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TO THE METHOD OF GEOCHEMICAL CHARACTERIZATION OF ROCKS IN REGIONAL INVESTIGATION

(Tab.2, Figs. 2)

Abstract: In the present time the investigation of geochemical background is carried out in main types of rocks in the region of the Bohemian Massif. On the whole about 3500 samples have to be treated.

The data about the contents of selected elements are prevailingly obtained by multielement, physical-chemical methods (X-ray fluorescence analysis, optical emission spectrography, γ-spectrometry, atomic absorption spectrophotometry and instrumental neutron activation analysis).

From the obtained analytical data in the first place the fundamental statistical parameters are calculated for groups of rocks. The changes in chemical properties of the observed rocks are then established in spatial dependence and the total error of treatment of samples by the method of hierarchic analysis of variance.

Резюме: В современности, в области Чешского массива производят исследования геохимического фона у главных типов пород. Всего должно быть обработанных около 3500 проб.

Данные по содержаниям отобранных элементов получают преимущественно многоэлементными, физическо-химическими методами (анализом рентгеновой флуоресценции, оптической эмиссийной спектрографией, γ-спектрометрией, атомной абсорпционной спектрофотометрией и инструментальным анализом нейтроновой активации).

Из полученных аналитических данных высчислены для совокупностей пород прежде всего основные статистические параметры. Методом иерархического анализа рассеяния определяют потом изменения в хемизме обследованных пород в пространственном отношении и ошибка в целом обработки пород.

Introduction

In the last years regional geochemical investigation is getting to the foreground of interest on a state-wide scale. It provides the fundamental data for a whole series of scientific disciplines. In the study of the living environment it makes possible to distinguish the primary contents of individual elements in the rock environment from anomalies of secondary origin due to human activity. On data of the primary contents also the hydrogeochemical, biogeochemical, pedogeochemical, geohygienic and equally also metallogenetic and deposit investigations are based.

Until now regional geochemical investigation was carried out systematically only in the region of the Bohemian Massif by a team of members of the Central Geological Institute in Prague. Regarding to the fact that a similar investigation should be included also in the plan of fundamental investigation in the Slovak Socialist Republic (SSR) this work can serve as information in this way and applied method of up to present regional geochemical works in the Czech Socialist Republic (ČSR).

The main object of investigation is the study of distribution and establishing of the background contents of selected elements in the fundamental litho-

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stratigraphical units of the Bohemian Massif. The principal requirement in solving of this task is a uniform plan of taking samples for all types of rocks, thoroughful homogenization, uniform method of analytical treatment and expression of results. (The way of cartographic representation of results in form of geochemical maps has not been unambiguously solved so far and is a subject of further study).

Determination of the geochemical background for the individual elements in rocks is dealt with in many foreign and Czechoslovak works. So far, however, they were prevailingly only works specifically directed or carried out in relatively small and isolated areas (e.g. Klomínský, 1963, 1969; Vejnar, 1969; 1971; Čadková, 1971a, 1971b; Čadek et al., 1974). In these works, however, selection of the traced elements was not uniform, not the same analytical methods were applied and analytical determinations were not carried out in equal laboratories. With regard to the fact that the contents of some observed elements are very low in common, unmineralized rocks (often varying at the detection limit of the analytical method), the results can be rendered more difficult by considerable and inconstant analytical error.

Common characterization

In projecting of regional geochemical investigation it was necessary to set out from analytical capacities, which were available, on the one hand and from the degree of geological investigation of the area under study on the other hand (Čadková, Jakeš, 1974).

Regarding to the limited capacity of chemical laboratories on the whole about 100 lithostratigraphical units or groups of roughly 30—50 samples each were distinguished in the region of all the Bohemian Massif (Čadková, Jakeš, Mrázek, 1975). In order to distinguish these units with sufficient reliability, as the basis was chosen the geological general map 1 : 200 000 for its uniform conception.

The plan of sampling was compiled in a way that in the frame of the distinguished units it was possible with a minimum number of samples to express not only the variance of contents of chemical components in spatial dependence but also the so called error of sample treatment.

Applied method of sampling

Regarding to unequal representation of rock types in the mapped units the asymmetric model of hierarchic sampling was chosen. This system of sampling for geochemical investigation in large regions was described by Miesch (1967a ,1976b, 1972) and Connor et al. (1972).

The plan of sampling sets out from the following assumption: In each lithostratigraphical unit the contents of elements in samples are varying in certain range of concentration around the value of the average. In the magnitude of this total variance always several factors take part, which influence distribution of the given element to an unequal extent. The total variance is thus the addition of so called partial variance.

For each lithostratigraphical unit it is necessary in cooperation with the mapping geologist and/or also with the petrographer to establish, which factors could have been effective with regard to distribution of elements in the rocks. The plan of sampling must be compiled so that with suitable grouping of samples it would be possible to trace and express mathematically the influence of these factors.

In order to make determination of element content dispersion, caused by treatment of samples (i.e. with sampling proper in the field and manipulation with the sample before and during analytical treatment) possible, from each locality two samples of macroscopically equal character are taken, from places maximum 2 m distant from each other.

In all types of rocks essentially samples are taken from facies, which are mostly spread in the given stratigraphic unit. So we avoid rocks, which are anomalous from the viewpoint of chemical properties in the area under consideration (e.g. samples near ore mineralization, near coal seams etc.).

Fresh, unweathered and homogeneous samples of weight 5 kg are, if possible, taken from surficial outcrops where all the studied rocks are exposed to equal conditions near the surface. So as far in the studied area a greater number of localities, suitable for sampling, are available, we select of them the required amount by random selection. In case of lacking outcrops the groups are completed with samples from boreholes; drill cores of wider diameter are halved at length and each half is further treated as a particular sample.

Analytical treatment

In selection of analytical methods it was necessary to take into account several requirements: these methods should be sufficiently precise with relatively little error of detection, sufficiently sensitive, relatively cheap and also recording the whole group of the observed elements in all types of rocks.

For establishing of all elements the complex of physical-chemical methods was selected: optical emission spectrography (chemical laboratories of the Central Geological Institute-Prague), X-ray fluorescence analysis (Geological Exploration Ostrava, establishment Brno), γ — spectrometry (Geophysics — Brno), atomic absorption spectrophotometry (Central Geological Institute — Prague) and instrumental neutron activation analysis (Geoindustria Prague, establishment Černošice). Only at several few elements (e.g. Cl, F, P) individual analytical methods are applied; these determinations are carried out in the chemical laboratories of the Central Geological Institute (ÚÚG) — Prague.

In the following table (Tab. 1) the elements observed so far with the applied analytical method and detection limit are mentioned.

Perspectively the extension of this scale by macroelements is intended (X-ray fluorescence analysis-ÚÚG-Prague).

Evaluation of analytical data

The analytical data obtained from the individual groups are treated mathematically. The result are mainly the fundamental statistical parameters, which characterize the groups of rocks: the arithmetic or geometric mean

Table 1

Applied analytical methods of the observed elements

Element	Method of determination	Detection limit (in ppm)
Ag	X-ray fluorescence analysis	0,06
As	X-ray fluorescence analysis	5
Au	instrumental neutron activation anal.	0,05
B	optical emission spectrography	10
Ba	X-ray fluorescence analysis	50
Be	optical emission spectrography	1
$C_{carb.}$	coulometry	100
Ce	instrumental neutron activation anal.	1
Cl	ionic selective electrode	100
Cr	X-ray fluorescence analysis	5
Cs	instrumental neutron activation anal.	1
Cu	optical emission spectrography	1
Eu	instrumental neutron activation anal.	0,1
F	pyrohydrolysis	100
Ga	optical emission spectrography	1
Hf	instrumental neutron activation anal.	1
Hg	atomic absorption spectrophotometry	0,05
La	instrumental neutron activation anal.	1
Li	atomic absorption spectrophotometry	2
Lu	instrumental neutron activation anal.	0,1
Mo	X-ray fluorescence analysis	1
Nb	X-ray fluorescence analysis	5
Ni	X-ray fluorescence analysis	5
P	spectrophotometry	20
Pb	optical emission spectrography	1
Rb	X-ray fluorescence analysis	5
S	X-ray fluorescence analysis	100
Sb	instrumental neutron activation anal.	1
Sc	instrumental neutron activation anal.	0,1
Sm	instrumental neutron activation anal.	0,1
Sn	X-ray fluorescence analysis	1
Sr	X-ray fluorescence analysis	5
Ta	instrumental neutron activation anal.	1
Tb	instrumental neutron activation anal.	1
Th	γ — spectrometry	1
Ti	X-ray fluorescence analysis	60
U	γ — spectrometry	1
V	X-ray fluorescence analysis	10
Y	X-ray fluorescence analysis	5
Yb	instrumental neutron activation analysis	1
Zn	X-ray fluorescence analysis	5
Zr	X-ray fluorescence analysis	5

M (depending whether the type of distribution of the given element is normal or lognormal) and standard deviation D.

By means of the standard deviation it is also possible to establish the expected range of concentration values in certain interval around the mean. (AM — arithmetic mean, AD — arithmetic standard deviation.)
in conc. range AM± AD are lying nearly 68 % cases in the group,
in conc. range AM±2AD are lying nearly 95 % cases in the group,
in conc. range AM±3AD are lying nearly 99 % cases in the group.
(AM — arithmetic mean, AD — arithmetic standard deviation.)

In case of lognormal type of distribution the above mentioned intervals are given by the relations:

nearly 68 % cases are lying in conc. range $\frac{GM}{GD}$ to GMxGD,
nearly 95 % cases are lying in conc. range $\frac{GM}{GD^2}$ to $GMxGD^2$,
nearly 99 % cases are lying in conc. range $\frac{GM}{GD^3}$ to $GMxGD^3$.
(GM — geometric mean, GD — geometric standard deviation.)

These data are very important from the viewpoint of anomality limit detection; as anomalies usually members are considered, the values of which exceed the upper limit for the range of 95 % cases, distinctly anomalous contents exceed the upper limit for the range of 99 % cases.

According to orientational testing of the distribution character in several groups and according to mathematical tests, carried oua in the frame of former works with similar purpose (e.g. Čadková, 1971 b; Lepka, 1973; Čadek et al., 1974) it may be supposed that distribution of trace elements is closer to the lognormal type, distribution of major elements is rather of normal type.

The analytical data are then treated further by the method of hierarchic analysis of variance (further HAR). This type of analysis was applied to geology first by Olson, Potter (1954), mathematical expression was presented in the work by Krumbein, Slack (1956). For regional geochemical (background) investigation application of HAR was proposed by Miesch (1972).

The hierarchic analysis of variance makes possible valuation of the obtained data at several levels, i.e. in dependence on spatial and manipulation factors; each level expresses the effectiveness of certain factor on distribution of the given element in the group. It sets out from the assumption that the concentration of the chemical component in the sample is a function of the average for the whole group, then the function of deviations found out in the area studied and of the function of treatment error. In general, this relation may be expressed:

$$x = \mu + \alpha + \beta + \gamma + \vartheta + \varepsilon$$

where x is the amount of given component in individual sample,
μ the average value for the whole group,
the values α, β, γ and ϑ represent the deviation from total average at various levels in the frame of the given unit,
ε is the deviation caused by treatment of sample.

In a similar way the dispersion of concentration values of the chemical component for the whole group may be expressed by common relation (Beuss, Grigorjan, 1975):

$$s_x^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2 + s_\delta^2 + s_\varepsilon^2$$

where s_x^2 is variance of contents in the frame of the whole group,
s_α^2, s_β^2, s_γ^2 and s_δ^2 represent variance values around the average at various grades of subordination (levels),
s_ε^2 is variance caused by treatment of sample; it includes also objective and subjective analytical error.

In the variance analysis proper computers IBM 370/135 (Bohemian Energetic Works — Prague) on one hand, programming calculator HP — 67 (ÚÚG — Prague) on the other hand, were applied. The programme for the calculator in Fortran IV language was compiled by workers of the mathematitc centre of Geoindustria — Prague, for calculator HP-67 an own programme HAR was prepared.

Example of application

As a concrete example I mention treatment of Lower Carboniferous sediments:

The Lower Carboniferous in the Bohemian Massif belongs to marine deposits and is developed in flysch (Culm) facies. There is mainly alternation of light-grey to dark-grey greywackes, siltstones and shales. The pelites are often thin — leaflike disintegrating; the matrix is mostly argillaceous with admixture of chlorite and sericite, rarely carbonate. The greywackes

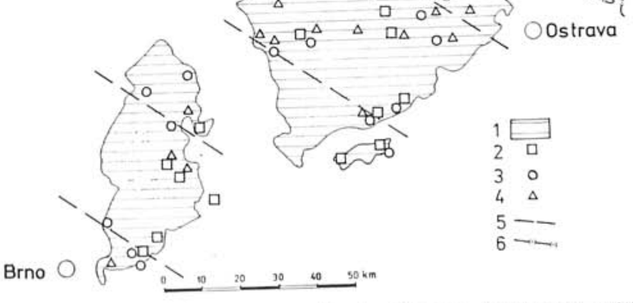

Fig. 1. Schematic map of areas of Lower Carboniferous sediments with plotted sites of sampling. 1 — Lower Carboniferous sediments; 2 — conglomerates; 3 — greywackes; 4 — pelites (shales); 5 — profile lines; 6 — state frontier.

are fine-to medium-grained, with variable admixture of micas. The conglomerates are more rare than psammites and pelites; they are also mostly light- to dark — grey, fine- grained, sometimes with admixture of greywacke material.

Fig. 1 shows a schematic map of the area of Lower Carboniferous sediments in the Bohemian Massif (area of the Nízke Jeseník and Drahanská vrchovina Mts.) with indicated sites of taking samples of the observed lithological types. In the place of each symbol at least one couple of samples was taken. In order to trace the changes in distribution of elements in dependence on stratigraphy, in each of both areas two lines of profiles were established to record the as most complete as possible vertical sequence of beds in the frame of the given unit (roughly transversal profile through the sedimentary basin); in sampling dispersion to the sides of the profile line proper in the frame of the given stratigraphic unit maximum 10 km is possible.

The method of further treatment is shown on the example of Lower Carboniferous pelites. Grouping of samples in this group for application of HAR method is visible from Fig. 2, the results of mathematic treatment of data of the contents of selected elements are summarized in Tab. 2. Besides the fundamental statistical parameters also the values of detection ratio are mentioned here for individual elements, which expresses the degree of reliability of the calculated statistical data.

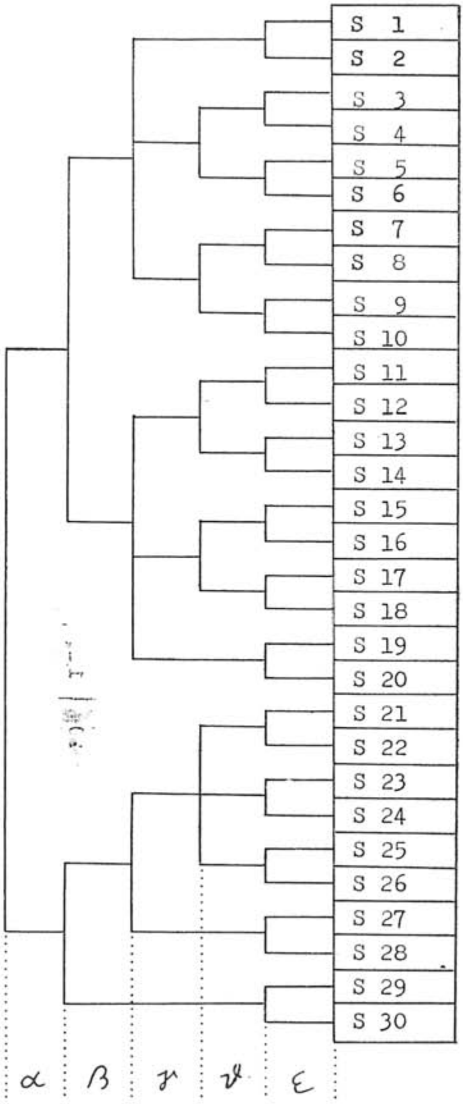

Fig. 2. Scheme of mutual relation of samples in the group of Lower Carboniferous pelites, S 1-S 30 — number of samples in the group; α—ε— designation of levels of mutual dependence of samples.

Table 2

Fundamental statistical values of selected elements in the group of Lower Carboniferous pelites

Element	Type of distribution	Detection ratio	M (ppm)	D	Expected range (in ppm)		Variance in % at level				
					v 68 %	v 95 %	α	β	γ	ϑ	ε
Ag	L	2 : 30	<0,06	—	—	—	—	—	—	—	—
As	L	27 : 30	11	2,16	5 — 24	<5 — 52	46,5	0,0	3,1	11,0	39,4
B	L	30 : 30	68	1,18	57 — 80	49 — 94	0,0	14,4	47,2	1,0	37,4
Ba	L	30 : 30	552	1,19	465 — 656	391 — 780	0,0	17,3	32,6	6,3	43,8
Be	L	30 : 30	6	1,38	4 — 8	3 — 11	0,0	0,0	0,0	48,5	51,5
Cr	L	30 : 30	119	1,20	99 — 142	83 — 170	0,0	0,0	37,4	18,1	44,5
Cu	L	30 : 30	52	1,40	37 — 72	26 — 120	2,0	0,0	25,7	30,8	41,5
Ga	L	30 : 30	20	1,23	16 — 25	13 — 30	8,9	0,0	0,0	37,9	53,2
Hg	L	5 : 30	<0,05	—	—	—	—	—	—	—	—
Mo	L	30 : 30	2	1,29	2 — 3	1 — 4	0,0	33,9	18,4	11,1	36,6
Li	L	30 : 30	29	1,13	26 — 33	23 — 37	0,0	7,6	0,0	70,5	21,9
Nb	L	30 : 30	15	1,16	13 — 18	11 — 20	11,7	0,0	0,0	17,4	70,9
Ni	L	30 : 30	56	1,25	45 — 71	36 — 88	0,0	0,0	58,0	20,8	21,2
Pb	L	30 : 30	24	1,29	18 — 31	14 — 40	0,0	0,0	41,6	0,0	58,4
Rb	L	30 : 30	153	1,30	118 — 199	91 — 258	0,0	0,0	74,7	3,5	21,8
Sn	L	30 : 30	10	1,16	9 — 12	7 — 14	0,0	55,1	9,2	0,0	35,7
Sr	L	30 : 30	99	1,24	80 — 122	65 — 150	5,5	0,0	40,5	0,0	54,0
Th	L	30 : 30	13	1,27	10 — 17	8 — 21	0,0	0,0	48,3	2,3	49,3
Ti	L	30 : 30	5240	1,15	4560 — 6000	3080 — 6890	0,0	27,1	26,7	0,5	45,7
U	L	30 : 30	4	1,81	2 — 7	1 — 12	6,4	0,0	18,2	24,9	50,5
V	L	30 : 30	135	1,27	106 — 171	84 — 217	13,4	0,0	50,7	0,1	35,8
Y	L	29 : 30	24	1,64	15 — 39	9 — 64	0,0	0,0	0,0	16,3	83,7
Zn	L	30 : 30	103	1,19	83 — 123	72 — 147	5,5	15,8	0,0	0,4	78,3
Zr	L	30 : 30	185	1,33	140 — 245	105 — 325	0,0	15,7	0,0	56,5	27,8

Fundamental statistical values of selected elements in the group of Lower Carboniferous pelites.
Type of distribution: L — lognormal; detection ratio — the first number indicates the number of samples in the group, with content of the given element higher than the detection limit, the second number indicates the total number of analysed samples;

M — average (for type of distribution L — geometric mean);
D — standard deviation (for type of distribution L — geometric standard deviation).

From the results obtained by HAR method is also mentioned in the table, which part (in %) from total variance falls to individual levels ($\alpha-\varepsilon$).

The data of variance may be interpreted roughly as follows:

From the observed elements only As displays dependence of contents on competence to certain area (level α). In the frame of the areas differences in contents in samples, taken from various profiles (level β), are manifested in Sn only. The dependence on the stratigraphic position (level γ) is shown in Rb and to a less extent also in B, Ni, Th and V. At the level of small distances (level ϑ), i.e. between the individual localities variability in Li and Zr, less then in Be contents is evident. In Nb, Pb, Y and Zn the greater dispersion of contents values is mainly caused by treatment of samples (i. e. by manipulation during and after sampling in the field- level ε).

With comparison of the tables of statistical values for more groups the data on changes in distribution of the individual elements in dependence on stratigraphy and on the lithological type of sediments may be obtained.

Conclusion

The presented paper provides data on the method of study of the geochemical background in rocks, carried out at present in the region of the Bohemian Massif. In the course of several years the contents of 35 — 40 selected elements in about 100 lithostratigraphical groups (main rock types) are going to be established with application of prevailingly physical- chemical analytical methods.

The data obtained are treated mathematically, by common statistical method on the one hand and by the method of hierarchic analysis of variance on the other hand.

As an example of practical application the brief results of the study of Lower Carboniferous pelites are mentioned in the conclusion.

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