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# STATISTICAL ANALYSIS OF VARIABILITY OF URANIUM CONTENTS IN ACCESSORY APATITE OF THE CRYSTALLINE ROCKS OF THE WEST CARPATHIANS

(Tabs. 1—8; Figs. 1—2)

**Abstract:** The homogeneity grade and types of the uranium distribution were followed by the fission track method on the level of individual grains of 41 samples of accessory apatite from granitoid, metamorphic and volcanic rocks of the West Carpathians. The statistical measure as the average values of uranium concentrations, variability, skewness and the form of distribution curves, were used for characterization of distributions. The shown fact is that a type of element distribution and its form is probably stronger joined with genetic conditions than such universal statistical measurement as, e.g. an average concentration.

**Резюме:** Методом треков следили за степенью гомогенности и типом распределения урана на уровне отдельных зерн в 41 пробе акцессорического апатита из гранитоидных, метаморфизованных и вулканических пород Западных Карпат. Статистические меры, какими являются средние величины концентрации урана, вариабильность и вид кривых распределения применяли для характеристики распределения. Работа свидетельствует что тип распределения элемента и его вид наверно более сильно связан с генетическими условиями как такая универсальная статистическая мера какой является напр. средняя концентрация.

## Introduction

The majority of analytical methods determines concentrations of elements from samples which were homogenised, for instance, by solution or by melting. By this type of analysis we can determine the element concentration which may have the different forms of occurrence in the original sample. The resultant concentration, obtained by the analytical procedure is, however, the weighed arithmetical mean of all forms of element occurrence in a given phase. This fact is outstanding in the case of uranium, which can be isomorphically bound in a structure of minerals, it can be only kept in them, to occur in the grain borders and often these forms occur commonly. But even on the individual mineral grains concentrations of the individual forms of uranium occurrences by the fission track method can be distinguished and analyzed. Similarly as the X-ray-microanalyzer on other elements, this method enables thus not only selection, or the control of the analyzed form of an element, but also tracing of the element on individual grain level. This kind of study can bring valuable informations about the variability of element contents from the individual mineral grains of a sample contents from the individual mineral grains of a sample and it can obtain quantitative data about such important parameter as the homogeneity.

This study informs about the result, obtained from a grain collection of accessory apatite from 41 samples of granitoid, metamorphic and volcanic

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rocks. Nearly 5900 grains of the accessory apatite were analysed from these samples. The accessory apatite was chosen for this kind of study for various reasons. First, it is one of the most occurred accessory minerals in these rocks. Second, as L. L. Ames [1960] demonstrated, uranium is isomorphically bound in the apatite structure; it is not clear, whether it changes calcium [Z. L. Altschuler et al., 1958], or, whether it creates  $\text{UO}_4$  tetraheders, as was proposed by D. McConnell [1973].

### *Analytical procedure*

100—300 grains were chosen from the concentrate of apatite grains by binocular magnifier. No characteristic properties of grains were preferred as e.g. colour, shape etc. for the selection of grains. From some samples there were chosen two fractions in granularity classes 0.10—0.20 mm and 0.25 — 0.50 mm. In such case, from the finer fraction only the whole idiomorphic grains were chosen, so as to exclude a possible grain contamination of this class with fragments of coarser crystals. Spontaneous tracks were annealed from the grains (cca 5 hours at 500 °C). The grains were then irradiated by an appropriate dose of thermal neutrons in nuclear reactor IBJ in Swierk [Poland]. After irradiation, the grains were cast in synthetic resin, their inner areas were uncovered and polished to a high optical lustre by standard procedure. This procedure excludes any contamination of the analyzed material.

*Conditions of track etching.* The apatite grains were etched in 1 % solution of  $\text{HNO}_3$  during 4,5 minutes for all samples, at  $20 \pm 1$  °C temperature. Glass uranium standards were etched in 4 % HF — 5 minutes at the same temperature.

*Establishing of the integral dose of thermal neutrons.* The size of the dose was established by standard uranium glasses. In these glasses the uranium content is precisely known and they were irradiated together with apatite samples [R. L. Fleisched — P. B. Price, 1964].

*Establishment of track density* (i. e. number of tracks to unit of area). Tracks were counted on the individual grains of samples in transcendent light in immersion oil at magnification 800 x. Because only equally dispersed tracks on the analyzed area, or its part, were counted in the individual grains, the tracks from inclusions rich in uranium (mainly zircons) were not counted in the total density of the tracks. For technical reasons, it was not possible to count the tracks on the whole etched area of the grain. Therefore, the appropriate part of the grain for counting the tracks was chosen, which, with its density represented the whole area. This condition is easy to fulfil, because in the great majority of samples the uranium distribution on the individual grains is homogeneous and from the view-point of the used analytical method, the concentration gradient is not evident. Only in some samples there is an inhomogenous uranium distribution on the individual grains. Since these inhomogeneities are systematic as far as possible, the tracks were counted in both different zones of concentrations. In such cases, two measurements are from one grain.

*Calculation of uranium concentration.* For calculation of uranium concentration in apatites was used G. A. Wagner's (1969) formula:

$$C_{g/t} = (7.4 \pm 0.7) \cdot 10^{10} \cdot p_i/n \quad (1)$$

where  $p_i$  is the number of tracks on  $\text{cm}^2$ ,  $n$  = the integral dose of thermal neutrons.

*Calculations of errors.* The average error is expressed in this study at the confidence interval for the mean at 95 % confidence level [G. S. Koch — R. F. Link, 1970]. That is because in measurements of that type it is necessary to take into regard the homogeneity of a set as well as the number of measurements. Hence:

$$\text{C.I.M.} = \frac{s}{\sqrt{n}} t_{95\%} \quad (2)$$

where  $s$  = the standard deviation of the average,  $n$  = the number of measurements,  $t_{95\%}$  = the table value of the Student factor.

The error of the coefficient of variation represents one standard deviation of average, obtained by repeated measurements.

*Elaboration of experimental data.* By the help of the measured densities of the induced tracks, which in fact represent the uranium concentration, the histograms were constructed. Further, for each sample represented by the set of grains were calculated the arithmetical mean, the geometrical mean, the standard deviation, the skewness and the coefficient of variation. Since a left-sided asymmetry of distributions was expected, the original data were transformed to the corresponding values of decade logarithms. From these, again, were constructed histograms and calculated the mentioned statistical parameters. For testing agreement of empirical distributions with the alternative normal or lognormal distribution model there was used  $\chi^2$  test according to the formula:

$$\chi^2 = \sum_{i=1}^K \frac{(O_i - T_i)^2}{T_i} \quad (3)$$

where  $O_i$  = the measured frequency,  $T_i$  = the theoretical frequency. Approximation curves of the lognormal or normal distributions, calculated according to S. Đurovič (1957) are drawn in histograms for direct judgement of the agreement of the empiric distribution forms with the accepted model. Variability of the examined sets of accessory apatite is expressed by the variation coefficient:

$$C = \frac{s}{x} \quad (4)$$

where  $s$  = the standard deviation,  $x$  = the arithmetical mean.

The skewness used for valuation of the distribution symmetries, was calculated as a ratio of the third central moment and the third power of the standard deviation.

## Results of the study

The calculated parameters for the studied distributions of uranium in the accessory apatite are given in Tables 1—4. The results in the tables are given in  $\text{g.t}^{-1}$ . The tables are constructed according to the individual types of rocks, within the framework of the individual types; the samples are listed according to the increasing variation coefficient. Transformed values into logarithms are not given. In Tables 5 — 8 the results of the test for agreement of distributions are given.

Histograms, presented in this work were constructed from the original measured values, i. e. the number of tracks on  $\text{cm}^2$ .

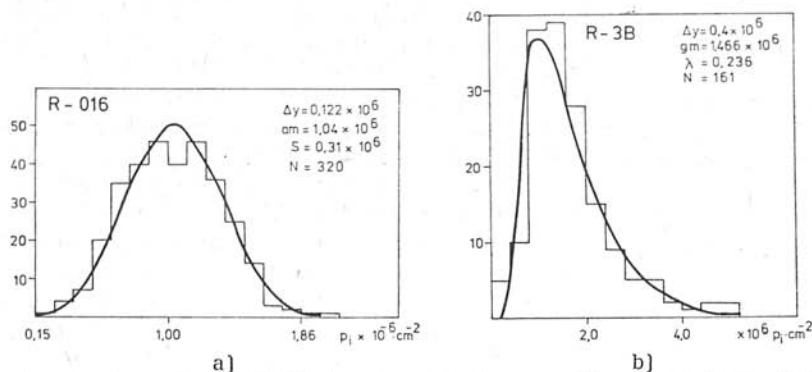


Fig. 1. Types of uranium distributions in accessory apatite. a) uranium distribution in apatite from granite of the crystalline of veporides. This distribution can be approximated by the normal distribution on the level of significance  $\alpha = 0.01$ , b) uranium distribution in accessory apatite from the paleosome part of migmatite. This distribution can be approximated by the lognormal distribution on the significance level  $\alpha = 0.01$ . The drawn approximative curves (according to S. Ďurovič, 1957) indicate a good agreement of the observed empiric distributions with the accepted statistical model.  $\Delta y$  = interval,  $\lambda$  = standard deviation of the logarithms of the concentrations.

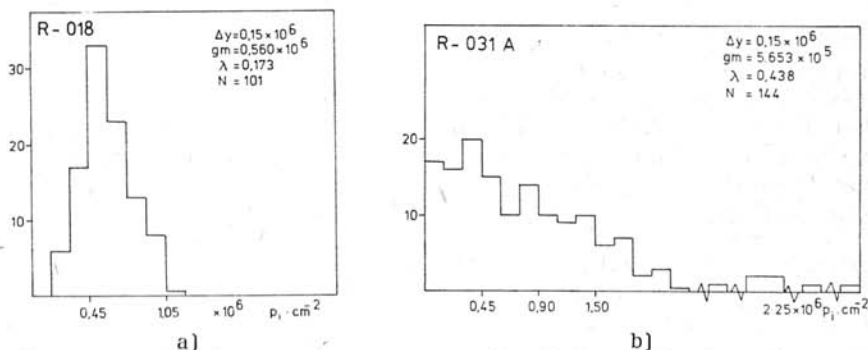


Fig. 2. Uranium distribution in accessory apatite. Both samples have the same average concentration of uranium. a) this empirical distribution agrees with both distributions; b) this empirical distribution does not agree with any alternative distribution.

Table 1

Uranium concentration in accessory apatite from granitoid rocks. Basic statistical data.

| No. of samples | m  | gm | am          | s  | min.        | max.         | C               | $\gamma_1$ |
|----------------|----|----|-------------|----|-------------|--------------|-----------------|------------|
| R — 016        | 47 | 44 | 47 $\pm$ 2  | 14 | 10 $\pm$ 2  | 108 $\pm$ 17 | 0.30 $\pm$ 0.02 | 0.020      |
| R — 050        | 24 | 22 | 24 $\pm$ 1  | 8  | 2 $\pm$ 1   | 50 $\pm$ 6   | 0.33 $\pm$ 0.02 | 0.095      |
| R — 20         | 21 | 19 | 21 $\pm$ 1  | 8  | 2 $\pm$ 0.2 | 54 $\pm$ 22  | 0.38 $\pm$ 0.02 | 0.043      |
| R — 25         | 17 | 17 | 19 $\pm$ 1  | 7  | 5 $\pm$ 1   | 37 $\pm$ 6   | 0.38 $\pm$ 0.02 | 0.440      |
| R — 40         | 18 | 22 | 24 $\pm$ 2  | 10 | 3 $\pm$ 0.8 | 55 $\pm$ 6   | 0.40 $\pm$ 0.02 | 0.004      |
| R — 018        | 27 | 25 | 27 $\pm$ 2  | 11 | 9 $\pm$ 2   | 71 $\pm$ 10  | 0.41 $\pm$ 0.02 | 0.300      |
| R — 3          | 33 | 33 | 37 $\pm$ 2  | 15 | 5 $\pm$ 0.6 | 78 $\pm$ 9   | 0.43 $\pm$ 0.02 | 0.290      |
| R — 032A       | 23 | 23 | 25 $\pm$ 1  | 11 | 5 $\pm$ 1   | 78 $\pm$ 8   | 0.44 $\pm$ 0.02 | 1.370      |
| R — 29         | 18 | 24 | 27 $\pm$ 2  | 12 | 4 $\pm$ 1   | 57 $\pm$ 6   | 0.45 $\pm$ 0.02 | 0.360      |
| R — 019        | 30 | 31 | 41 $\pm$ 3  | 21 | 6 $\pm$ 2   | 125 $\pm$ 17 | 0.50 $\pm$ 0.02 | 1.70       |
| R — 032        | 18 | 24 | 27 $\pm$ 2  | 14 | 2 $\pm$ 1   | 93 $\pm$ 8   | 0.50 $\pm$ 0.03 | 1.58       |
| R — 26         | —  | 23 | 26 $\pm$ 2  | 13 | 5 $\pm$ 1   | 57 $\pm$ 11  | 0.50 $\pm$ 0.03 | —          |
| R — 28         | 18 | 19 | 21 $\pm$ 2  | 12 | 4 $\pm$ 0.4 | 92 $\pm$ 11  | 0.55 $\pm$ 0.03 | 1.21       |
| R — 22         | 13 | 13 | 15 $\pm$ 1  | 9  | 2 $\pm$ 0.5 | 49 $\pm$ 13  | 0.58 $\pm$ 0.03 | 1.66       |
| R — 28         | 20 | 22 | 34 $\pm$ 4  | 20 | 3 $\pm$ 3   | 156 $\pm$ 18 | 0.59 $\pm$ 0.03 | 1.57       |
| R — 38         | 11 | 16 | 18 $\pm$ 2  | 11 | 1 $\pm$ 0.2 | 64 $\pm$ 10  | 0.59 $\pm$ 0.03 | 1.52       |
| R — 57         | 22 | 23 | 28 $\pm$ 2  | 17 | 3 $\pm$ 0.4 | 116 $\pm$ 30 | 0.59 $\pm$ 0.03 | 0.76       |
| R — 015        | 18 | 26 | 27 $\pm$ 2  | 16 | 4 $\pm$ 1.6 | 118 $\pm$ 16 | 0.61 $\pm$ 0.03 | 2.02       |
| R — 014        | 45 | 53 | 67 $\pm$ 12 | 44 | 5 $\pm$ 0.8 | 219 $\pm$ 26 | 0.66 $\pm$ 0.03 | 1.10       |
| R — 2          | 25 | 35 | 41 $\pm$ 7  | 29 | 11 $\pm$ 3  | 170 $\pm$ 25 | 0.70 $\pm$ 0.04 | 1.90       |
| R — 017        | 9  | 13 | 15 $\pm$ 1  | 11 | 2 $\pm$ 0.3 | 62 $\pm$ 13  | 0.70 $\pm$ 0.04 | 2.18       |
| R — 020        | 12 | 19 | 23 $\pm$ 3  | 16 | 2 $\pm$ 0.5 | 120 $\pm$ 42 | 0.70 $\pm$ 0.04 | 0.03       |
| R — 23         | 15 | 15 | 20 $\pm$ 3  | 14 | 2 $\pm$ 0.5 | 85 $\pm$ 19  | 0.72 $\pm$ 0.04 | 0.44       |
| R — 47         | 4  | 11 | 15 $\pm$ 2  | 12 | 1 $\pm$ 0.4 | 64 $\pm$ 13  | 0.79 $\pm$ 0.04 | 0.92       |

Explanations: m — modulus, gm — geometrical mean, am — arithmetical mean, s — the standard deviation, min. — minimal concentration of uranium, measured on one grain, max. — maximum uranium concentration measured on one grain, C — variation coefficient,  $\gamma$  — the skewness of measured distribution. These signs are the same for the tables 1 — 4.

Table 2.

Uranium concentration in apatites from paragneisses. The basic statistical data. A — grain class of apatites from 0.1 to 0.2 mm.

| No. of sample | m       | gm | am         | s  | min.           | max.         | C               | $\gamma_1$ |
|---------------|---------|----|------------|----|----------------|--------------|-----------------|------------|
| R — 027       | 50      | 46 | 50 $\pm$ 3 | 17 | 6 $\pm$ 2      | 92 $\pm$ 10  | 0.35 $\pm$ 0.02 | —0.19      |
| R — 051       | 26      | 26 | 26 $\pm$ 1 | 9  | 3 $\pm$ 0.5    | 73 $\pm$ 13  | 0.36 $\pm$ 0.02 | 0.05       |
| R — 049       | 27      | 24 | 27 $\pm$ 1 | 10 | 0.1 $\pm$ 0.01 | 79 $\pm$ 10  | 0.39 $\pm$ 0.02 | 0.46       |
| R — 027A      | —       | 36 | 40 $\pm$ 6 | 16 | 12 $\pm$ 3     | 65 $\pm$ 7   | 0.40 $\pm$ 0.02 | —          |
| R — 030       | 39      | 35 | 39 $\pm$ 4 | 18 | 0.3 $\pm$ 0.3  | 114 $\pm$ 13 | 0.47 $\pm$ 0.03 | 1.14       |
| R — 031A      | 12      | 18 | 27 $\pm$ 2 | 21 | 0.3 $\pm$ 0.3  | 114 $\pm$ 13 | 0.78 $\pm$ 0.04 | 0.55       |
| R — 031       | bimodal | 10 | 17 $\pm$ 2 | 16 | 0.8 $\pm$ 0.4  | 71 $\pm$ 9   | 0.95 $\pm$ 0.05 | 0.61       |

Table 3.

Uranium concentration in apatites from migmatites

| No. of sample | m  | gm | am         | s  | min.          | max.         | C               | $\gamma_1$ |
|---------------|----|----|------------|----|---------------|--------------|-----------------|------------|
| R — 3B        | 16 | 22 | 25 $\pm$ 2 | 14 | 2 $\pm$ 0.4   | 80 $\pm$ 20  | 0.55 $\pm$ 0.03 | 1.36       |
| R — 2B        | 16 | 22 | 25 $\pm$ 2 | 14 | 4 $\pm$ 1.2   | 120 $\pm$ 20 | 0.56 $\pm$ 0.03 | 1.38       |
| R — 1B        | 23 | 36 | 44 $\pm$ 4 | 25 | 3 $\pm$ 0.2   | 138 $\pm$ 17 | 0.58 $\pm$ 0.03 | 0.50       |
| R — 1A        | 16 | 23 | 27 $\pm$ 2 | 16 | 1.4 $\pm$ 0.2 | 124 $\pm$ 18 | 0.58 $\pm$ 0.03 | 0.96       |
| R — 2A        | 20 | 20 | 25 $\pm$ 4 | 17 | 1.4 $\pm$ 0.3 | 106 $\pm$ 16 | 0.70 $\pm$ 0.04 | 1.35       |
| R — 3A        | 30 | 36 | 48 $\pm$ 6 | 42 | 7 $\pm$ 1.1   | 185 $\pm$ 53 | 0.87 $\pm$ 0.04 | 1.55       |

The basic statistical data. A — apatite from the paleosome part of migmatite, B — apatite from the paleosome part of migmatite, B — apatite from the neosome part of migmatite.

Table 4.

Uranium concentration in apatites of volcanic rocks. The basic statistical data.

| No. of sample | m  | gm | am         | s | min.        | max.       | C               | $\gamma_1$ |
|---------------|----|----|------------|---|-------------|------------|-----------------|------------|
| R — 008       | 14 | 14 | 14 $\pm$ 1 | 4 | 4 $\pm$ 0.5 | 28 $\pm$ 4 | 0.30 $\pm$ 0.02 | 0.72       |
| R — 009       | 8  | 8  | 8 $\pm$ 1  | 3 | 3 $\pm$ 1   | 15 $\pm$ 2 | 0.32 $\pm$ 0.02 | 0.48       |
| R — 010       | 14 | 14 | 14 $\pm$ 1 | 5 | 4 $\pm$ 1   | 47 $\pm$ 5 | 0.35 $\pm$ 0.02 | 1.65       |
| R — 011       | 7  | 7  | 7 $\pm$ 1  | 3 | 3 $\pm$ 1   | 21 $\pm$ 3 | 0.40 $\pm$ 0.02 | 1.90       |

Similarly, all the statistical parameters were calculated from the original values, thus in Tabs 1—4 small differences can occur in the calculated values of variation coefficient and the mentioned values of arithmetical mean and the standard deviation already expressed in the uranium concentration.

### Discussion

#### A. Distribution of trace elements in minerals and rocks.

Establishment of the new geochemical law by L. H. Ahrens (1954) that the concentration of a trace element in rocks or minerals is lognormally distributed, spread a live discussion. Although the law was modified later on, several important conclusions followed for the geochemical study. The most important is that one, that from a certain view-point, it is not decisive to know the absolute concentration of an element and to know the form of its distribution where there is coded the character of the geochemical process causing the accumulation of the trace elements in rocks or minerals. However, simultaneously it was clear that the interpretation of element distributions is, from the geochemical point of view, complicated not only by influences, connected with the origination of the object and with its later existence (R. L. Miller — E. D. Goldberg, 1955) but also, what

Table 5

Results of the  $\chi^2$  test on agreement of distributions. Uranium distribution in apatites from the granitoid rocks. Empirical distributions were tested against the alternative normal or lognormal distribution. Distributions were tested on the significance level  $\alpha = 0.01$ .

| No. of sample  | Number of observations  | Number of intervals                                    | Number of degrees of freedom | $\chi^2$ | Type of distribution |
|--|-------------------------|--|------------------------------|----------|----------------------|
| Core mountains   |                         |  |                              |          |                      |
| R — 3  | 105                     | 7  | 1                            | 4.41     | lognormal            |
|  |                         | 11   | 4                            | 2.10     | normal               |
| R — 20   | 106                     | 10   | 4                            | 5.67     | normal               |
| R — 22   | 131                     | 5  | 1                            | 2.25     | lognormal            |
| R — 23   | 86                      | 7  | 1                            | 4.66     | lognormal            |
| not conform with neither of the examined distributions |                         |  |                              |          |                      |
| R — 24   | 90                      | 8  | 2                            | 1.16     | lognormal            |
| R — 25   | 70                      | 9  | 3                            | 4.10     | normal               |
|  |                         | 9  | 2                            | 3.66     | lognormal            |
| R — 38   | 98                      | 8  | 3                            | 4.83     | normal               |
| R — 40   | 80                      | 8  | 1                            | 3.32     | lognormal            |
|  | 88                      |  | 3                            | 10.50    | lognormal            |
| not conform with neither of the examined distributions |                         |  |                              |          |                      |
| R — 020  | 104                     |  |                              |          |                      |
| Veporides  |                         |  |                              |          |                      |
| R — 2  | 50<br>few observations  | 5  | 1                            | 1.50     | lognormal            |
| R — 26   |                         |  |                              |          |                      |
| R — 28   | 116                     | 7  | 2                            | 4.50     | lognormal            |
| R — 29   | 106                     | 9  | 3                            | 6.02     | lognormal            |
| not conform with neither of the examined distributions |                         |  |                              |          |                      |
| R — 57   | 155<br>few observations |  |                              |          |                      |
| R — 014  |                         |  |                              |          |                      |
| R — 015  | 176                     | 13   | 4                            | 2.57     | lognormal            |
| R — 016  | 321                     | 16   | 8                            | 8.21     | normal               |
| not conform with neither of the examined distributions |                         |  |                              |          |                      |
| R — 017  | 285                     | 7  | 3                            | 7.78     | normal               |
| R — 018  | 101                     | 9  | 4                            | 3.57     | lognormal            |
|  | 101                     | 9  | 3                            | 10.05    | lognormal            |
| R — 019  | 181                     |  |                              |          |                      |
| R — 020  | 104                     | not conform with neither of the examined distributions |                              |          |                      |
| R — 032  | 182                     |  |                              |          |                      |
| R — 032A   | 180                     | 9  | 2                            | 4.17     | lognormal            |
| R — 050  | 170                     | 12   | 4                            | 2.25     | normal               |

is seldom taken into account by such studies, by the selection of samples, by the method of analysis and its accuracy [J. R. Butler, 1964].

Already the first semiquantitative analysis of Ahren's data [R. L. Miller — E. D. Goldberg, 1955] and later, the accurate quantitative test, carried out by A. B. Vistelius [1960] have demonstrated that in the ma-

Table 6

The results of the  $\chi^2$  test on agreement of distributions. Uranium distribution in apatites from paragneisses.

| No. of sample | Number of observations | Number of intervals                                    | Number of degrees of freedom | $\chi^2$ | Type of distribution |
|---------------|------------------------|--|------------------------------|----------|----------------------|
| R — 027       | 188                    | 12   | 5                            | 2.85     | normal               |
| R — 027A      | few observations       |  |                              |          |                      |
| R — 030       | 107                    | 10   | 4                            | 12.00    | lognormal            |
| R — 031       | bimodal distribution   |  |                              |          |                      |
| R — 031A      | 144                    | not conform with neither of the examined distributions |                              |          |                      |
| R — 049       | 250                    | 13   | 7                            | 7.54     | normal               |
| R — 051       | 225                    | 13   | 4                            | 9.76     | normal               |

Table 7

The results of the  $\chi^2$  test on agreement of distributions. Uranium distribution in apatites from migmatites. A — apatite from the paleosome part, B — apatite from the neosome part.

| No. of sample | Number of observations | Number of intervals                                    | Number of degrees of freedom | $\chi^2$ | Type of distribution |
|---------------|------------------------|--|------------------------------|----------|----------------------|
| R—1A          | 207                    | 9  | 3                            | 7.61     | lognormal            |
| R—1B          | 123                    | not conform with neither of the examined distributions |                              |          |                      |
| R—2A          | 84                     | 7  | 1                            | 3.49     | lognormal            |
| R—2B          | 165                    | not conform with neither of the examined distributions |                              |          |                      |
| R—3A          | 175                    |  |                              |          |                      |
| R—3B          | 161                    | 9  | 2                            | 4.43     | lognormal            |

Table 8

The results of the  $\chi^2$  test in agreement with distributions. Uranium distribution in apatite of volcanic rocks.

| No. of sample | Number of observations | Number of intervals                                    | Number of degrees of freedom | $\chi^2$ | Type of distribution |
|---------------|------------------------|--|------------------------------|----------|----------------------|
| R—008         | 134                    | 12   | 4                            | 8.07     | normal               |
|               | 134                    | 12   | 6                            | 9.42     | lognormal            |
| R—009         | 94                     | 11   | 4                            | 2.97     | normal               |
|               | 94                     | 10   | 5                            | 1.94     | lognormal            |
| R—010         | 200                    | 13   | 4                            | 9.60     | lognormal            |
| R—011         | 138                    | not conform with neither of the examined distributions |                              |          |                      |



majority of cases on a high degree of certainty the hypothesis about the lognormal distribution of trace elements cannot be accepted nor refused. This is probably caused by the fact that the elements in a geochemical process are not distributed by some simple function (R. L. Miller — E. D. Goldberg, 1955) or that these complications are caused by the geochemical evolution of the examined objects. But that fact is incontestable — nearly without exception, all the mentioned distributions of trace elements in minerals and rocks are evidently positively skewed, what means that the modulus of distribution is postponed in the direction to the lower values of concentrations and the arithmetical mean to the higher ones. Till now, two schemes appeared for the explanation of such skewed distributions, by which can be explained their genesis. These schemes lead to different consequences. The first one, which explains the genesis of the lognormal distribution leads to the creation of only one population which is lognormal and occurs independently in the whole analyzed body as well as in its small part.

The possibility of origination of the skewed but also the lognormal distributions demonstrated by a different way A. B. Vistelius (1960). According to him, the geochemical processes in a given narrow separated grade of geochemical evolution give concentrations of elements under the conditions of the central limit theorem. By joining of the individual evolutionary grades of the geochemical process we can obtain positively the skewed distributions with the presumption that the function of weight of compound values of the normal distribution of a certain evolutionary grade is given by a series of not increasing values. The basic difference of this scheme from the lognormal one is evident — the distributions of a certain grade of the geochemical process are in accordance with the normal law.

Although A. C. Oertel (1969a, b) proved that under the conditions of a closed system the lognormal distribution cannot be generated, the presumption about the lognormal distribution of trace elements is often preferred in geochemistry.

Recently, G. I. Menaker (1978) has mathematically elaborated the models of distribution functions of elements. He started from the presumption that the behaviour of trace elements can be described by the equations of the classical ideal gas. This access enabled to construct theoretical models of the distribution of trace elements in which the form of distribution curves depends on their concentrations. For trace elements, the author considers as the best approximation the lognormal law. On the other hand, for increasing concentrations of elements correspond the right-sided asymmetrical distributions. Thus, the known reality was proved that with the increasing contents of the element its distribution becomes right-asymmetrical (L. Ahrens, 1963). But from the geochemical point of view the fact that very small parts of the examined systems can be exactly approximated by the normal distribution law is significant, what means, that the „local hypothesis” of A. B. Vistelius (1960) is theoretically proved.

#### *B. Uranium distribution in the accessory apatite of crystalline rocks*

The used analytical method and the analysis procedure grain by grain exclude to a great extent the influences which can change the parameters

of uranium distributions in the accessory apatites. The only sort of mineral from a sample of small volume (cca 10 kg) was analyzed. The uranium concentration was measured which we supposed to be isomorphically bound in the apatite structure. At last, because the analyses procedure enables it, the analytical error was kept approximately at the same level (cca 10 — 15% on the individual grains).

From results, given in Tables 1—8 can be seen that the samples are mutually different in all parameters which may be quantified or which were used for their characterization. The samples are mutually different by the average uranium concentrations, by variability of uranium concentration within the framework of one grain and among the grains they differ in their skewness and in the form of distribution. For all samples statistics of the normal distribution was used but, as can be seen, the majority of the distribution is asymmetrical. Therefore some measures are in fact innatural measures; these questions will be discussed in the next part.

a. *Uranium distributions on the individual apatite grains.* Uranium in apatites is most often dispersed on the whole area of the analyzed grain or its part. On the scale of the used method the concentration gradient is not evident. We suppose that these tracks are caused by uranium isomorphically bound in the apatite structure. In some samples (from migmatites) there occur grains, in which the homogeneity is reached only within the framework of a certain area but not of the whole grain. The character of these inhomogeneities is typical and systematically repeated: the margins of the grains have lesser concentrations as the center of the grain. Similar features of inhomogeneity were found, for example by B. L. Gulson — T. E. Krogh [1975].

A further form of uranium occurrence in apatites is its bond to inclusions rich in uranium. From this view-point, the most significant ones are the inclusions of zircons. It is characteristic that since apatite from granulites, migmatites and paragneisses contain many mineral inclusions, in apatites of volcanic rocks no mineral inclusions, except for the gas-fluid bubbles were observed.

Other forms of uranium occurrences in individual grains have no importance.

b. *Uranium concentrations in apatites.* The average contents can be partially deformed, because the distribution curves are often asymmetrical and do not always agree with normal or lognormal distributions. As was shown by G. S. Koch — R. F. Link [1970], if the variation coefficient is lower than 1 (which condition was fulfilled in our case), then the estimation of the usual arithmetical mean and for clear lognormal distributions is effective to more than 90%.

Average uranium concentrations in apatites are generally low and vary in a quite narrow interval from 7 to 67 ppm. The concentrations obtained are very similar to those described by J. Burchart [1972] from apatite of granitoid and metamorphic rocks from the crystalline of the Tatra Mts. and metamorphic rocks from the crystalline of the Tatra Mts. and also from the crystalline from the Alps, as described by G. A. Wagner and C. M. Reimer [1972]. 50% of samples from granitoid rocks and 46% of all analyzed samples are concentration in the interval from 20 ppm to

30 ppm U. The highest concentration of uranium has the apatite from granite [Hrončok type] — 67 ppm U [sample No. R-014].

Samples from migmatites and paragneisses do not show differences in uranium concentration with respect to apatite from granitoid rocks. As for migmatites from Nízke Tatry Mts., uranium concentration in apatite from the paleosome and neosome parts of the migmatite are in two cases different, in one case they are in agreement. Accessory apatite from volcanic rocks is the poorest one in uranium. In Table 1 are also shown maximum and minimum uranium concentrations, found with the individual grains of one sample. As is seen from the table, the differences in concentrations are really great. Although these anomalous grains have practically no importance from the point of view of the frequency, nevertheless, these differences demonstrate the inhomogeneity of the measured population. From this view-point the most homogeneous population represent the samples from volcanites, where the highest ratio of maximum and minimum concentrations is 12. In further samples, these ratios are much higher — e.g. in samples No. R-031 A up to 380.

In the studied samples no dependence between uranium concentration and the colour of grains was found. In those samples, in which the different grain-size classes were analyzed, it was not a rule that the difference in the crystal size meant also a different uranium concentration.

c. *Variability of uranium concentrations.* For the estimation of the variability of uranium concentrations among the individual grains of the same sample the variation coefficient was used. By its use, we have to take into account that such variability measure is used for those distributions which may be approximated by the normal distribution law. In asymmetrical distributions, which are in majority in this work, it is — in fact — an innatural measure, because in these distributions the arithmetical mean is not the central measure. Therefore, great differences may originate in this value, according to the fact, whether we use the formulas for normal or lognormal distributions (G. S. Koch — R. F. Link, 1970).

The uranium variability in apatites from granitoid rocks varies from 0.30 [leucocratic granite of Rimavica type, Veporides] the highest variability has the Tatra sample — 0.79. In apatite from paragneisses the variability range is higher (0.35 — 0.95). In apatite from migmatites the least value is 0.55, the highest one is 0.87. For apatites from volcanic rocks, great uranium homogeneity from 0.3 to 0.4 is typical.

The whole studied set of apatite has several characteristic features from the point of view of the variation coefficient. In the first place, the value of variation coefficient is not higher than 1 in any sample. In the second place, to a certain degree this value divides the examined samples into three groups. Samples from granitoid rocks and paragneisses create one — mutually overlapping group — and from the point of view of variability, they have the highest dispersion.

Within the framework of this group, it is possible to differentiate the samples from migmatites, the variability of which is limited in the direction to the lower values. An individual group with small variability is represented by samples of apatites from volcanites in which the variability is very low and does not exceed the value 0.4.

d. *Skeweness of distributions.* The skeweness informs us about the distribution of the frequency of uranium concentrations with respect to the calculated arithmetical mean. Distributions are considered as symmetrical up to the value 0.5; from 0.5 to 1.0 as medium asymmetrical and over the value 1 as strongly asymmetrical. As can be seen in Tables 1 — 4, except for one sample (R—027), all the distributions are left-sided asymmetrical. The left-sided asymmetry is shown also by the lower values of the modus, as well as by the lower values of the geometrical mean in comparison with the arithmetical mean. Although the skeweness values vary from 0 to 2.2, no relationship was found between the skeweness value and the rock type in the set.

When seeking criteria for sample differentiation, we supposed that an appropriate measure would be the skeweness. But this statistical value cannot be used as a criterium. The extreme values of the uranium concentrations on several grains have a great influence on the size of this value. In several samples these grains were found, although with a minimum frequency of occurrence but their concentration with regard to the arithmetical mean is very high. One such grain is able to change principally the skeweness value. Since these grains are rare and of no importance from the view-point of the frequency, the value of the skeweness coefficient is an unreproducible value. That means that the use of the skeweness coefficient for the estimation of the distribution form is not real. Comparable results can be obtained only in case when the skeweness is defined by the form of the whole population.

e. *Form of uranium distribution among grains.* Uranium distributions in the studied samples were tested on the agreement of distribution by the help of  $\chi^2$  test. We were not seeking a function which would be the best fitted one for the empiric distribution. Chiefly, we tried to establish whether the distributions from genetically different media are also different in their form. The empiric distributions were tested as to the alternative normal or lognormal distributions which are the most often considered ones in geochemistry. On the accepted level of significance  $\alpha = 0.01$  three distributions from 24 samples of the granitoid rocks can be approximated only by the normal distribution (R—20, R—016, R—050; see Fig. 1a). Both the alternative distributions are suitable for 4 samples, 11 samples can be approximated only by the lognormal distribution. 6 samples do not agree with any of the distributions. One sample was not examined for lack of data. Distributions which may be approximated by the normal distribution are prevalent in paragneisses. One sample was not tested for lack of data. As to the apatites from migmatites, only a half of the samples agrees with the lognormal distribution (Fig. 1b). The second half does not agree with any of the distributions.

Uranium distributions in the apatite from 3 samples of volcanites are in agreement with both tested distributions.

Although the majority of the distributions agrees with the law of the lognormal distribution, the great number of distributions which can be described by the normal law is surprising. The forms of distribution curves are mutually comparable, because the selection of the individual grains was identical in all samples and errors of measure were kept on the same level

in all the samples. The establishment of the fact that the different form of curves is not caused only by the difference of the parameter creating their form (the standard deviation) but that they belong, in fact, to two, principally different types of distribution. From the mentioned results it follows, that for trace elements, more precisely for the uranium distribution in apatite, the hypothesis about merely the left-asymmetrical or merely the log-normal distribution of the element cannot be accepted.

Of course, the fact that each sample was judged from different points of view, causes that the question of conformity or nonconformity of samples depends from the criterium chosen. If we, e.g. judged the samples from the view-point of average uranium contents, then the sample R-018 is identical with the sample R-031 A. But, from the view-point of the uranium distribution they are principally different (Fig. 2a, b). It is clear that the selection of the criteria for the judgement of the different samples has, in fact, a principal significance in the study of the geochemical processes. From this point of view, the study of distribution form may have, in some cases, much greater significance than the mere study of their average concentrations.

### *Conclusion*

The new informations about the inhomogeneity grade and the distribution types of the uranium were obtained by statistical analysis of the variability of uranium concentrations on the individual grains of accessory apatite. The results of the work demonstrate that by some statistical measures the difference in the individual parameters of distributions can be truthfully found. Other ones, e.g. the skewness coefficient cannot be used then in this case. The results demonstrate that although in geochemistry the thesis of the skewness, or — even — the lognormal distribution of the trace elements in minerals or rocks is generally accepted; in the case of uranium in accessory apatite this hypothesis cannot be accepted. The distribution curves are of different form, while their form does not depend on the average concentration in a sample. Therefore we may assume that the distribution of an element and its form are more strongly joined with the genetical conditions and rock crystallization than such universal measure as the average concentration of element.

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*Localization of samples**Granitoid rocks — core mountains*

- R-3 the biotitic granite of the Nízke Tatry Mts., cca 100 m SW from the final stop of the rope-railway.
- R-20 the biotitic granodiorite, the Veľká Fatra Mts, road to the altitude Smrekovica, quarry near the village Matejková.
- R-22 the biotitic granodiorite, the Tatras, road to the Roháče Mts, 500 m from the park near the Tatliak hut, 3,1 km from the altitude Baník.
- R-24 the biotitic granodiorite, the Nízke Tatry Mts., the Prašivá type, the road Sopotnica — Hronov, 1 km of climbing from the last houses.
- R-25 the biotitic granodiorite, the Nízke Tatry Mts., road Sopotnica—Hronov, 1 km from the climbing of the last houses in the close of the valley.
- R-38 the biotitic granodiorite near tonalite, quarry Dubná Skala, the Malá Fatra Mts.
- R-40 the biotitic granodiorite, about 1500 m west from the hut near the road Zuberec — Roháče, the Tatras.
- R-47 the biotitic granodiorite, cliff near the park at Hrebienok, Starý Smokovec, the Tatras.
- R-020 the biotitic granodiorite, Holičná, 400 m W from the altitude 12000,0, the Nízke Tatry Mts.

*Granitoid — veporides*

- R-2 the biotitic granite, north part of the Hladomorná valley, NE from Chyžné, 6 km from Revúca, veporides.
- R-26 the biotitic granite, veporides, Hrončok type, Kamenistá valley, the Kráľova Hoľa zone.
- R-28 the biotitic tonalite, Tlstý Javor, road Čierny Balog—Hriňová, the Kráľova Hoľa Range.
- ZK-29 the biotitic granodiorite, quarry in the Páleničnô valley near Dobroč, the Kráľova Hoľa Range.
- R-57 the biotitic tonalite, incision of the road near the turn to Zubrie, road Podkrikriváň—Lučenec, the Kráľova Hoľa Range.
- R-014 the porphyritic biotitic granite of the Hrončok type, the Kamenistá valley opposite to the Spády valley mouth, quarry, the Kráľova Hoľa zone.
- R-015 the biotitic tonalite of the Sihla type, incision of the road Čierny Balog—Hriňová near the altitude 1020,2 (Tlstý Javor), the Kráľova Hoľa zone.
- R-016 the leucocratic granite of the Rimavica type, quarry 200 m NW from the northern part of the village České Brezovo.
- R-017 the porphyritic biotitic granite of the veporide type, incision of the road in the Ipeľ valley close, 320 m SE from the altitude 769,1.
- R-018 the porphyritic granodiorite with pink feldspathic phenocrysts, the eastern range of Trsteník, 100 m W from the altitude 1300,3, stone cliff.
- R-019 pegmatitic granite of the Pálenisko type, the valley of the Mlynová brook, 200 m N from the altitude 910,0 incision of the wood way.
- R-032 granodiorite of the Sihla type the Petříkov valley, the shot over rocks in the incision of the road, the Kráľová Hoľa zone.
- R-32 A — dtto —
- R-050 granodiorite, road Utekáč-Lom incision of the road

*Paragneisses*

- R-027 paragneiss, the Chorepa quarry near Klenovec.
- R-027 A — dtto —
- R-030 migmatitized gneiss, the Vydrovo valley, quarry near the valley mouth, the Kráľova Hoľa Zone.
- R-031 A — dtto —
- R-049 weakly migmatitized paragneiss, road Utekáč-Lom, incision of the road.
- R-051 paragneiss, road Utekáč-Lom, incision of the road.

*Migmatites*

- R-1 A,B migmatite with eyed texture, the Nízke Tatry Mts., the Vajskov valley, small quarry in the valley turning 500 m NW from the Črnné gamekeeper's cottage, 500 m from the altitude 687,0.
- R-2 A,B migmatite with the blank striped and eyed texture, with aplitic sill, the Nízke Tatry Mtsc., the Vajskov valley, stones on the meadow near the road, W from Pálenice (1653,5), 200 m under the „tajch“.
- R-3 A,B migmatite with uneven striped texture. The Nízke Tatry Mts., the Lomnístá valley, stones near the channel moh-NE from the gamekeeper's cottage Blatá (1125,3), 150 m behind the hut near the water-lock.

*Volcanites*

- R-008 propylitized andesite, Zlatá Baňa, the Slánske vrchy Mts.
- R-010 rhyolite, Vyhne, the Kremnica Mts.
- R-010 pyroxene-amphibolitic andesite, Zemplínska Teplica, the Slánske vrchy Mts.
- R-011 rhyolite, Sklené Teplice, the Kremnica Mts.

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