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TO THE QUESTION OF ORIGINE AND STABILITY OF SECONDARY MINERALS IN THE WEATHERING ZONE OF MALÉ KARPATY MTS. GRANITOIDES

(Tab. 1 - 5, Figs. 1 - 4)



Abstract: The submitted contribution concerns geochemical study of spring waters, draining the granitoid rocks of Little Carpathians, where emphasis is laid on thermodynamic analysis of the system rock — water. The obtained results, enabling to characterize the processes and products of chemical weathering are evaluated in the context of complex evaluation of the main chemical weathering factors of granitoides.

The geochemical study of granitoide waters showed that unstable minerals in the weathering zone are anorthite, albite, microcline, illite and gibbsite. Practically stable are Ca-montmorillonite, kaolinite and quartz. Comparison of mineralogical study and thermodynamic analysis of waters leads to the conclusion that the contemporary hydromical weathering zone is thermodynamically unstable and theoretically there exists a tendency of transformation of illite to montmorillonite or kaolinite.

Резюме: Предлагаемая статья касается геохимического изучения вод ключей, дренидующих гранитоидные породы Малых Карпат, причем подчеркивается термодинамический анализ системы порода — вода. Полученные результаты, способствующие более подробно характеризовать процессы и продукты химического выветривания, оценивают в контексте комплексной оценки главных факторов химического выветривания Малых Карпат.

Геохимическое изучение вод гранитоидов показало, что нестабильными минералами в коре выветривания являются анортит, микроклин, иллит и гиббсит. Сравнение результатов минералогического изучения и термодинамического анализа вод ведет к заключению что современная гидрослюдовая кора выветривания термодинамически нестабильная и теоретически существует тенденция перехода иллита к монтмориллониту, или-же к каолиниту.

Introduction

Granitoide rocks of Malé Karpaty Mts. (Slovakia, West Carpathians, Fig. 1) are formed mainly by granites and granodiorites (B. Cambel— J. Valach, 1956; B. Cambel— J. Veselský— V. Vilinovič, 1980). In the process of their chemical weathering it comes to hydrolytic dissociation of alumosilicate minerals, where one part of the substance gest to the solution and the other remains on the place in the form of the so called mineral residue. The higher-to papers concerning chemical weathering of granitoides of Malé Karpaty Mts. were devoted mainly to mineralogical or mineralogic-geochemical study of solid products of weathering, before all of the clay fraction of weathering products and soils. By means of rtg analysis, DTA and electron microscopy there was stated a prevalence of hydromical weathering crusts on rocks of

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Little Carpathians'crystallinicum. On granodiorites there was found the following association of clay minerals (J. Čurlík et al., 1980):

illite (hydromicas) — mixed structures — montmorillonite. As admixture there appears chlorite. Kaolinite was found with certainty as admixture in the most upper horizons of soils, especially on phylites.

M.Harman — J. Derco (1976), who studied mineralogically the loose filling of the mylonite zones in granitoides, found in the Bratislava massif (massifs are understood in the sense of the work of B. Cambel — J. Valach, 1956) the following mineral association:

montmorillonite — illite (hydromicas) — chlorite — hydrogoethite, and in the Modra massif:

illite — chlorite — montmorillonite — hydrogoethite.

In the region of the Dolinkovský Hill (Modra massif) it came to the formation of an anomalous association of secondary minerals in mylonites (aragonite — calcite — hydromicas — IM structures — quartz) in consequence of penetration of carbonate solutions from upperstrata rocks of the Harmonia series to mylonite zones (M. Harman — J. Derco, 1974).

Recently M. Harman (1980) stated, that the process of formation of secondary minerals in plagioclases of Malé Karpaty Mts. granitoides consists essentially in their illitization. There does not come to kaolinite formation under the given conditions. Special circumstances of weathering were found in the region of Horvátka (Bratislava massif), where there occurs the so called hydro — (auto) metamorphosed type of granite. The arousal of clay minerals in isolated "nests", perhaps from the residual solutions (?) without a distinct influence of the surrounding environment on the plagioclases has also an illitic character.



Fig. 1. Schematical geological map of Malé Karpaty Mts. Comments: B — Bratislava massif, M — Modra massif, 1 — granitoide rocks, 2 — crystalline schists, 3 — amphibolites, 4 — mesozoicum undivided, 5 — panone, 6 — baden and sarmat undivided, 7 — loesses, 8 — alluvial sediments of the quaternary.

Research methods

In the period of 1975-1980 there were taken 58 samples of spring waters from the region of Malé Karpaty Mts. granitoides. The author has taken 46 samples, 12 samples were taken — with permission — from the work of D. Cambelová (1975). In the field were measured these parametres: water and air temperature, acidity and alcalinity, pH. Conservation of samples was performed according to the demand of the laboratory. pH-values were measured by a portable apparatus, pX-meter RADELKIS, type OP-107, using a combined glass electrode with the precision \pm 0,05 pH. In quoted samples the pH was measured by the same apparatus immediately after transport of samples to the laboratory (i.e. after 2-3 hours). All samples were taken into polyethylene flasks. Complex chemical analyses were performed in hydrochemical laboratories IGHP n. p. Žilina (31 samples) and GÚDŠ Bratislava (27 samples).

Data of chemical analyses were processed on programmable calculator WANG 2 200B according to the programme used at present by the Hydrochemical Department of the GÚDŠ in Bratislava for waters with a temperature to 25°C and with a ionic power smaller than 0.1.

Study of thermodynamic dependences in the system rock - water

Disequilibrium index. T. Pačes (1972 defined the disequilibrium indexes $I_{\alpha\beta}$ for the single systems silicate mineral — water (where α is the primary and β the secondary mineral) as $I=\log/Q/K_t/;$ Q is the activity product of the reaction and K_t the equilibrium constant at the temperature of water measured in the field. The relations of the index calculation are quoted in Table 1.

Table 1

Relations for the calculation of disequilibrium indexes according to T. Pačes (1972)

Index/system	$I_{\alpha \cdot \beta}$ = log [Q/K] at temperature t in °C
I _{an-k} anorthite-kaolinite	$I_{an-k} = log a_{Ca}^{2+} + pH - \{18,81 - 0,07114 t\}$
I _{ab-k} albite-kaolinite	$I_{ab-k} = log a_{Na+} + 2 log a_{H4SiO4} + pH - (0.043 + + 0.00323 t)$
I _{m-k} microcline-kaolinite	Im-k — log a _{K+} + 2 log a H ₄ SiO ₄ + pH — [0,01629 t — 2,931]
I _{il-k} illite-kaolinite	$I_{il-k} = 0.6 \log a_{K}^{+} + 0.25 \log a_{Mg}^{2}^{+} + 1.1 pH + 1.2 \log a_{H_4}^{2} \sin_4 - \{1.692 - 0.005086 t\}$
I _{cm-k} Ca-montmorillonite- -kaolinite	$I_{cm-k} = [\log a_{Ca}2^{+} + 8 \log a_{H_4}S_{iO4} + 2pH - (0,01143 t - 16,6)]/6$
I _{k-g} kaolinite-gibbsite	$I_{k-g} = 2 \log a_{H_4} SiO_4 - (0.02 t - 8.79)$
I _s amorphous SiO ₂ -water	$I_s = \log a_{H_4} s_{iO_4} - [-3,09 - 779 (273,15 + t)]$

Although the index $I_{\alpha-\beta}$ for a certain system is thermodynamically precisely defined in the relation to the Gibbs free energy (G) (I = Δ G/2.303RT, further T. Pačes, 1972; S. Gazda — T. Pačes, 1975), in practice at judging the degree of deviation of the actual state of the system from the equilibrium state, its quantitative evaluation mostly does not matter and it is not necessary to calculate Δ G. Therefore the disequilibrium indexes are used with

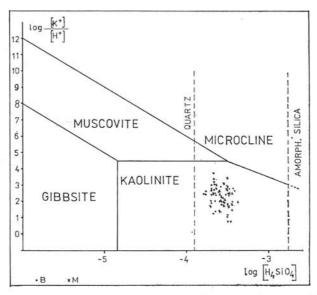


Fig. 2. Stability phase diagram for microcline, kaolinite, gibbsite at $25^{\circ}C$ and 0.1MPa as function of [K⁺], pH and [H₄SiO₄]. B — Bratislava massif, M — Modra massif.

advantage, as they were defined by T. Pačes (1972), because they express the deviation from the thermodynamic equilibrium for the calculated systems. If I=0, then the reaction is in thermodynamic equilibrium and all partaking substances are thermodynamically stable. If I<0, the reaction tends to pass to the right, and if I>0, on the contrary to the left. The values of indexes then characterize the unsaturation or the saturation of the spring waters towards individual minerals and by this also the stability of these minerals under the given conditions.

Stability phase diagrams. In nature there never are occurring pure mineral phases and e.g. products of weathering often cannot be precisely defined crystalochemically. Therefore in the study of processes of rock weathering we often approach to the study of simplified systems. As the weathering of granitoide rocks consists essentially in hydrolytic dissociation of alumostilicate minerals, in the study of this weathering we can use with advantage the so called stability phase diagrams (Figs. 2, 3 and 4) to interpreting purposes. The diagrams are constructed on the base of experimental data on free energy of the originating of individual mineral phases. In their construction it is supposed that the aluminium in the process of weathering is

immobile and entirely fixed within the arising solid phase. Details of construction of stability phase diagrams, together with factors delimitating their use, are quoted e.g. in the works R. M. Garrels [1960]; R. M. Garrels — C. L. Christ [1965]; J. R. Kramer [1968]; C. H. Helgeson et al.

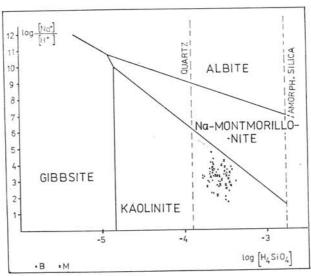


Fig. 3. Stability phase diagram for albite, Na-montmorillonite, kaolinite, gibbsite at 25°C and 0.1 MPa as function of [Na+], pH and [H_4SiO_4].

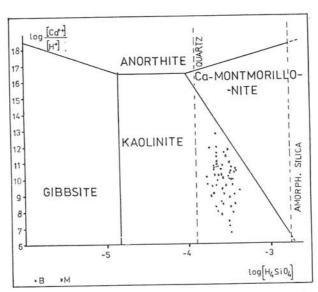


Fig. 4. Stability phase diagram for anorthite, Ca-montmorillonite, kaolinite, gibbsite at 25°C and 0.1 MPa as function of [Ca²⁺], pH and [H₄SiO₄].

[1969]; N. van Breemen — R. Brinkman [1976]. They were introduced into hydrogeochemical literature by J. H. Feth et al. [1964]. Stability phase diagrams (Figs. 2, 3, 4) were constructed on the base of the relations quoted in Table 2.

Results

Chemical composition of waters.

Results of the chemical analysis of spring waters, quoted in Table 3 indicate, that from the point of view of mineralizating processes of waters the differences in chemical and mineralogical composition of rocks of both massifs (Table 4) have no important role. Certain differences in chemical composition of both sample groups are caused by these factors:

- a) the samples were not taken in the same period
- b) the topographical position of the springs is different and the time of the contact of waters with the rock environment is unequal
- c) the Alpin tectonic disrupting of granitoide rocks (intensive cataclase of minerals, arousal of tectonic dislocations, B. Cambel — J. Valach, 1956) presented itself in a greater extent in the Bratislava massif; a greater dispersity of minerals facilitating the hydrolysis of silicates and a deeper circulation of waters are the cause of the somewhat higher mineralization of the waters of the Bratislava massif on the average.

From indications in Tab. 5 where there are quoted the results of the index calculations it follows that the chemical composition of spring waters on the

Table 2

Equilibrium dependences for the calculation of stability phase diagrams for 25 °C and 0.1 MPa (according to Y. Tardy, 1971, who used thermodynamic constants published in the papers of R. A. Robie — D. R. Waldbraum, 1938 and J. R. Kramer, 1968)

System	Equilibrium dependences
Microcline-kaolinite	$2 \log [H_a SiO_a] + \log [K+] / [H+] = -2,45$
Microcline-gibbsite	$3 \log [H^4 SiO^4] + \log [K+] / [H+] = -7,28$
Microcline-muscovite	$3 \log [H_4 SiO_4] + \log [K+] / [H+] = -5,39$
Muscovite-kaolinite	$\log [K+] / [H+] = 4.52$
Muscovite-gibbsite	$3 \log [H_4 SiO_4] + \log [K+] / [H+] = -9.96$
Albite-montmorillonite	$5 \log [H_4SiO_4] + 3 \log [Ga+] / [H+] = 7,90$
Albite-kaolinite	$2 \log [H_4 SiO_4] + \log [Na+] / [H+] = 0.93$
Albite-gibbsite	$3 \log [H_4 SiO_4] + \log [Na+] / [H+] = -3,90$
Anorthite-montmorillonite	$4 \log [H_4SiO_4] + 3 \log [Ca^{2+}] / [H^+]^2 = 65,37$
Anorthite-kaolinite	$\log \left[\text{Ca}^{2+} \right] / \left[\text{H}^{+} \right]^{2} = 16.41$
Anorthite-gibbsite	$2 \log [H_4 SiO_4] + \log [Ca^{2+}] / [H^+]^2 = 6.78$
Montmorillonite-Na-kaolinite	$4 \log [H_4 SiO_4] + \log [Na+] / [H+] = -9.31$
Montmorillonite-Na-gibbsite	$11 \log [H_4SiO_4] + \log [Na+] / [H+] = -43,11$
Montmorillonite-Ca-kaolinite	$8 \log [H_4 SiO_4] + \log [Ca^2 +] / [H +]^2 = -15,70$
Montmorillenite-Ca-gibbsite	$22 \log [H_4 Si04] + \log [Ca^2 +] / [H +]^2 = -83,28$
Kaolinite-gibbsite	$log [H_4SiO_4] = -4,82$

40,63

15,93

42,01

16,79

Bratislava massif (n=37)Modra massif (n=21)Granitoides undivided value value (n = 58)average average dispersion dispersion average Total minerali-144.87 157,01 114,23 - 222,28163,89 104,72 - 208,02zation 5,65 - 7,905,00 - 8,006,67 6,65 6,66 pH 3.6 - 12.18.26 3.9 - 9.77.22 7.88 Na 0.9 - 3.01,1 - 3,21.93 1,90 1,89 K 2,43 - 7,175,34 2,43 - 9,485,64 4.80 Mg 19,48 10.42 - 29.4620,96 11.02 - 29.4616,89 Ca 2.41 - 12.264.00 1.77 - 5.673,57 3,84 NO3 0.00 - 28.679.34 0.00 - 30.809.18 9,28 22,22 - 90,5550,50 21,39 - 64,2034,05 44,55 SO,

Table 3 Results of chemical analyses of granitoide waters of Malé Karpaty Mts.

10,05 - 25,79Note: Except pH the data are presented in mg/1.

12,20 - 109,80

HCO₃

SiO₂

whole is not in equilibrium with the rock environment, but the waters are dissolving the surrounding minerals. The stability of minerals in the weathering zone of granitoide may be characterized as follows:

12,20 - 97,60

11,09 - 21,56

39,85

15,44

Unstable mineral phases: anorthite, albite, microcline, illite, gibbsite. Stable mineral phases: kaolinite, Ca-montmorillonite, practically also quartz.

Note: The average content of SiO₂ is 15,93 mg/1, whereas the quartz solubility in natural water [pH = 4 - 9] is about 6-8 mg/1 [O. P. Bricker - R. M. Garrels. 1967). In relation to quartz the spring waters are thus supersaturated by the SiO2 compound. The unsaturation of waters in comparison to amorphous SiO2 results from the fact, that its solubility in natural waters is about 115 mg/1.

All points on Figs. 2, 3 and 4, plotted on the base of [Ha/H] or [K/H] values and the SiO₂ concentration from chemical analyses of spring waters of Little Carpathians' granitoides occur in the stability field of kaolinite. This indicates that under the given conditions the kaolinite is as a weathering product the most stable one. It does not mean however that the waters are in equilibrium with kaolinite. At the same time the values of the index Ii.k [-2,10; Tab. 5] indicate that illite is under the given conditions less stable than kaolinite, whereas the values of the index $I_{\rm cm-k}$ (-0,15) suggest that montmorillonite is under the given conditions as stable as kaolinite.

Between these data and the results of the mineralogical investigation of weathering products and soils there exists one basic difference resulting from the following:

a) Study of the clay fraction of weathering products and soils on granodiorites showed that in the crust of weathering it came, or comes to a massif arousal of illite or of hydromicas and that montmorillonite occurs regularly in abundancy. The contents of chlorite, which is always present, are locally

Average chemical and mineralogical composition of Malé Karpaty Mts. granitoides

Si	SiO ₂	TiO_2	A12O3	Fe203	FeO	MnO	MgO	CaO	Na ₂ O	K20	P ₂ O ₅	H ₂ O+	H ₂ O-	Total
A 72 B 68	72,31	0,28	14,87 15,70	1,27	0,78	0,05	0,71	1,53	3,70	3,52	0,13	0,83	0,15	100,13

B. Cambel - J. Veselský - V. Vilinovič (1989). A

Monzogranites ($\hat{n}=6$) and granodiorites (n=29) of the Modra massif. Calculated by the author according to B. bel -1. Veselsk $\hat{y}-V$. Vilinovič (1980). B

Cam-

	Quartz	K-feldspar	Plagioclase	Biotite	Muscovite	Amphibole	Accessories	Total	
									-
A	32,35 23,41	22,07 21,87	34,83 39,72	5,82 12,43	4,23	0,95	1,25	100,55	
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A — Arithmetical mean of 6 planimetric analyses according to B. Cambel — J. Valach (1956) B — Arithmetical mean of 7 planimetric analyses according to B. Cambel — J. Valach (1956).

granitoides Malé Karpaty Mts. silicate equilibria for the spring waters of of Results of thermodynamic calculations

	Dise	quilibrium in	Disequilibrium index I = log U/N		Grannoides
System	Bratislava massif (n=37)	if (n=37)	Modra massif (n=21)	(n=21)	average
5	value dispersion	average	value dispersion	average	(n=58)
albite-kaolinite microcline-kaolinite illite-kaolinite kaolinite-gibbsite anorthite-kaolinite Ca-montmorillonite-kaolinite amorphous SiO ₂ partial pressure of CO ₂ (MPa)	-5,11 to -2,50 -3,21 to -0,55 -3,69 to -0,68 4,16 to -5,21 -1,192 to -5,96 -0,57 to 0,262 -0,79 to -0,30 7,1,10 ⁻⁵ to 1,3,10 ⁻² 1,82,10 ⁻³ to 4,55,10 ⁻³	-3,81 -1,79 -2,14 4,63 -6,78 -0,17 -0,58 1,5,10-3 3,26,10-3	-4,80 to -2,77 -2,60 to -0,67 -3,11 to -0,85 4,26 to 5.07 -10,76 to -6,42 -0,44 to -0,03 -0,71 to -0,37 9,8.10 ⁻⁵ to 1,2.10 ⁻² 1,83.10 ⁻³ to 3,69.16 ⁻³	-3,73 -1,66 -2,05 4,70 -6,73 -0,12 -0,12 1,3.10 ⁻³ 2,64.10 ⁻³	-3,78 -1,74 -2,10 4,65 -0,15 -0,15 1,4.10 ⁻³ 3,02.10 ⁻³

much more variable. Kaolinite was stated only in traces, or its presence was indicated as questionable (J. \check{C} urlík et al., 1980).

b) The thermodynamic analysis of spring waters, draining these rocks indicate ($I_{il^*k}=-2,19$), that illite is thermodynamically unstable in the crust of weathering products and there exists the tendency of its transformation to montmorillonite, or kaolinite. Although there are treated to a considerable amount schematized calculations, these prompt us to pronounce the conclusion, that the contemporary hydromical crust of weathering on Malé Karpaty Mts. granitoides is thermodynamically unstable.

Discussion

In the interpretation of differences between the mineralogical composition of the clay fraction of weathering products and soils of granitoides and the results of equilibrium and stability dependences in the system silicate minerals — water we are obliged to take into consideration two basic facts:

- 1. Equilibrium calculations show only, that the spring waters are not (or are) in equilibrium with the inner structure of the minerals, that correspond to stechiometric formuli, for which formuli the free energies of the arousal of minerals are determined. The thermodynamics is useful only to describe the deviations of the real system from the partial or entire equilibrium. Whether it comes to a real process does not depend on thermodynamics, but on the energies of activation and the kinetics of the reactions (T. Pačes, 1970).
- 2. The spring waters do not represent in a full extent the "weathering" (intersticial, porous) waters. In thin breaches and cracks, where there it comes to hydrolytic decomposition of aluminosilicate minerals, there exists a different geochemical environment as in the surrounding circulation waters, incessantly supplied by atmospheric precipitations.

When we realize this, on the base of the values of disequilibrium indexes [Tab. 5] and the interpretation of stability phase diagrams (Figs. 2, 3, 4), we may characterize the chemical weathering of Little Carpathians'granitoides as follows:

The basic factor, causing the alumosilicate decomposition, are the precipitation waters, which have an expressively acid character in the given region (pH = 4 - 5, data of GÚDŠ Bratislava). In the soil layer they are saturated by soil CO2 - a further source of H+ ions. In climatic conditions of Little Carpathians (a temperate warm and temperate humid region of Central Europe) the CO2 concentrations in the soil air keep within 0,5 - 5,0 volume % (S. Gazda, 1980), i.e. 5.10^{-4} to 5.10^{-3} MPa. In the atmosphere pCO2 equals approx. 3.10^{-5} MPa. The reverse calculation from the chemical composition of the granitoid waters (Tab. 5) showed, that pCO2 = 10^{-3} to 10^{-2} MPa (in average $1.4.10^{-3}$ MPa) and thus is 10- to 100-fold higher than in the atmosphere. Such aggresive solution quickly becomes mineralized by hydrolytical decomposition of silicate minerals and is enriched by cations and SiO2. High positive values $I_{k-g}=4.65$ (Tab. 4) indicate, that if even in the initial stage of alumosilicate decomposition gibbsite arises, it becomes unstable by a quick increase of concentration of cations and SiO2 and the

oretically there may arise kaolinite. Its formation under the given conditions is somewhat questionable. Hydrolysis of silicate minerals proceeds relatively quickly (W. D. Keller et al., 1963), pH shifts to the alkaline zone and the concentration of cations and SiO2 in the liquid phase increases to such an extent, that montmorillonite is probably a more stable phase than kaolinite. The question of the priority of arousal of this or that mineral is connected with the speed of the decrease of hydrolytic capacity of the liquid phase and the increase of the concentration of the structure cations and SiO2 to the values corresponding to stability conditions of the relevant mineral phase. The cause of the predicted formation on kaolinite under the conditions of weathering of Malé Karpaty Mts. granitoides (Fig. 2, 3, 4) is due to the fact, that the spring waters are in comparison with real [weathering) solutions diluted and by concentration of structure cations and SiO2 they do not give possibility of neoformation of montmorillonite or illite (illite is thermodynamically and crystalochemically close to muscovite, Fig. 2]. However the fact, that in the crust of weathering is found illite or montmorillonite in priority indicates, that in the cracks and breaches of minerals, where there it comes to a real arousal of clay minerals [M. Harman -J. Derco, 1974; M. Harman — J. Derco, 1976; M. Duray, 1977; J. Čurlik et al., 1980; M. Harman, 1980), it comes to the formation of a more basic and more concentrated environment, which is not suitable for the arousal of kaolinite. Thus in hypergene conditions of Malé Karpaty Mts. it practically does not come to kaolinization of feldspars of granitoide rocks. At the same time we are obliged to emphasize, that the circulating underground waters represent by their hydrogeochemical character an aggresive agent for the surrounding rock environment and unambiguously point out the progressive character of the chemical weathering of the Malé Karpaty Mts. granitoides (see the negative values of the indexes $I_{ab-k} = -3.78$; I_{m-k} =-1,74; $I_{an-k}=8,76;$ Tab. 5). At the same time the index values I_{il-k} (in average -2,10) permit to express the conclusion that by their chemical character and hydrogeological cycle the underground waters of Malé Karpaty Mts. granitoides may be the cause of the thermodynamic unstability of the contemporary hydromical crust of weathering.

Conclusion

Our results may be summarized as follows:

- 1. The mineralogical character of the clay fraction of the weathering products and soils of Malé Karpaty Mts. reflects the tendency of bisiallitization (formation of illite, montmorillonite, chlorite) in the sense of G. Pedro (1971) and Y. Tardy (1971).
- 2. The thermodynamic analysis of granitoide waters indicates rather a theoretical tendency of monosiallitization (formation of kaolinite) in the process of weathering.
- 3. The mentioned contradiction points 1, 2 is the reflection of the fact, that mineral products of weathering of Malé Karpaty Mts. granitoides are not in the geochemical equilibrium with hydrological and hydrogeochemical conditions in the zone of weathering. Geochemical equilibrium primary

mineral — secondary mineral — liquid phase is formed only in thin cracks and breaches of minerals, where there it comes to the arousal of secondary products.

4. By their chemical and hydrological character in the crust of weathering the underground waters of Malé Karpaty Mts. granitoides are probably the cause of the total thermodynamic unstability of the contemporary hydromical crust of the weathering of Malé Karpaty Mts. granitoides.

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