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THE INFLUENCE OF THE ANALYTICAL ERROR ON THE DISTRIBUTION OF TRACE ELEMENTS

Abstract: For the geochemical study of trace elements in geological materials their distribution is of main importance. The published data describing the distribution of trace elements represent the convolution of the distribution corresponding to the own concentration changes and to the error of the used analytical method. On the basis of the logarithmic normal model of distribution a procedure enabling the separation of the analytical error and the calculation of the pure own distribution of the trace element contents is described and applied on the distribution of some selected trace elements in ultrabasic rocks from the Spiš — Gemer rudohorie. It was proved that the error of the used spectrochemical determination does not influence significantly the obtained statistical parameters of the studied distribution. The precision of the analytical results is so adequate to the solved problem.

Резюме: Для геохимического изучения следовых элементов в геологических материалах самым важнейшим является их распределение. До сих пор опубликованные в литературе данные о распределении следовых элементов включающие надлежащие параметры (средние величины, рассеянность и т. п.) представляют собой, таким образом, результаты соответствующие конволюции распределения собственных величин концентраций исследованных следовых элементов и распределения ошибки использованного аналитического метода. В работе описан метод способствующий учитывать ошибку аналитического метода и определения собственного распределения содержаний следовых элементов. Предлагаемый метод применяли для изучения распределения выбранных следовых элементов в ультрабазических породах из Спишско-гемерского рудогорья, исследованных при применении спектрохимического анализа. На основании полученных результатов ошибка спектрохимического определения не проявляется значительно в величинах полученных статистических параметров описывающих изучаемое распределение.

Introduction

At the geochemical study of the type of occurence of trace elements in rocks and minerals the distribution of their contents plays a considerable role. All analytical procedures used for the determination of the studied trace element contents are loaded by error of precision. This inevitable error leading to specific distribution of concentration values for each sample from the observed population is so involved in the determined distribution of the studied contents. According to the value of the error of the analytical precision the parameters of the distribution of trace element contents calculated using insufficiently precise input data can become non reliable. We therefore tray to clear the influence of the analytical error upon the parameters of the distribution of trace elements in ultrabasic rocks chosen as exemple.

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Theoretical part

At the mathematical description of the distribution curve, some of the model distributions is used and appropriate function of the statistically treated value (in our case the concentration) leading to as far as the best accordance with the experiment is proposed. The Gaussian normal distribution is generally accepted as basis because of its comparatively simple mathematical description, as well as because of the best knowledge of its properties. The basic condition of the normal distribution, i.e. the followed quantity must be defined in the whole range of values from minus infinity to plus infinity is, however, often neglected. Many physical quantities can obtain only positive values (e.g. time, temperature, mass, concentration). The correct description of the distribution of their values by the Gaussian normal distribution is therefore not suitable from the mentioned principial reason. In such cases the description of the distribution of the logarithmic values of the quantity in question can often help. The logarithmic — normal distribution can be applied with sufficient accordance to the quantities which may obtain only positive values mainly in the case when the values do not differ too much from zero and their sccatering is considerable in comparison with their mean value (E. Plško, J. Kubová 1978). These conditions are sufficiently fullfilled by the contents of trace elements in rocks and minerals of the same kind and/or of the same genetic type. It is therefore not surprising that Ahrens used the logarithmic — normal distribution of trace elements in rocks and minerals at their geochemical study already more than a quarter century ago (L. H. Ahrens, 1954).

Apart from the distribution of trace element own contents, the analytical results of spectrochemically determined concentrations can also be described with sufficient accordance by the logarithmic — normal distribution as it was proved on extensive experimental material (E. Plško, 1973) and theoretically explained on the basis of the use of internal reference elements (E. Plško, J. Kubová, 1978).

The till now published data on the distribution of trace elements described by its main parameters (mean values, deviation etc.) represent so results corresponding to the convolution of the distribution of the own concentration values of the studied elements and of the distribution of the analytical results. The described situation testifies that it is not possible to make sufficiently reliable conclusions concenrning the own distribution of the trace elemens contents without the knowledge of the parameters of the distribution of the analytical results obtained by the used procedure. In the extreme case, if the concentration of the element in question did not change at all, the gained scattering of the results would be caused only by the analytical error and on the other side the correct description of the distribution of the trace element could be obtained only by using an analytical method not loaded by any error of precision which situation cannot be attained. The real state appears somewhere between the cited twoo extreme cases. We therefore endeavour to give a proposal of the procedure enabling the valuation of the influence of the analytical error on the distribution of trace elements in geological materials.

Proceeding from the logarithmic — normal model of the distribution of the error of spectrochemical determination, the standard deviation of the logarithm of the concentration value can be estimated on the basis of parallel measurements performed on different samples of the same investigated type of material by the application of the equation (E. Plško, 1973):

$$s_\lambda = \sqrt{\frac{\sum_{i=1}^{p} \left(\log \frac{c_1}{c_2} \right)_i^2}{2\,p}} \qquad (1)$$

c_1 is the concentration determined in the i-th sample in the first and c_2 in the second parallel measurement, p is the whole number of samples which hangs with the number of measurements (n) by the relation:

$$n = 2p \qquad (2)$$

The standard deviation characterizing the total scattering of the logarithm of the concentration value in the whole population of the given type of geological material including both the different geochemical influences acting at its formation and during its existence (pressure, temperature, pH, surrounding, tarnsport phenomena etc.), as well as the error of the analytical determination can be estimated by the application of the well known equation:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (\overline{\log c} - \log c_i)^2}{n - 1}} \qquad (3)$$

In accordance with the law of the addition of errors and with the stochastic independence of the components, the total variation (s^2) is composed from the variation (s_e^2) caused by the geochemical factors which characterize the sought net scattering of the element in the investigated material and from the variantion caused by the analytical procedure (s_λ^2):

$$s^2 = s_e^2 + s_\lambda^2 \qquad (4)$$

From the equation (4) the calculation of the standard deviation of the logarithm of the concentration value, not disturbed by the corresponding analytitical determination, is thus possible.

Results and discussion

The described correction procedure was used for the determination of the parameters of trace elements distribution in granitoid, basic and ultrabasic rocks from different Western Carpatian localities (J. Medveď, 1975; B. Cambel, L. Kamenický, J. Medveď, 1979). As exemple the evaluation of the distribution of some trace elements (Cu, Mn, Ni) in ultrabasic rocks (peridotic serpentinites) from Spiš — Gemer rudohorie is presented.

The mentioned elements were determined spectrochemically using the method described by J. Medveď and E. Plško (1979). The error of precision estimated on the basis of parallel measurements expressed in the form of relative standard deviation (s_{rp}) is presented for the selected elements in the tab. 1.

Table 1

Element	Cu	Mn	Ni
s_{rp}	0.073	0.122	0.046

These values enable to calculate the standard deviation of the logarithm of the concentration (s_λ) by means of the equation (E. Plško, 1973):

$$s_\lambda = \log(1 + s_{rp}) \qquad (5)$$

107 samples of the described rocks were analysed. The standard deviation of the logarithm of concentration values (s) characterizing the whole scattering were calculated by using the equation (3) and the standard deviation of the analytical determination of the logarithm of concentration from the equation (5). All these values are presented in the tab. 2 together with the standard deviations (s_e) calculated using the equation (4) and corresponding only to the scattering caused by the geological factors.

Table 2.

Element	Cu	Mn	Ni
s	0.490	0.229	0.149
s_λ	0.0305	0.0501	0.0195
s_e	0.489	0.223	0.148

As it can be seen from the Table 2., the standard deviation of the analytical determination is much smaller than the standard deviation characterizing the whole scattering. It therefore practically does not distort the real scattering of the given element in the studied rocks which statement is proved bythe very well agreement of the s values with the s_e values. It can be therefore concluded that the applied spaectrochemical method is sufficiently precise for the gaining of the claimed geochemical conclusions. The use of more precise procedures, or the claim for a further improvement of the applied spectrochemical method do not lead so to more precise final results corresponding to the whole aim not only from the scientific, but mainly from the economic point of view and therefore it is useless.

As it follows from the performed study the election of the appropriate parameters of analytical procedures should correspond to the claims of the given problem and their further useless optimization cannot bring any new informations.

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