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THE STUDY OF SELECTED SYSTEMS "ROCK-WATER" AT LOW TEMPERATURES (4—5 °C)

(Tabs. 6, Figs. 8)

Abstract: In the paper are presented the results of experimental study of leaching of Ca, K, Mg, Na and SiO_2 from samples of crystalline rocks of the High Tatra and Malá Fatra Mts. Releasing of components was followed at low temperature 4—5°C, in various intervals of time 114—202, in some also 7 to 202 days). In some details the results differ from up to present observations, what the authors explain mainly as a consequence of interactions of components released by leaching. These facts are the basis to expressing conclusions on some circumspection in application of knowledge from thermodynamic stability of individual minerals to stability of rocks.

Резюме: В работе представлены результаты экспериментального исследования выщелачивания Ca, K, Mg, Na и SiO_2 из проб кристаллических пород Высоких Татр и Малой Фатры. Освобождение компонентов было исследовано при низкой температуре 4—5 °C в разных промежутках времени (114—202, у некоторых и 7 до 202 дня). Результаты отличаются в некоторых деталях от предыдущих данных, что авторы объясняют прежде всего как следствие интеракций компонентов освобожденных выщелачиванием. Эти факты являются основой для высказания выводов об определенной осторожности в применении знаний из термодинамической стабильности отдельных минералов на стабильность пород.

The data of stability of minerals in relation to water and various water solutions represent important sources of information on the possibilities of formation of the mineral content of groundwaters. According to present-day opinions the mineral content of groundwaters is a result of very complicated processes, taking place in the systems: water-rock — atmosphere. Experimental verification of such complicated system is an uncommonly pretentious task. Some starting point is therefore disintegration of systems into more simple partial systems. Among these partial systems a very important place have relations water — rock with exclusion of the influence of atmosphere and other gases, as CO_2 etc.

In the frame of systematic investigation of stability of minerals we were focused on the experimental study of stability of rock-forming mineral complexes in water at low temperatures 4—5 °C. The impulse to the decision to

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follow these systems was the acute need of theoretical hydrogeochemical investigation, mainly in relation to concrete areas of the West Carpathians.

Selection of samples for the study and their description

The study of stability of rock-forming mineral complexes from the viewpoint of processes of formation of the mineral content of groundwaters was focused on tracing of releasing of some components from these rocks by the action of water at the mentioned low temperatures. In the study the possibilities of the Analytical Department of the Geological Institute of the Faculty of Natural Sciences of the Comenius University (PvFUK) to establish by the method of atomic absorption very low concentrations of some elements (Ca, K, Mg, Na), were used, which were released by the action of water from the rock complex of minerals. Determination of low Cl concentrations was made possible by means of ion-selective electrode. For determination of very low SiO_2 contents the working methods applied so far have been adjusted.

For the study samples of various crystalline rocks from the High Tatra and Malá Fatra areas were used. The first part of experiments was realized as orientational, also the descriptions of samples, including the sites of sampling, are very brief here. The second part of experiments was carried out on defined, detaily petrographically determined and chemically analysed samples (Vondrovic, GÚ SAV). The descriptions of samples and their chemical analyses are mentioned in Tab. 1.

Working approaches

The samples for the study of rock-forming mineral complex stability were crushed in agate pulverizer to analytical fineness (less than 0.056 mm). 1 gram of adjusted sample was then weighed to 100 ml of polyethylene bottles, 100 ml redistilled water were added, the content was thoroughly mixed and after standing of one hour the liquid was poured above the sedimented sample. Such a decantation clearing of samples was repeated still three times in order to remove the finest parts, which could be of disturbing influence in proper analytical works.

After the fourth decantation the samples were placed into a refrigerator with tempered temperature 4—5 °C. After tempering redistilled water 4 °C warm was added to the sample and the whole content was thoroughly mixed. The mixing was repeated always once after three days. Before the established interval elapsed, the samples were not moved at least 7 days, so that also the finest parts should settle and the analytical determinations should not be disturbed.

Analytical determinations of Ca, K, Ma and Na were made directly by suction of the solution into the atom absorption apparatus Perkin Elmer, model 303. The suction device has made possible to take samples without filtration, immediately after they were taken out from the refrigerator, so that after the analysis and mixing it was possible to continue in tracing sample stability for the next period. Under equal conditions also the so called blind experiment was carried out, in which were used the corresponding vessels and redistilled water.

Table 1

Chemical composition of the studied eruptive and metamorphosed rocks of the Malá Fatra Mts.

	1	2	3	4	5	6	7	8	9	10
SiO_2	38.66	64.92	60.49	62.99	65.24	61.41	60.65	57.88	67.97	62.92
TiO_2	3.17	0.96	0.81	1.01	0.62	0.84	0.68	1.26	0.80	0.87
Al_2O_3	14.61	16.92	16.15	14.11	15.36	17.33	15.81	17.52	13.59	16.06
Fe_2O_3	12.93	5.77	5.71	10.41	5.14	5.62	8.26	9.36	5.55	5.67
MnO	0.38	0.07	0.08	0.14	0.06	0.07	0.32	0.16	0.06	0.06
MgO	9.28	1.67	1.65	1.83	1.67	1.45	3.38	4.81	2.56	2.56
CaO	9.47	1.54	3.09	2.27	1.66	2.62	1.71	1.52	1.87	1.22
Na_2O	2.30	3.10	6.51	0.66	2.55	3.87	3.60	0.65	4.75	2.28
K_2O	1.75	2.47	2.26	1.81	4.44	2.85	2.79	2.88	2.08	4.36
Loss by drying	0.89	0.50	0.47	0.67	0.31	0.37	0.63	0.86	0.28	0.33
Loss by annealing	6.69	2.01	2.79	4.13	2.87	3.73	2.08	3.14	0.45	2.72

+ Total iron as Fe_2O_3.
Analytical method: X-ray-fluorescence analyses. Analyst: M. Vondrovic (Geological Institute of the Slovak Academy of Sciences).

Characterization of samples

1. (HMF—4—1/28): Fine-grained (2 mm) distinctly schistose metaamorphibolite (amphibole plagioclase). It is intensively tectonically and subsequently hydrothermally altered. The alterations are documented by the presence of tectonic polishes with chlorite filling, the presence of amphiboles and plagioclases of IInd generation in tectonized zones, of hair veins (up to 1 mm) with filling of hydrothermal carbonates, iron oxides and hydrates and dimming of plagioclases. The product of hydrothermal alteration are also isolated quartz veins.

2. (HMF—4—II 35, 5—37): Intensely mylonitized two-mica granodiorite (plagioclase quartz K-feldspar biotite — muscovite). The product of recrystallization processes are mainly chlorite, light-coloured mica II, quartz II and albite. Characteristic of the rock is the planparallel system of fissures filled up with products of hypergene-hydrothermal alterations: calcite, iron hydrates and oxides and quartz.

3. (HMF—4—III 52—53): Fine-grained (2—3 mm) hydrothermally altered muscovite-biotite granodiorite. The alteration is mainly expressed by bleaching and chloritization of biotite, sericitization and argillitization of plagioclases, the presence of hair veins with filling of quartz II, carbonate, albite. In the rock in accessory amount also apatite, titanite, zircon, ore minerals, iron oxides and hydrates are present.

4. (HMF—23—I 11—12): Fine-grained biotite paragneiss with high content of biotite (15 %). Composition: quartz plagioclase biotite. In the rock are zones of tectonic crushing of mm dimensions, in which intense hydrothermal alteration was manifested.

Its product is chloritization of biotite (50 %), intense decomposition of plagioclases and formation of percolating iron hydrates and oxides.

5. (HMF—23. II/17—18): Medium-coarse-grained (7 mm) pegmatitoid granodiorite with low content of micas. K-feldspars are predominating over acid plagioclases in it. On cleavage cracks of feldspars continuous zones of intense sericitization are developed. Partial chloritization of biotite. In the rock are developed intense kakiritized (crushed) zones with present carbonates and clay minerals.

6. (HMF—23—III/42—44): Kakiritized and hydrothermally altered porphyric biotite granodiorite. Kakiritization is shown mainly in zones of mm thickness — intense crushing mainly of feldspars and quartz or formation of small clusters to hair veins of carbonates and quartz are observed. In the granodiorite mass bleaching of biotite took place — the released Fe hydrates form leakage on intergranulars of minerals.

7. (HMF—42—I/23—25): Garnet-biotite, distinctly preferrentially oriented beaded paragneiss. The essentially represented minerals: plagioclase quartz K-feldspar biotite — muscovite garnet. Characteristic of the rock is only the insignificant extent of secondary alterations 10 %), chloritization of garnet and biotite.

8. (HMF—42—II/48—50): Eyed muscovite-biotite paragneiss with high (20 %) content of micas. Composition: quartz plagioclase biotite muscovite. It is medium-intensely diaphthorized. The alteration is manifested in chloritization of biotite (50 %), sericitization of plagioclases (20 %), deformation and detailed folding, mainly of micaceous layers of O.X — mm mm dimensions.

9. (HMF—42—III/80): Beaded garnet-biotite plagioclase paragneiss. It is a distinctly fresh rock type. Composition: plagioclase, quartz, biotite, garnet. Only insignificant post-crystalline deformation of the mentioned fundamental minerals of rock.

10. (HMF—42—V/102): Medium—grained porphyric (K-feldspars) two-mica granodiorite. The rock underwent pressure alterations- manifested in translations of mineral grains, intense undulosity of quartz, bending of mica leaves. Biotite is partly chloritized, plagioclases are only insignificantly sericitized. Hydrothermal alteration is shown in the presence of hair chlorite and epidote group minerals.

SiO_2 was determined, on the one hand so called dissolved, i. e. a part of the released SiO_2, which passed into the solution, on the other hand so called sorbed, which though was released, but remained sorbed in the solid part of the sample and was determined after dissolving in 2 % solution of Na_2CO_3.

The dissolved SiO_2 was determined in the aliquot part of the sample (solution) after filtering away of the insoluble part, colorimetrically in form of the silicomolybdenum complex. Sorbed SiO_2 was determined from the insoluble part by dissolving in cold state in Na_2CO_3 solution of the mentioned concentration. We have proved that under these conditions SiO_2 from fresh samples, which were not exposed to long-time activity of water, was not released. The carbonate solution with content of dissolved, originally sorbed SiO_2 was then acidulated and the solution was prepared for colorimetrical determination as in the first case.

Chlorides in leaches of some samples were determined by Ing. J. Polakovičová, CSc. by ion-selective electrodes of the firm Radiometer, on the apparatus Radiometer PHM 64. The results of determination of chlorides in the soluble part of samples of the 772 series are presented here (Tab. 2) as orientation only.

The working approach at some samples was adjusted so that the content of components was determined after filtering away of the undecomposed portion by a filter of density "blue strip". In the first series of experiments (Tab. 2) only the Ca contents were traced for a long time as of an element, which is sufficiently analytically sensitive and could provide a picture of the course of stability changes of minerals during the traced period. In further series of experiments were determined all components also in continuous times.

Table 2

Survey of Ca, Cl, Mg, K and Na releasing (mg.1000^{-1} g water) from various samples of High Tatra provenance (d. — number of days of experiment)

Number of exper.	Designation of sample	Ca for			after 193 days			Ca	after filtr. — 214 days						
		46 d.	72 d.	120 d.	Ca	K	Na	214 d.	Ca	Mg	K	Na	pH	Cl
772 a	"blind"	0.01	0.01	0.02	0.04	0.05	0.02	0.01	0.01	0.01	0.01	0.01	5.78	0.62
b	pegmat. granite no. 205	0.37	0.38	0.30	0.42	1.24	0.44	0.50	0.05	0.02	0.87	0.45	6.76	1.56
c	pegmatit. aplite no. 1141	0.39	0.32	0.36	0.44	0.72	0.57	0.56	0.15	0.02	0.55	0.62	6.78	1.58
d	Ridge above Kotly no. 1458	0.42	0.42	0.40	0.48	0.53	0.44	0.51	0.25	0.10	0.58	0.45	6.92	3.59
e	granite, groove between Pach.-Spál.	1.18	1.30	1.47	1.87	0.99	0.51	1.91	0.87	0.16	1.43	0.61	7.31	2.56
f	biot. amph. quartz diorite, Suchý	0.39	0.37	0.34	0.40	1.50	0.72	0.54	0.21	0.18	1.61	0.71	7.20	1.68
g	Račkova dolina valley	0.35	0.26	0.30	0.33	0.49	0.22	0.50	0.15	0.08	0.52	0.41	6.30	2.15
h	Ridge from Harich skala-rock, no. 1021	0.31	0.27	0.26	0.29	1.09	1.55	0.41	0.06	0.03	1.04	0.92	6.62	2.15
i	migmatite, Račková dolina valley	0.83	1.02	1.06	1.25	2.74	0.23	1.47	0.84	0.52	2.83	0.37	7.05	4.73
j	two-mica paragneiss no. 1150	0.09	0.10	0.08	0.03	0.57	0.37	0.06	0.01	0.03	0.56	0.21	6.72	0.94
k	biot. paragneiss Suchý	0.40	0.37	0.33	0.40	2.30	0.45	0.63	0.15	0.15	1.68	0.30	7.02	1.34
l	granodiorite no. 1026	0.23	0.24	0.23	0.34	0.59	0.26	0.35	0.03	0.03	0.42	0.28	6.87	1.56

Continuation of Tab. 2

Number of exper.	Designation of sample	Ca for			after 193 days			Ca	after filtration — 214 days					
		46 d.	72 d.	120 d.	Ca	K	Na	214 d.	Ca	Mg	K	Na	pH	Cl
772 m	Kamenistá dol.-valley Rokľa, no. 1150	0.31	0.31	0.34	0.35	1.01	0.28	0.49	0.05	0.03	0.75	0.30	6.70	1.18
n	garnets, no. 1403	0.34	0.31	0.31	0.32	0.65	0.27	0.53	0.05	0.02	0.49	0.31	6.25	3.58
o	pegmatite with pink feldspars, no. 7666	0.17	0.13	0.17	0.17	0.69	0.20	0.25	0.01	0.02	0.48	0.23	6.30	0.98
p	Menguš. dol. valley, no. 1310	2.83	2.70	4.60	6.78	0.67	0.73	7.45	4.92	0.18	0.98	0.33	7.02	2.16
r	light-coloured aplite, pegmat. granite Magura	0.20	0.20	0.23	0.25	0.85	0.38	0.33	0.01	0.01	0.52	0.27	6.55	1.56
s	microcl. hybrid granite Magura	0.29	0.23	0.30	0.37	0.29	0.17	0.48	0.03	0.02	0.26	0.15	6.25	4.57
t	Kamenistá dol. valley, no. 1069	0.42	0.34	0.34	0.48	0.28	0.11	0.57	0.06	0.02	0.38	0.18	6.52	0.62
u	tuffs from Poprad. pleso-lake, no. 1448	0.17	0.15	0.15	0.21	0.57	0.37	0.31	0.04	0.02	0.55	0.34	6.64	1.30
v	granite, no. 1459	0.15	0.14	0.12	0.17	0.99	0.18	0.24	0.05	0.02	0.75	0.30	6.65	1.17
x	ridge, east of Smrek, no. 1154	0.10	0.11	0.09	0.11	1.28	0.06	0.14	0.02	0.01	1.02	0.18	6.84	1.36
y	aplite, light-coloured granite	2.92	2.76	4.84	7.31	0.35	0.85	9.23	6.19	0.06	0.33	0.35	7.40	3.43
z	ridge to Bystrá, no. 1053	0.24	0.25	0.23	0.24	1.52	0.11	0.38	0.05	0.14	1.34	0.21	6.86	1.18

Table 3

Controlling and complementary determinations of some results from Tab. 2 (details in text, data in mg.1000^{-1} g water)

Number of exper.	Designation of sample	Repeated exper.	after 114 days				after 175 days				after 202 days			
			Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
795 a	biot. amph. qu. diorite, Suchý	772 f	0.60	0.61	1.21	0.33	0.82	0.68	1.32	0.26	0.62	0.69	1.20	0.25
b	migmatite, Rač. dol. valley	772 i	1.29	0.79	2.62	0.29								
c	ditto		1.40	0.76	3.15	0.32	1.85	1.35	3.90	0.40				
d	ditto		1.30	0.75	2.74	0.24	1.65	0.96	3.57	0.30	1.35	1,40	3.16	0.31
e	two-mica paragn. Kamenistá	772 j	0.13	0.35	0.62	0.09								
f	ditto		0.13	0.36	0.70	0.14	0.14	0.34	0.62	0.14				
g	ditto		0.15	0.39	0.70	0.14	0.14	0.37	0.70	0.16	0.11	0.41	0.68	0.17
h	biot. paragn. Suchý	772 k	0.52	0.51	1.34	0.22	0.65	0.53	1.66	0.27	0.43	0.58	1.37	0.26
i	granodiorite Menguš dol.-val. no. 1310		6.80	0.24	1.21	0.30								
j	ditto		7.55	0.18	1.02	0.34	6.50	6.28	1.50	0.44				
k	ditto		7.10	0.13	0.73	0.47	7.20	0.35	1.55	0.57	7,20	0.33	1.40	0.54
l	pegmat. granite Magura	772 r	0.45	0.12	1.21	0.69	0.50	0.11	1.27	0.78	0.35	0.14	1.10	0.76
m	migmatite Magura		0.43	0.61	2.05	0.73	6.60	0.64	2.32	0.72	0.33	0.61	1.99	0.68
n	tuffite-Baranec		10.65	4.50	1.80	0.46	10.30	4.60	2.32	0.50	11,83	7.90	2.08	0.46

The established data about stability of the complex of rock-forming minerals, the third series samples among one another on the other hand (Tab. 3 — samples at temperature 4—5 °C for the given time, are summarized in Tabs. 2 to 4. The analytical data were recalculated to an equal basis — mg metal to 1000 grammes of water.

Controlling experiments were carried out for the first series of samples on the one hand (Tabs. 2 and 4, experiments 772 f — 795 a, 772 i — 795 b to d, 772 j — 795 e to g, 772 k — 795 h, 772 p — 795 i to k, 772 r — 795 l) and in the third series samples among one another on the other hand (Tab. 3 — samples 795 b do d, 795 e to g, 795 i to k). Regarding to the type of the investigated material and own processes, which are directing releasing of components from minerals by the action of water, the obtained results can be considered as satisfactory.

The analytical characteristics for individual components:

a) method of atomic absorption

	proof limit	precision of measurement
calcium	0.002 μg . ml^{-1}	1.47 ± 0.03 mg . ml^{-1}
		0.63 ± 0.03 mg . ml^{-1}
magnesium	0.0003 μg . ml^{-1}	0.13 ± 0.01 mg . ml^{-1}
sodium	0.002 μg . ml^{-1}	0.27 ± 0.1 mg . ml^{-1}
potassium	0.005 μg . ml^{-1}	2.83 ± 0.02 mg . ml^{-1}
		0.48 ± 0.01 mg . ml^{-1}

b) determination of chlorides (Ing. J. Polakovičová, CSc.)
proof limit 0.5 mg Cl^{-} . l^{-1}
precision of measurement
± 0.15 mg for contents less than 2.5 mg . l^{-1}
± 0.11 mg for contents more than 2.5 mg . l^{-1}

c) determination of SiO_2

soluble SiO_2	boundary of proof	0.11 mg . l^{-1}
	precision of measurement	2.44 ± 0.05 mg . l^{-1}
		3.36 ± 0.04 mg . l^{-1}
sorb. SiO_2	proof limit 0.18 mg . l^{-1}	
	precision of measurement	7.74 ± 1.23 mg . l^{-1}

Review of results

The results, mentioned in Tab. 2, regarding to the beginning of solution of the whole problem, are necessary to consider as tentative. Their goal was to verify mainly time dimension of experiments, as so far we have had no experience with similar study.

On their basis was then compiled a new set of experiments (Tabs. 3 to 5) focused on controlling some results of the first series of samples on the one hand, on investigating the dependence of changes of leaching of the examined components from drilling samples, coming from various depths characterized petrographically in detail, on the other hand.

Table 4

Survey of Ca, Mg, K and Na releasing from drilling samples of the Malá Fatra area (data in mg.1000^{-1} g water)

Number of exper.	Sample	after 114 days				after 175 days				after 202 days			
		Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
794 a	„blind"	0	0	0	0	0	0	0	0	0	0	0	0
b	HMF—4—I	11.0	1.04	0.71	0.68	1.52	0.96	3.57	0.30	1.35	1.45	3.24	0.30
c	HMF—4—II	11.7	1.41	0.70	0.14	13.90	2.12	0.62	0.13	17.30	2.25	0.68	0.14
d	HMF—4—III	9.00	0.30	0.71	0.63	13.25	0.34	0.72	0.54	16.60	0.36	0.66	0.50
e	HMF—23—I	14.00	0.82	0.69	0.37	0.13	0.42	0.76	0.13	0.10	0.43	0.62	0.13
f	HMF—23—II	13.00	0.46	0.56	0.27	14.02	0.60	0.62	0.28	17.30	0.60	0.61	0.28
g	HMF—23—III	8.45	0.61	0.60	0.46	10.80	0.74	0.60	0.43	13.50	0.83	0.53	0.42
h	HMF—42—I	0.50	0.68	0.73	0.38	0.70	0.63	0.70	0.45	0.47	0.79	2.33	2.65
i	HMF—42—II	0.35	1.28	0.73	0.27	6.40	0.31	1.55	0.40	6.60	0.32	1.35	0.41
j	HMF—42—III	0.68	0.58	0.71	0.53	0.80	0.65	1.27	0.57	0.69	0.79	1.13	0.56
k	HMF—42—V	0.35	0.70	0.70	0.42	0.40	0.76	0.80	0.45	0.27	0.80	0.68	0.44

Table 5

Survey of releasing of dissolved SiO_2 from drilling samples of the Malá Fatra area (data in $mg.l^{-1}$ g sample and 1000 g water)

Sample	7 days	36 days	74 days	114 days	175 days	202 days
HMF—4—I	0.80	1.09	1.20	2.94	3.32	6.04
HMF—4—II	0.58	1.10	1.37	2.94	4.00	6.94
HMF—4—III	0.52	1.08	1.12	2.42	4.40	7.24
HMF—23—I	0.44	1.25	1.38	2.20	4.64	9.00
HMF—23—II	0.66	1.18	1.42	2.54	3.90	7.00
HMF—23—III	0.56	1.38	1.52	2.96	4.24	9.00
HMF—42—I	0.64	1.09	1.22	5.50	7.60	14.18
HMF—42—II	0.64	1.08	1.39	3.94	8.04	14.03
HMF—42—III	0.70	1.08	1.21	3.30	8.30	12.60
HMF—42—V	0.82	1.09	1.27	3.30	5.40	10.70

Table 6

Survey of releasing of sorptional SiO_2 from drilling of the Malá Fatra area (data in $mg.l^{-1}$ g sample)

Sample	7 days	36 days	74 days	114 days	175 days	202 days
HMF—4—I	0	0.02	0.16	0.30	1.30	1.66
HMF—4—II	0	0.00X	0.15	0.42	0.79	1.64
HMF—4—III	0	0.00X	0.15	0.52	0.92	1.18
HMF—23—I	0	0.00X	0.16	0.15	1.31	1.14
HMF—23—II	0	0.00X	0.15	0.41	0.70	0.62
HMF—23—III	0	0.00X	0.16	0.10	0.98	0.96
HMF—42—I	0	0.00X	0.16	0.33	0.92	2.20
HMF—42—II	0	0.00X	0.15	0.25	0.90	2.08
HMF—42—III	0	0.00X	0.16	0.10	0.75	2.14
HMF—42—V	0	0.00X	0.16	0.21	0.99	2.10

Discussion of results

As it was mentioned, the results of Tab. 2 are necessary to consider as orientational only, however, also in spite of that some conclusions can be drawn from them.

The prevailing part of the investigated samples showed certain stability in releasing of the main traced element-calcium, as for example, the curves corresponding to experiment no. 772 b and j in Fig. 1 illustrate. Representatives of samples, in which a slight increasing of calcium in leaches took place with time, were samples from experiments 772 e and i. On the contrary, in samples 772 p and 772 y with proceeding time of action a very distinct enrichment of the solution in calcium took place. The correctness of the data was confirmed also by controlling experiments (795 k, Tab. 3).

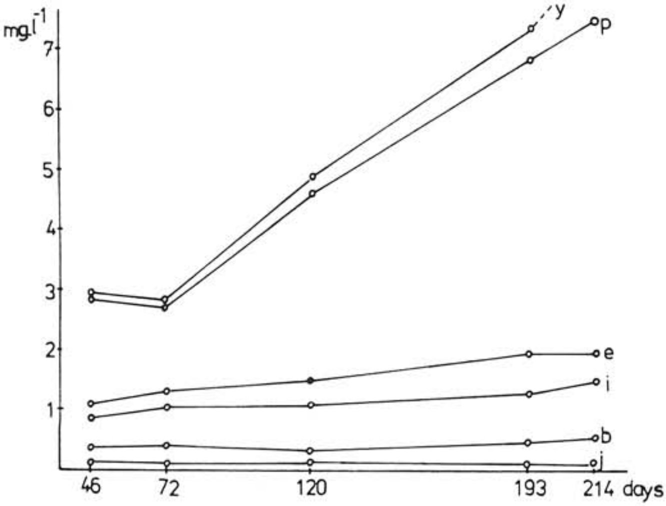

Fig. 1. Graphical representation of the time course of Ca releasing from some samples of experiment 772.

As remarkable in Tab. 2 is necessary to mention the content of traced elements in leaches after filtration (after 214 days lasting experiment). Mainly in calcium, which was determined in equal time intervals, its distinct decrease after filtration by paper filter can be observed. The sorptional capacities of paper stock are obviously so intensive, that for purposes of further experimenting as well as for natural waters the paper filtration materials cannot be used at all.

Catching of other traced elements by paper stock of the filter is already not so intensive. For example, in Na deviations are very little, in K somewhat higher. Chlorides were determined also in the portion filtered away and when some results were controlled, it is not possible to use them in the discussion. For information we mention at least the survey of controlling determinations of Cl: For the couple 795 c — 772 i the results were 3.95 — 4.73 mg . 1^{-1}, and for the couple 795 f — 772 j: 1.06 — 0.94 mg.l^{-1} and for the couple 795 j — 772 p: 1.09 — 0.94 mg.l^{-1} chlorides.

The results of Tab. 3 had to confirm, to what an extent the established data can be relied upon, regarding to the applied working approach on the one hand, to proper analytical determinations on the other hand.

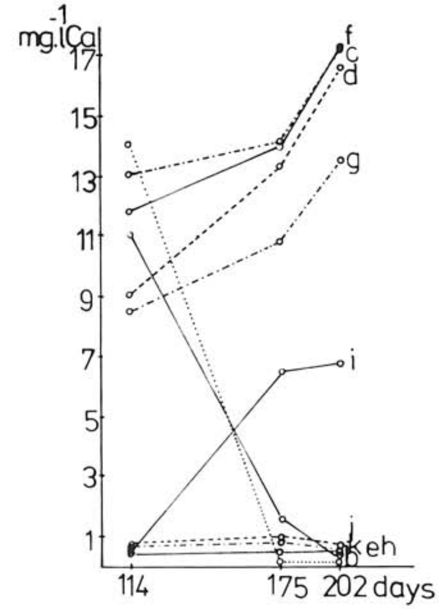

Fig. 2. Graphical representation of Ca releasing from drilling samples of the Malá Fatra area (experiment 794).

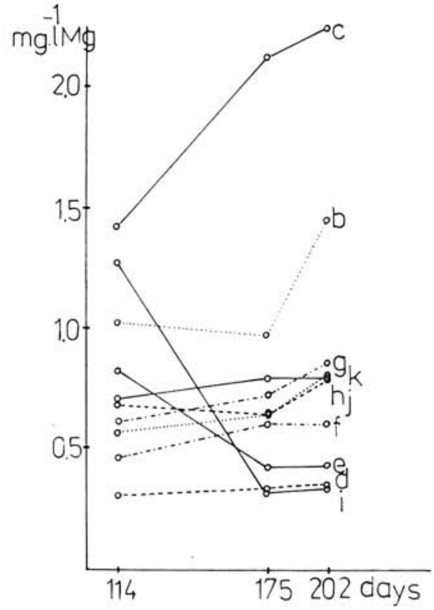

Fig. 3. Graphical representation of the time course of Mg releasing from drilling samples (experiment 794).

Certain positive establishing is the result of experiment 795 n, in which material designated as tuffite was used (Doc. RNDr. Š. Kahan, CSc.). Releasing of potassium, mainly of magnesium and calcium is very high. It cannot be excluded, that the higher content of these components comes to solution from so called typical magmatites, which did not undergo the metamorphic cycle. This concerns the mentioned tuffite, further granite (772 e), migmatite (772 i, 795 b—d), granodiorite (772 p, 795 i to k), aplite (772 y). It will be necessary to confirm these suppositions by further experiments.

For the purpose of comparison, the results concentrated in Tabs. 4 and 5 are of the greatest importance, which concern drilling samples. The course of releasing of individual components and pH change with time are for clearness expressed graphically in Figs. 2 to 8.

According to theoretical presumptions it could be expected that releasing of the individual components from the investigated samples will increase with time. It is so in the majority of the samples, with the exception of calcium from samples HMF-23-I (experiment 794 e) and HMF-4-I (experiment 794 b), of magnesium, mainly samples HMF-42-II (experiment 794 i) and sodium of

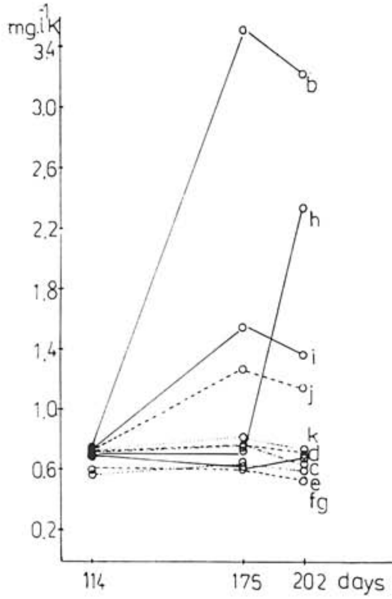

Fig. 4. Graphical representation of the time course of releasing of potassium from drilling samples (experiment 794).

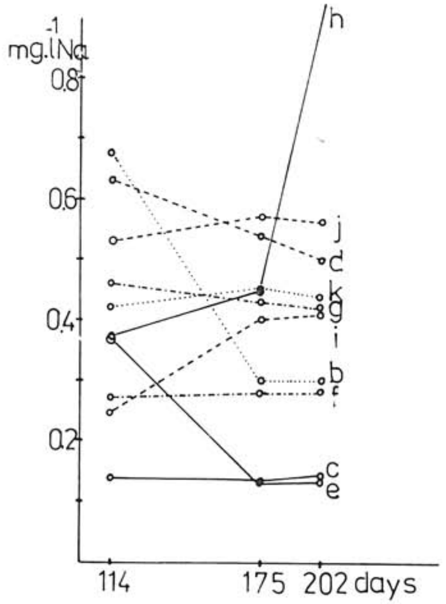

Fig. 5. Graphical representation of the time course of releasing of sodium from drilling samples (experiment 794).

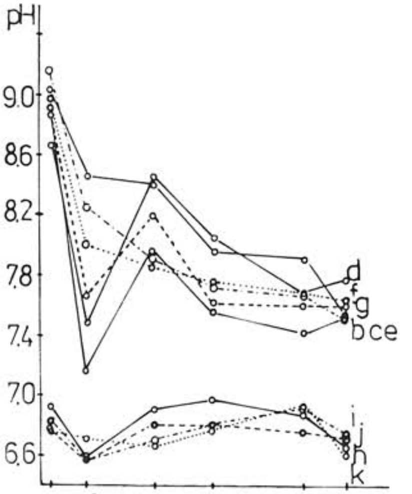

Fig. 6. Graphical representation of the time course of p^H changes of the suspension of samples.

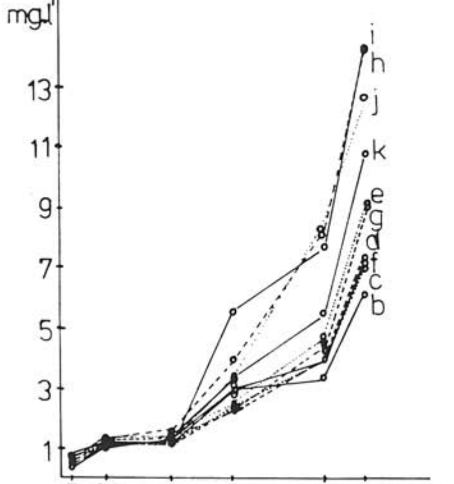

Fig. 7. Graphical representation of the time course of releasing of dissolved SiO_2.

samples HMF-4-I (experiment 794 b), HMF-23-I (experiment 794 e), HMF-4-III experiment 794 d).

In the quoted samples (0 to 114 days) relatively high releasing took place in the first period, in the further period (114 to 175 days) the content of the released components was reduced, obviously in consequence of their reaction with some further components in reaction environment. It is remarkable that together with calcium also sodium takes part in these reactions, at least in the most extreme cases. In case of sample HMF-4-I (experiment 794 b) the decrease of Ca and Na is to a certain extent compensated by enormous increase of potassium content in the solution.

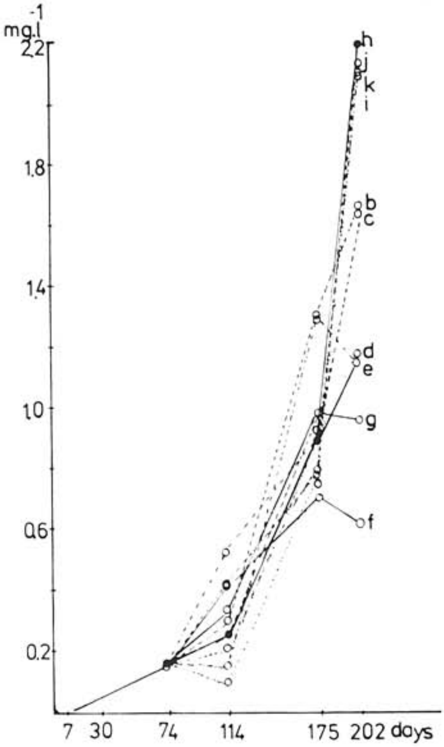

Fig. 8. Graphical representation of the time course of releasing of so called sorptional SiO_2.

According to petrographical description Ca and Na decreased in leaches in case of highly weathered samples from near-surface beds of drillings. They are samples, in which simultaneously sorbed SiO_2 distinctly increased, what could confirm the above mentioned presumption about reactions between released components. This is also evidenced by the course of potassium releasing (Fig. 4). Potassium has according to the graph a very clear tendency to enter the reaction, because practically in all samples except HMF-42-I (experiment 794 h), after some time its content in water leaches sunk after beginning increase. It is interesting to add, that also the sample with extraordinary behaviour of potassium (HMF-42-I) is highly weathered according to petrographical analysis.

The content of released SiO_2 from samples by the action of water increased in all samples in the course of time. The Figs. 7 and 8 permit only relative correlations because the substance of experiments itself does not make possible to convert the so called sorbed SiO_2 to 1000 grammes of water. The absolute values of SiO_2 (in case of soluble SiO_2 must be multiplied by 10^{-1} regarding to the performed experiments with 100 g water) are in shorter time intervals more favourable for dissolved SiO_2, for longer time, on the contrary, for sorbed SiO_2.

When clearing up theoretically the phenomena connected with releasing of SiO_2 in form of so called sorbed SiO_2, a certain possibility to explain their substance is also shown in a way that part of it can be derived from easy-decomposing silicates, which are releasing SiO_2 by the action of 2 % solution of Na_2CO_3. These silicates, if present, must be a product of reactions in situ, what, however, would also only support the opinion, that components released from silicates by the action of water can immediately react among one another.

Particular remarks deserves the pH change of suspension of samples in the course of time. In all cases in the course of time total decrease of pH values takes place, when also theoretically we expected a contrary phenomenon effect. In some samples (HMF-4-I, HMF-23-II, HMF-23-III, HMF-42-I, HMF-42-II and HMF-42-III) temporarily after 36 days, even very distinct sinking of pH was evident. The substance of these phenomena, mainly of the last mentioned, has been unclear so far.

Conclusion

The experimental study of some systems rock — water, which we performed, has brought some remarkable results. Their theoretical treatment requires a longer time, in spite of that, however, already now it is possible to express the conclusion, that in a complicated heterogeneous system of minerals, which natural rocks represent, besides simple solubility of minerals, shown in releasing of some components, a mutual reaction of the released components with mineral surfaces (exchange of ions) or reaction of the released components among one another can take place already in so called microdimensions, given, for example, by the capacity of our experiments. The more distinctly such processes can be manifested in macrodimensions, represented by rock systems and so complicate the theoretical explanation of formation of the mineral content of groundwaters. This, however, simultaneously forces to some circumspection in application of information from thermodynamic stability of individual minerals to the stability of rocks, e.g.with regard to the contents of soluble SiO_2, Na^+ and pH.

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