of weathering and material translocation. Field studies indicate that the white gel colloids are translocated deeper (Si gels?).

In the other localities the weathering phenomena in regoliths are similar but higher horizons are different. The fossil crusts are covered with Quaternary (?) sediments with a variable amount of foreign and mixed-character material.

Micromorphology

The micromorphological study makes it possible to observe reflections of weathering phenomena throughout a weathered profile (by means of thin-sections of solid samples vacuum-impregnated by resins), i. e. from unweathered rock to humus horizon. This study provided us with a more complete information on the weathering crust development and we could have generalized some observations. The micromorphological studies of weathered basalts compiled by Kubiena (1970) had been taken as a background, too. Thus we have obtained information on mineral stability during initial phases of alteration, on clay translocation, formation of eluvia and their covering with foreign material. The konwledge of the micromorphological features has made it possible to interpret much better the geochemical study results, too. The principal micromorphological phenomena are portrayd in Figs. 3—15.

The least resistant mineral is olivine and volcanic glass. Augite and plagioclases are more resistant, while magnetite (ilmenite) is most resistant. Olivine is often altered to iddingsite already in a rock with no weathering manifestations. This alteration is accompanied by oxidation of iron in the olivine. Later partial oxidation of iron takes place also in augite. Goethite oxidation rims are formed relatively often around mafic minerals. In some places, oxidation-reduction processes are associated with a reduction microenvironment and therefore iron is removed and mafic minerals are bleached. In the first stage, weathering solutions penetrate into interstitials and fissures to form a network of microfissures. The solutions flow along all planes of weakness, mainly cleavage joints, around which material is selectively removed (Figs. 5—6).

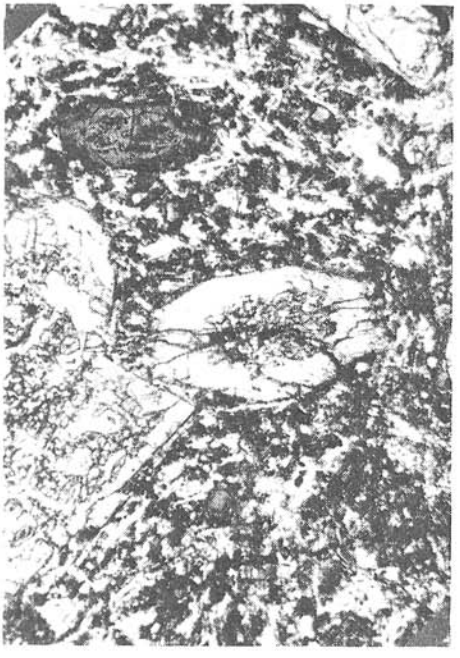


Fig. 5. Selective removal of components from mafic minerals along microfissures and cleavage plains. Olivine (left above), altered to iddingsite. Magn. 80x, // N.
Photographed by L. Oswald.

Fig. 6. Infillings — an illuviated clay components and Fe-oxides fill some empty spaces after porphyric phenocrysts. Magn. 44x, // N.
Photographed by L. Oswald.

All components are gradually mobilized and migrate into fissures. It has turned out that volcanic glass weathers at the same time as mafic minerals, releasing abundant Si and Al gels (Figs. 8—10) that are colloidaly translocated. Amorphous character of the gels is proved by their isotropic character (Fig. 11). Basic cations released in the outer margin of the weathering front form a highly alkaline environment probably facilitating removal of the main components — Al and Si. In the next stage, all components are locally removed and there remain empty spaces after numerous minerals (Figs. 5—6). If microfissures are associated with them, they are secondarily filled with colloid gels. The first indications of these phenomena can be seen in Fig. 9.

These observations suggest following facts: 1) all components migrate, 2) basic cations migrate in the form of ions, whereas Si and Al migrate as polymer clusters formin gels, 3) gels of various character originate in dependence on the degree of basic cation extraction (dealkalization) and desilification, 4) after their recrystallization, minerals 2:1 (minor dealkalization and desilification) or 1:1 (kaolinite) are formed by complete dealkalization and more intensive desilification (Pedro — Siefermann, 1979).

Later, when fissures become wider, gels and colloids are translocated also in suspended and aggregated states. Gravitational movement of colloidal papules

Fig. 7. Mafic minerals and plagioclases are completely leached and in places filled with gels (left above). Magn. 48x, N. Photographed by L. Oswald.

Fig. 8. Similarly as in Fig. 7. More intensive removal. Magn. 48x, N. Photographed by L. Oswald.

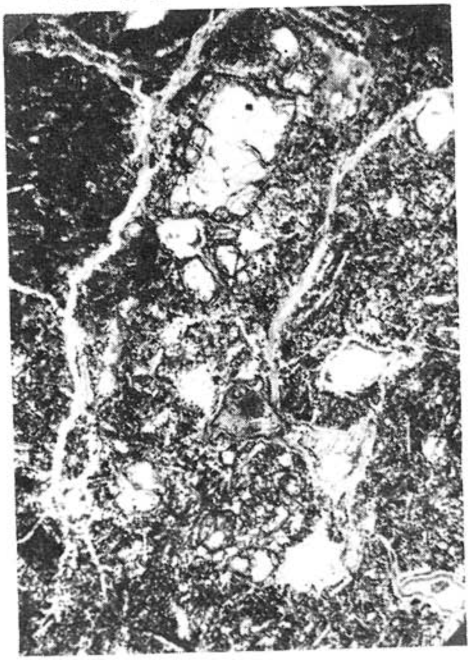


Fig. 9. Mobilized colloids are translocated into fissures where they form metakinematic textures (clay infillings). Magn. 88x, N. Photographed by L. Oswald.

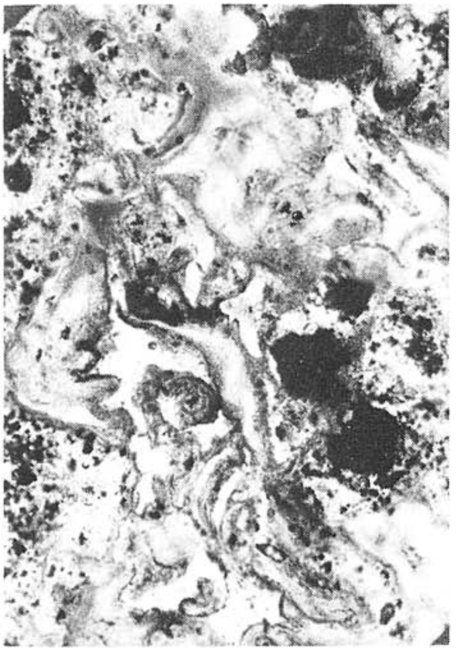


Fig. 10. In the advanced weathering stage only magnetite (black points) is preserved and metakinematic textures become more abundant as a result of clay illuviation. Magn. 178x, N.
Photographed by L. O s w a l d.

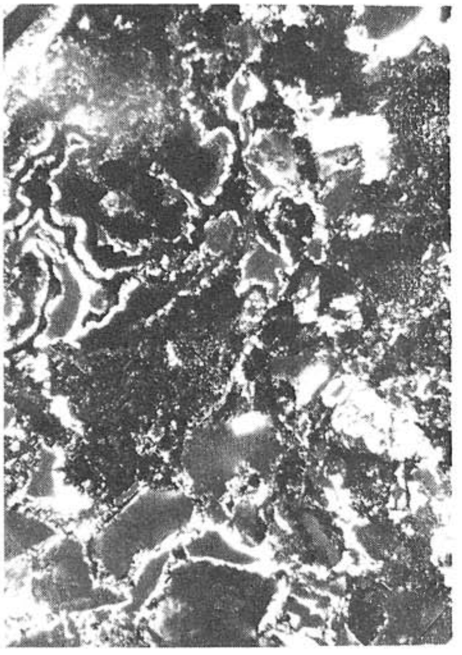


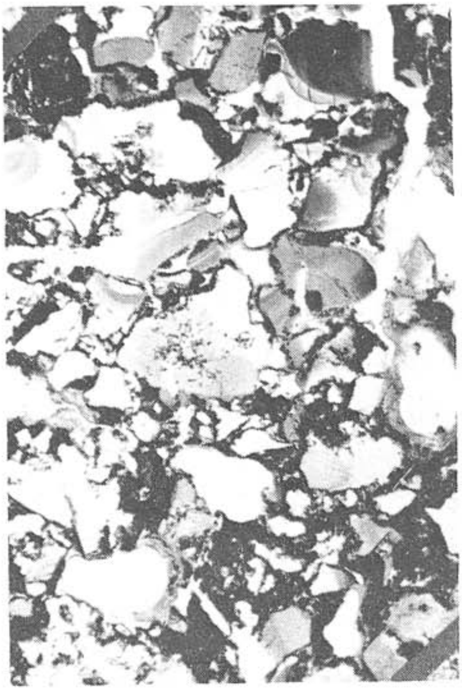
Fig. 11. Some gel-like papules partly displaced by gravitation preserve their isotropic character.
Explanations: White places — isotropic gels. Magn. 88x, +N.
Photographed by L. O s w a l d.

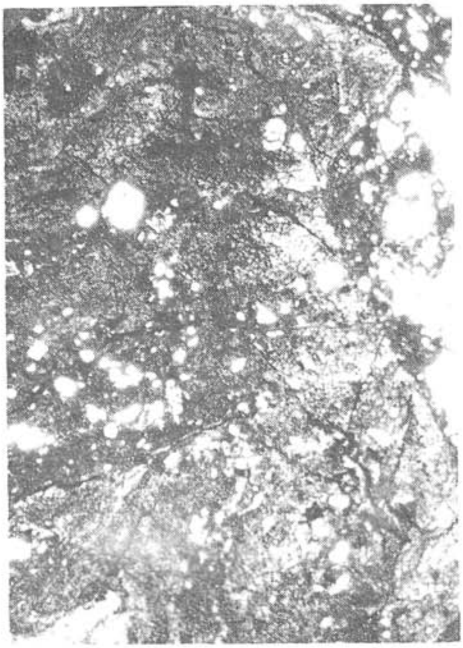
was facilitated by gel dehydration, by which a network of microjoints is formed. Due to following illuviation or only by gravitation, individual papules move into larger fissures. "Pseudobrecciated" fabric of the matrix is formed in this manner as can be seen in Figs. 11—13.

Weathering does not proceed linearly but colluviation of primary components and at the same time gravipedoturbation of secondary ones takes place in the depresions predisposed by weakness of the rock. Even deeper-seated fissures are occasionally filled with illuviated material from the surface.

The eluvium formation is therefore a complex sequence of processes in the course of which ions, molecules, colloids to suspensions, aggregated components and papules migrate. Because relatively highly weathered layers also contain less weathered blocks of the original rock capable of releasing some mobile components, these may enrich weathering solutions. Therefore physico-chemical conditions in individual parts of the weathering crusts and mineral zoning are fairly anisotropic.

As regards the development of the above-mentioned profile in the area of the Šiatorošská Bukovinka, it is interesting that the iron crust formed as part





Figs. 12. and 13. Clay papules redeposited by turbation processes show "pseudobrections" fabric. They have extinction pattern of former coatings. Magn. Fig. 12. — 44x, Fig. 13 — 88x, N.
Photographed by L. O s w a l d.

Fig. 14. Iron crust fabric.
Explanations: White spots — clastogene quartz grains. Magn. 88x, N.
Photographed by L. O s w a l d.

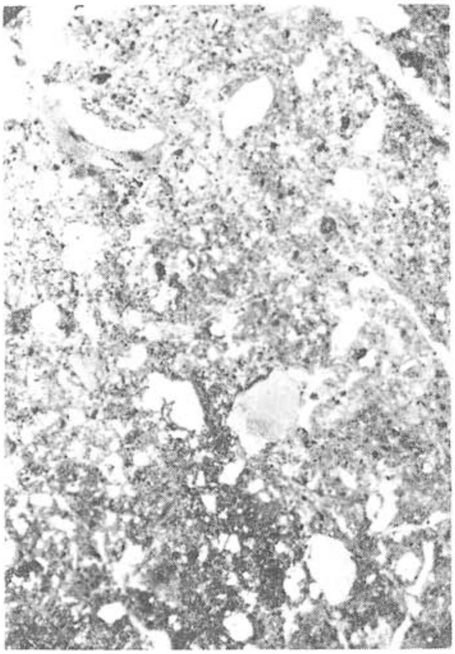


Fig. 15. Fabric of the humus horizon in top soil.
Explanations: Small papules of clayey character from the underlying clay residue as well as dusty skeleton-shaped particles of eolic (deluvial?) character are present.
Magn. 44x, N.
Photographed by L. Oswald.

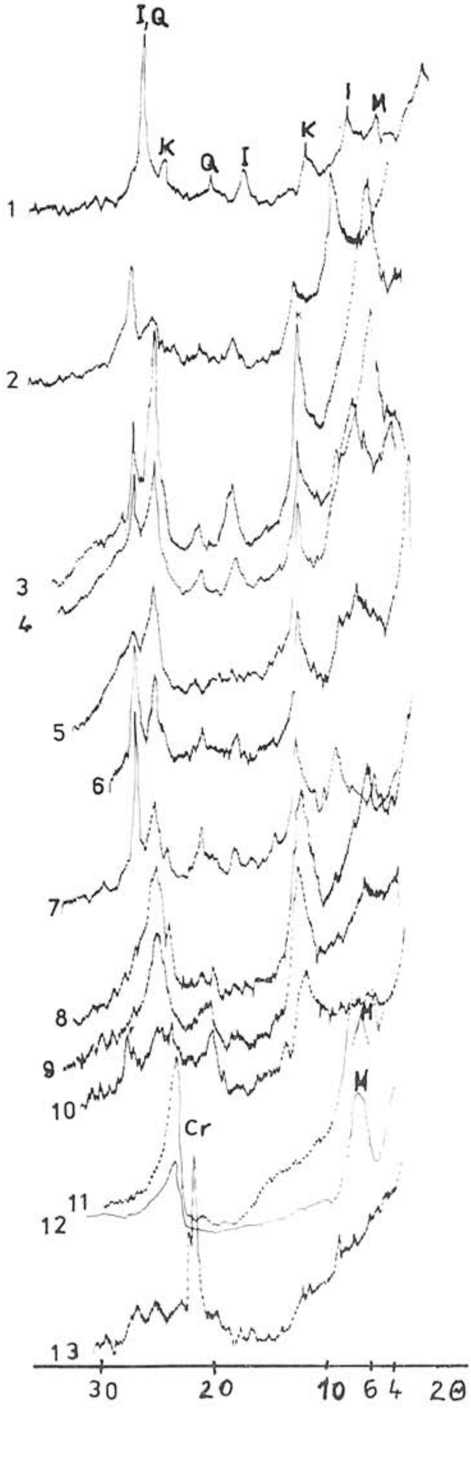


Fig. 16. X-ray diffractiograms of weathered clay (fraction 0.002 mm) on basalts.
Explanations: 1, 2 — locality Trebeľovce (1 — 30—40 cm, 2 — 90—110 cm); 3, 4, 5 — locality Veľké Dravce (3 — 30—40 cm, 4 — 80—90 cm, 5 — 110—120 cm); 6, 7, 8, 9, 10 — locality Šiatorošská Bukovinka 6 — 10—20 cm, 7 — 30—40 cm, 8 — 90—110 cm, 9 — 140—150 cm, 10 — 200—220 cm); 11 — illuviated clay of red colour along fissures in basalts (420 cm), locality Šiatorošská Bukovinka; 12 — red illuviated gel-like clay along fissures in basalts (500 cm), locality Trebeľovce; 13 — white illuviated gel-like clay (420 cm), locality Šiatorošská Bukovinka.
K — kaolinite, I — illite, M — montmorillonite, Q — quartz, Cr — cristobalite, F — feldspars. Conditions of X-ray diffraction: 1—10 — Cu K (Ni-fil, 35 kV, 15 mA), 11 — 13 — Co K (Fe-fil, 30 kV, 10 mA).

of former subsurficial horizons (probably illuvial) was created gradually from individual nodules to continuous crust (by accretion), which results from its fabric. In this crust and mainly above it the matrix contains fairly abundant clastogene quartz (Fig. 14), unweathered feldspars as well as clay papules of underlying clayey components with extinction patern of former coatings (Fig. 15). It is evidently a mixed material with an unrelated admixture re-worked by present pedogenesis. Therefore changes of chemical composition on the surface, formation of recent illuviated coatings and oxidation changes also in relict weathered material may reflect two different pedochemical regimes (relict and nowadays).

Mineralogy of clay

Mineralogical composition of the clay from the three above-mentioned localities (Šiatorošská Bukovinka, Trebeľovce, Veľké Dravce) has been studied by X-ray, DTA and electron microscopy. Some earlier results (Čurlík et al., 1977) based only on X-ray mineral study are thus made more complete and exact. The results are summarized in Tab. 1 and Fig. 16.

The study confirmed kaolinic character of the weathered material. The presence of kaolinite with peaks around 0.713 nm has been confirmed in all localities especially in upper zones of clay residuum which are rather unaffected by pedogenesis. In humus horizons of recent soils, clay micas (illite) highly prevail over kaolinite predominantly as part of an unrelated admixture or resulting from mixing and overlapping of relict crusts with younger weathered material, which results from the micromorphological study. Poorly crystallized kaolinites or metahalloysites (0.736 nm) occur in lower zones. Electron microscopy has not confirmed presence of particles with tube habitus. Kaolinite occurs in association with montmorillonite and illite. Montmorillonite gradually prevails downward. Red gel coatings are partly of amorphous character (allophanes), but also typical montmorillonite coatings have been found in fissures (Fig. 16). White silica coatings are opaline but partly recrystallized to opal-CT and cristobalite (Fig. 16). Clay fraction of the red-brown weathered material contains also goethite and perhaps gibbsite (faint reflex near 4.83 nm in clay filling of the iron crusts).

The presence of halloysite (metahalloysite) or kaolinite-halloysite mixture is still unresolved.

Geochemical balance of weathering changes

In literature there are many methods of evaluation of chemical changes accompanying weathering processes. These methods include:

a) immediate comparison of chemical composition of weathered and parent rocks or their logarithms (Forgáč, 1969, Schwaighofer, 1976 and others);

b) construction of diagrams of components comings — goings (Garrels — Mackenzie, 1971);

c) graphic illustration of chemical composition changes, during individual weathering stages, based on the supposition that given element is not removed (Reiche, 1950 and others);

Table 1

Mineralogy of clay (fraction < 0.002 mm)

Locality (depth in cm)		kaolinite	illite	montmorillonite	other accompanying minerals	remarks
Trebeľovce	30—40	+++	++	+	Q, I — M?	deluvial weathering crust
	90—110	++	++	++	Q	
Veľké Dravce	30—40	++	+	+++	Q, G	deluvial weathering crust
	70—80	++	+	+++	Q, G, F, I — M?	
	100—110	++	+	+++	Q, G	
Šiatorošská	10—20	++	++	+	Q	eluvial crust
Bukovinka	30—40	+++	++	+	Q, G	
	100—110	+++		+	G, Q?	
	140—150	+++		++	G, F	
	200—220	+++		++	F, allophane	
Trebeľovce	220	—	—	+++	allophane	red gel fillings along fissures
Šiatorošská	420	—	—	+++	+ allophane	red gel fillings along fissures
Bukovinka	420	—	—	—	cristobalite + allophane	white gel fillings along fissures

Explanations: Q — quartz, I — illite, M — montmorillonite, G — gibbsite, F — feldspars.

d) calculation of the losses and additions of components in relation to an immobile component (Krauskopf, 1967 and others).

Some methods of mineralogical character are based on comparison and quantification of mineral composition changes in individual weathering stages or on calculation of normative minerals according to the results of chemical analyses of rocks and weathered products (Mohr — Van Baren, 1954).

Besides the above-mentioned methods, also various weathering indices or oxidation indices are used, characterizing partial changes in a weathered material profile (Minářik—Houdková, 1986, Romashkevich, 1974).

All mentioned methods (some of them fairly complex) represent considerable simplification, being better or worse aproximation toward the reality.

Al, Ti and Fe are usually considered little mobile and are chosen for the so-called internal standards, in relation to which addition or extraction of other elements is calculated. Aluminium is used most often (Goldich, 1938, Krauskopf. 1967 and others). Chesworth et al. (1981) applied the sum of these elements in his investigation of basalt weathering trends. Degree of alterations and activity of other elements have been compared in relation to this sum.

If we again compare these methods with the results of our micromorphological study, we have to state that neither coherent samples, i. e. that have notable coherency some characteristics of the rock, make it possible to accept these conceptions without objections. In some sampled zones olivine and all mafic minerals and gradually even plagioclases are absent. Empty spaces in the rock or merely insignificant relics remained after them (Figs. 5—8). This means that the main components — Al, Si are translocated, too. In the last stage also magnetites, which besides iron contain also titanium, are absent. These elements are likely to have been translocated, too.

Weathering systems, designated also as eluvial systems (processes within them lead to the formation of eluvia), are characteristic for movement of ions, molecules, colloids and suspensions, which has alredy been mentioned above. Metakinematic textures of colloids, that occur in places of original primary minerals, prove that these spaces were filled as a result of illuviation (Figs. 9—13). All components move in the gravitational field in vertical as well as lateral directions (e. g. down-slope direction).

These observations indicate that small microfissures, ultramicropores and micropores act as conductive systems in coherent samples, too (Figs. 5—9).

Weathering systems are open-imbalanced. They are characteristic by material (energy) exchange between the system and surrounding environment. For their evaluation, a geochemical model of Chesworth et al. (1981) is valid, according to which:

all components are mobile	⟶ ⟵	all components are added or subtracted
weathering system		surrounding system

In the concrete case of basalt weathering, the mobility of all components is proved by micromorphological observations, i. e. we cannot state that from a certain volume of a rock a different (smaller) volume of weathered material originated.

In fact, most evaluations of weathering changes are based on the supposition that very little soluble components are not considerably mobilized also due to a relatively short duration of these processes in geological history. By their balance, the second model (Chesworth et al., 1981) is used most frequently:

one or more components are immobile	⟶ ⟵	one or more components added and/or subtracted
weathering system		surrounding system

Minařík and Houdková (1985) pointed out that these conceptions may result from the fact that slowly removed components increase their relative share in analyses re-calculated to the basis of 100 %. In other instances, the removal of some elements may be compensated by their illuviation from overlying zones. In this case, analyses do not make it possible to evaluate correctly the real state of alterations and all changes have to be regarded as relative.

Eluvial products is not a simple transformation of primary minerals and rocks but complicated products of illuviation from overlying or lateral parts of eluvium. The question of the mobility of individual elements in this system is not a simple one. Mobility of individual elements depends on minerals resistance to weathering (crystallochemical aspects), forms of chemical elements migration amount of energy supplied to the system etc. E. g. iron is released sooner from olivine than from magnetite, calcium is depleted sooner from pyroxenes than from plagioclases. Elements migrating as single ions (alkalies, alkali earths) are removed more rapidly than those forming complexes (Si, Al). After spatial anisotropy was formed in weathering crusts, the character of weathering solutions (pH, concentration) is changed. E. g. by decreasing pH value after removal of basic cations gradually reduces mobility of Si and mainly Al that form insoluble components (hydroxides) within the pH range of 5—9.

The relative Al enrichment against Si has to be evaluated very cautiously. The process of hydrolysis (pH 5—9.6) leads to partial or complete desilicification. Silica migrates in the form of complexes (polymers) and in places silica gels accumulate alone. Aluminium is translocated shortly afterwards in the form of colloids into fissures, leached hollows after primary minerals etc.

Its primary depletion is thus compensated for or even surpassed at the expense of the removal of other components. Consequently the relative increase of its content against silica is not due to real depletion of Si.

By weathering processes, all primary and secondary discontinuities (fissures, pores and other planes of weakness) are used. Along these planes, weathering proceeds more rapidly than in the solid rock mass. That is why rock relicts in some layers remain only slightly affected by weathering. They may later release part of their mobile constituents that may enter secondary products. This fact also influences the vertical mineral zoning of weathering crusts.

Neither the least mobile components remain in their original place. Percolating meteoric waters (+gravitation) transport them in the form of colloids solutions or suspensions (by colluviation) to depressed sites. If foreign material is supplied they mix with it and their overall chemical composition changes. All vertical changes in a weathering profile thus results from a very complex succession of changes, especially if they developed during different weathering regimes. If this history is not recognized on the basis of a complex study, the evaluation of chemical composition changes do not bring adequate results.

During evaluation of basalt weathering processes we compared individual models and methods and found out following facts:

1. In their study the geochemical model, according to which all constituents are added or extracted, is valid.

2. The profile has a complicated history corresponding to at least two different weathering regimes.

3. Chemical composition of individual zones reflects complicated development

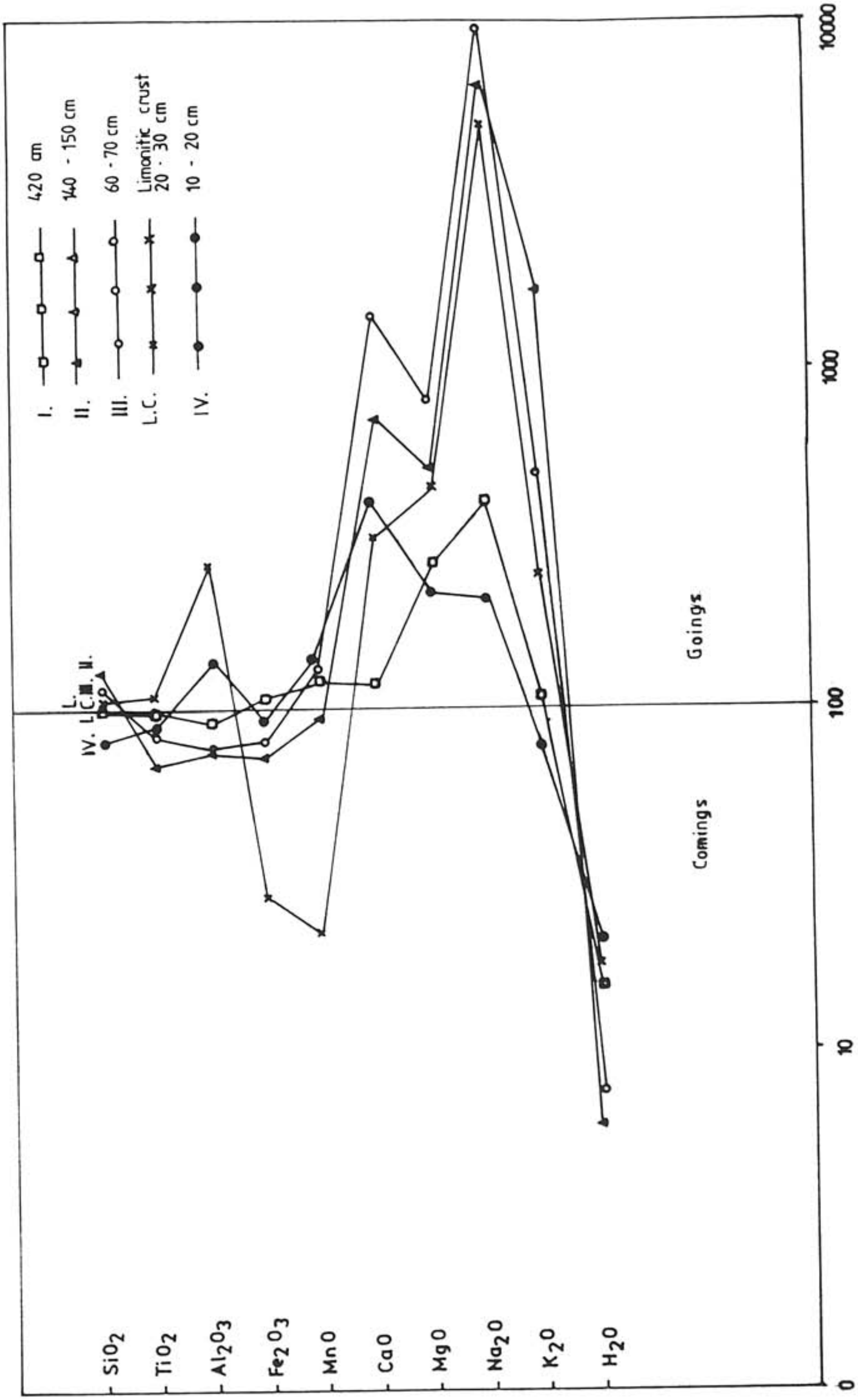


Fig. 17. Comings — goings diagram of individual components in different by stages of basalt weathering.

of weathering crust formation and not only groups of chemical changes in relation to the primary parent rock.

4. Mobility trends of individual components in relation to aluminium cannot ba regarded as decisive because the balance of changes follows the first model. Aluminium, iron or titanium are not universal internal standards and their application gives only approximate results.

5. Very valuable information on the development of any weathering crust is obtained by micromorphological study, which enable us to penetrate into the microworld and consequently also to the development of weathering crusts.

6. Diagrams of component comings and goings (G a r r e l s—M a c k e n z i e, 1971) seem to be convenient for a comparison of chemical composition changes in vertical zone, because they register individual changes against the parent rock regardless of the genesis of the observed zone (Fig. 17).

Diagrams of the components comings – goings and weathered profile (at Šiatorošská Bukovinka) history.

Diagrams of components comings—goings can be elaborated of values calculated in the following way: the weight percent of the oxide in the rock divide by its weight percent in the weathered products and multiply by 100 (G a r r e l s — M a c k e n z i e, 1971). The values thus calculated are plotted in a semilogarithmic scale whose axis x represents oxides in normal scale and axis y shows calculated ratio of the oxides in logarithmic scale (Fig. 17).

Graphic values result from the data of chemical analyses given in Tab. 2. These have been gained by X-ray fluorescent analysis (analysed by V o n d r o v i c, Geological Institute of the Centre of Geoscience Research, Slovak Academy of Sciences, Bratislava). The Tables slow average values of analyses of basalts (n = 3), individual weathering zones and solid iron crust. In the graph, ignition and drying losses are designated as H_2O.

Silica (SiO_2) was slightly removed, which is evident mainly in a depth 150 cm. In a depth 450 cm, probably as a result of the presence of silica gels, its content is almost compensated. On the other hand, present day soil (10—20 cm) containing quartz of clastogene character is enriched. In fact, this enrichment reflects the foreign admixture. The clastogene quartz occurs in the iron crust, too (Fig. 14). As other SiO_2 forms are absent, the presence of the clastogene quartz compensates for the relative depletion. Titanium (TiO_2) shows enrichment in all weathered materials and is therefore little mobile. The relatively highest enrichment in a depth 150 cm, however, means weathering and removal of other constituents except for part of magnetite (ilmenite?) which is still locally preserved (contains Ti).

Aluminium is enriched, with the exception of present day soil and iron crust, suggesting that it is little mobile. We must take into account, however, the compensation of its contents as a result of illuviation of Al gels and removal of other elements.

Iron and manganese accumulate in the oxidic type of these weathered materials. Indications of weak Fe and Mn removal in the first weathering stage well corresponds with the decreasing of oxidation capacity of penetrating so-

Table 2

Compostion of unaltered basalts and their weathered products (in weight %)

	Šiatorošská Bukovinka						Trebeľovce		
	unweathered basalts (n = 3)	420 cm 1st stage	140—150 cm 2nd stage	60—70 cm 3rd stage	20—30 cm iron crust	10—20 cm rec. soil. 4th st.	90—100 cm	50—60 cm	30—40 cm
SiO_2	46.53	47.45	36.06	42.05	50.55	58.85	54.34	60.16	63.46
TiO_2	1.84	1.96	2.74	2.21	1.11	2.13	2.08	2.44	1.94
Al_2O_3	18.9	20.80	24.72	24.94	7.01	13.02	17.94	15.04	13.15
Fe_2O_3	8.72	7.88	11.89	10.99	30.27	9.47	9.36	8.46	8.06
MnO	0.17	0.14	0.18	0.13	0.76	0.12	0.15	0.18	0.17
CaO	9.30	8.02	1.28	0.66	0.30	2.39	2.89	2.32	2.57
MgO	5.66	2.17	1.13	0.72	0.12	2.41	2.71	2.22	2.60
Na_2O	5.7	1.41	tr.	tr.	tr.	2.31	1.26	1.42	1.74
K_2O	1.85	1.74	0.11	0.42	0.42	2.43	1.89	2.16	2.16
H_2O^+	0.35	3.76	5.89	6.66	2.77	1.51	1.97	1.56	1.64
H_2O^-	0.68	4.43	16.13	11.55	6.16	5.39	5.45	4.21	2.78
Total	99.70	99.76	100.13	100.32	100.35	100.03	100.05	100.17	100.27

Analysed by M. Vondrovic, Geol. Inst., Centre of Geoscience Research, Slovak Academy of Sciences.

lutions, with manifestations of gleyey (reduction) processes leading to Fe^{2+} extraction from mafic minerals, which is evident by micromorphological study.

Calcium, magnesium, but mainly sodium are most mobile and are removed during all weathering stages. The relativelly least decrease of Na, Ca and Mg contents during the first stage (420 cm) well corresponds with microscopic study indicating preservation of plagioclases, as well as part of mafic minerals, though the latter bear signs of intensive corrosion. The trend of potassium is reverse. The higher the degree of weathering, the lower the apparent degree of depletion. Present day soil is even enriched (10—20 cm). This enrichment, however, results from the addition of less weathered components on the surface as well as partial bonding of potassium (sorption, fixation) translocated from the surface by secondary weathering products (illite) which is related to present day pedogenesis.

Enrichment in H_2O is associated with hydration of secondary weathering products.

The diagram illustrates in detail all peculiarities of weathered profile and agrees with micromorphological studies. Present day soil (10—20 cm) is enriched in a less weathered clastogene admixture (content of clastogene feldspars, quartz, micas). This has been reflected by a strikingly different course of the comings-goings curve. The changed Na, Ca, Mg removal in this zone is, in fact, supply of foreign constituents into the weathered material, probably in the form of devoluvial and/or eolic admixture. The whole profile formed in two stages. The first was related to intensive basalt weathering, whereas the other was linked to present day pedogenesis and supply of a less weathered clastogene material. A comparison of the result of chemical analysis from the localities Šiatorošská Bukovinka and Trebeľovce indicates an evident increase of SiO_2, drop in Al_2O_3 and some increase of alkalies and alkali earth contents. These mixed weathered materials contain an enriched clastogene admixture and their character in similar to present day soils. They are deluvial weathering crusts, which is proved by micromorphological study. Especially clastogene quartz can be seen microscopically also in lower deluvial zones (100—120 cm).

The trend of individual element removal during weathering of various rocks including basalts has been discussed by various authors: The well-known scheme of Polynov (1937) gives this sequence of element removal in the course of weathering:
Ca > Na > Mg > K > Si > Fe > Al.

Chesworth et al. (1981) give a different trend for coherent samples of basalt weathered materials:
Si > K, Na, Mg > Ca > Fe, Al, Ti for coherent spheroid cores of weathered basalt and
Si > Ca > K, Na, Mg > Fe, Al, Ti for spheroid envelopes of completely weathered basalts. We suppose that way of trends evaluation in this work did not take into account Al translocation in coherent samples and its enrichment (metakinematic infillings), which may bias the silicium-aluminium relation.

Basalts studied by us are highly alkaline. They contain a high percentage of sodium, which together with Ca are the most mobile elements. The quick depletion of these excellent water migrants resulted in the acceleration of weathering which, in spite of the young age of the basalts, has a partly kaolinic character. According to our study the element mobility trends are as follows:
Na > Ca > Mg > K > Si > Fe (Mn) > Al, Ti.
This confirms the high mobility of alkalies and alkali earths. The highly alkaline environment formed in the outer margin of the front influences also the mobility of Si and Al that are thus partly mobile.

Some trends of trace elements mobility

Results of microelement analyses in individual weathering stages obtained by spectrochemical method (Medveď—Plško, 1980) are shown in Tab. 3. These results are compared with the average values of microelement contents of 50 basalt samples from this area taken over from Forgáč's study (1970).

Barium, strontium and lead are probably present in plagioclases. The most depleted element of them is Sr (together with Ca), but Ba and Pb show a considerable decrease, too. Ba is in part trapped in secondary products or new mineral phases.

Prevailing part of Cr, V, Co, Ni, Sc, Y and Cu occurs in mafic minerals (pyroxenes, biotite). Although some of these elements tend to be removed, their significant part is trapped in secondary products. Ni, bound to clay minerals (smectites), has a marked tendency to enrichment. Increased Y and Sc contents are also interesting, but their trend cannot be analysed due to the absence of data on these elements in rocks. Vanadium is very depleted in all horizons. Only a small part of the original V amount is trapped in clays. Most probably it is removed as early as in the first stage under the influence of alkaline

Table 3

Trace elements in basalts and their weathering products (in ppm)

cm	Be	B	Pb	Sn	Cu	V	Ni	Co	Y	Sc	Cr	Ba	Sr
Šiatorošská Bukovinka													
10— 20	5	64	24	15	15	35.3	189	21	180	24	31	168	6
20— 30	3	37	37	15.4	12	57	58	16	61	21	79	381	10
30— 40	4.3	27	19	11	15	40	143	18.5	72	21	99	372	13
90—110	4	11.4	9	10	19	22	187	177	282	31.5	91	298	15
140—150	4.4	10.5	6	9	14	25.3	171	28	215	26.5	57	156	4
200—220	3	10	5.3	9	24	13.5	177	17	126	26	29	488	14
Trebolovce													
30— 40	4.3	60.4	14.5	9.4	12	38	91	14.5	72	25	100	23	39
Cerová vrchovina													
—	—	6	110	—	15	520	103	35	—	—	153	705	664

Explanations: 1 — average contents in basalts to Forgač (1970), (n = 50 samples).

solutions (as aniogene element). B contents in basalts are very low, but in the profile they are of a reverse increasing trend. B is most abundant in present day soil. It is concentrated at the biogeochemical barrier thus proving the above-mentioned facts that an foreign admixture is present and the fact that present day pedogenesis has influenced different microelement distribution characters in the top soil horizons. This is evidenced also by the above-mentioned analyses of the upper part of deluvial weathered material at Trebeľovce which is very similar in its composition.

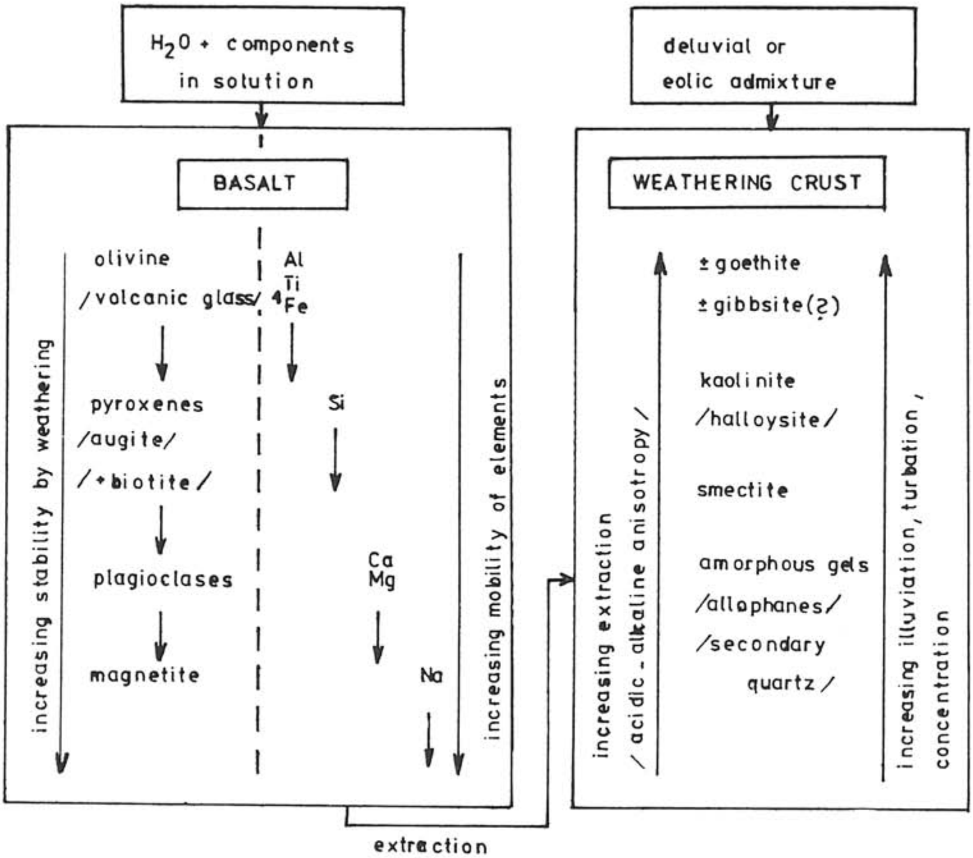
Weathering model

Based on presented results we are able to advance a schematic geochemical model documenting the gradual character of weathering and removal of elements. The activity of weathering solutions affecting alkali basalts first mobilizes alkalies and alkali earths. Their overall removal is controlled not only by their migration ability but also by the stability of individual mineral phases that release these components gradually (Tab. 4).

The presence the secondary minerals assemblage depends on the extraction degree of basic cations and silicium. By less intensive desilification, smectites originate, whereas complete dealkalization and advanced desilification result

Table 4

Model of basalt weathering in the Cerová vrchovina highland area



Explanations: 1_{Fe} — mobility is controlled by oxidation-reduction conditions.

in the formation of kaolinite. A considerable vertical mineral differentiation is partly due to rapid removal of basic cations and probably also anisotropy in pH differences thus formed. Fe-migration and oxidation are controlled by Eh (pe) values and therefore it cannot be stated that iron is immobile.

Weathering solutions affecting the rock in the outer margin of the front cause a highly alkaline environment. Under these conditions, Si and Al start migrating in the form of polymer components. They give rise to Si, Al gels, whose recrystallization results in secondary products (clay minerals) formation. The isotropic character of the gels is locally observable under the microscope. Over a period of time, some Si-gels gradually ages to cristobalite.

The kaolinic character of the studied kaolinic crusts is probably controlled mainly by alkaline character of the basalts (rapid removal of basic cations) and geomorphological development. Climatic influences cannot be excluded, but because of the young age of the basalts they were not a dominant factor. Some changes took place in the present day pedogenetic regime after the formation of weathering crusts on these basalts which, in accordance with a work of K u b i e n a (1970), can be termed braunlehm. Certain soil degradation (brunification) and a supply of foreign material onto the surface etc. is characteristic for this regime.

Our results indicate that the geochemical model, according to which all components are mobile, added or extracted, is only valid. The following order of decreasing mobility of the elements was found:

Na > Ca > Mg > K > Si > Fe (Mn) > Al, Ti,

that is almost identical to that of P o l y n o v' s global sequence.

The extraction of trace elements is controlled by the mobility of the main elements (origin of a migration environment) and ability of these elements to enter secondary mineral phases or sorption complex of the colloids.

Translated by Ľ. Böhmer

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