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STUDY OF MICROHARDNESS AND MATHEMATIC-STATISTICAL EVALUATION OF MICROHARDNESS MEASUREMENT RESULTS

(Figs. 1—7)

Abstract: The paper deals with possible mathematic-statistical treating of the results of microhardness measurement of minerals. Various minerals underwent mathematic-statistical evaluation of microhardness — silicates, sulphides and oxides. In all measured minerals the character of distribution of microhardness values was found out, the variation coefficient was calculated and the hypothesis of reliability was verified at the 95 % level of accuracy of determination found in advance. The mathematic-statistical valuation showed the required optimum number of measurements for one or another mineral. In the conclusion dependence of microhardness on chemism of the mineral and representation of microelements as well as the possibility of applying of the obtained microhardness values for genetic studies were discussed in some groups of minerals.

Резюме: В статье говорится о математическо-статистической обработке результатов измерения микротверности минералов. Математически-статистической оценке были подвержены различные минералы — силикаты, сульфиды и оксиды. У всех измеряемых минералов был обнаружен характер распределения данных микротвердости, подсчитанный коэффициент вариации и проверена гипотеза положительности на ранее определенном 95 % уровне точности определения. Из математически-статистического определения исходит требуемое оптимальное количество измерений для того или другого минерала. В заключении у некоторых групп минералов обсуждалась зависимость микротвердости от химизма минералов и наличия микроэлементов, а также возможность использования полученных фактических данных микротвердости для генетических изучений.

In the last period physical properties of minerals are being abundantly applied in detailed diagnosis of minerals. One of such physical properties is the microhardness of minerals. The method of microhardness measurement of minerals is well known from the works of many authors (S. J. Lebedeva 1963, G. A. Ifjinskij 1963, F. M. Nakhla 1956, E. M. Onitsch-Modl 1953, M. Háber 1965 a. o.).

The presented work deals with possible mathematic-statistical evaluation of the results of microhardness measurement of minerals, mainly from the standpoint of obtaining the most probable values and practical consequences for microhardness measurement following from that.

As base for mathematic-statistical evaluation of the results of microhardness measurement of minerals served the results of minerals taking part in the composition of skarns (F. Zábranský 1968) in the area of the Štiavnica „island" (fig. 1).

The microhardness of all minerals was measured on apparatus PMT-3 of Soviet production — using the weights mentioned in tab. 2. Regarding to that microhardness was measured on unoriented sections of minerals (in polished sections) in all cases we chose the method of larger number of measurements of the same mineral. The number of measurements, localization of the sample as well as the number of polished sections

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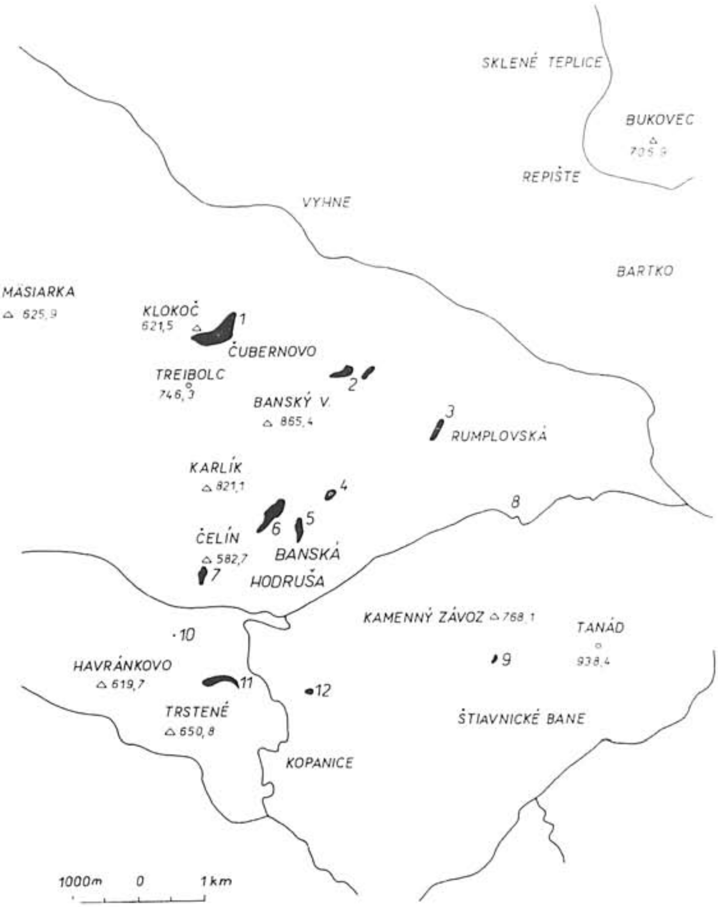

Fig. 1. Occurrences of skarns the Štiavnica „island". 1 — Klokoč-Treibolc, 2 — Alžbeta, 3 — Rumlovská, 4 — Michal, 5 — Raková, 6 — Karlík, 7 — Čelín, 8 — Laura, 9 — Rozália, 10 — Havránkovo, 11 — Železná Hora, 12 — Kohútovo.

used for microhardness measurement of one or another mineral are mentioned in tab. 2.

From the standpoint of the theory of probability we consider microhardness of minerals as accidental variable that may get (also in the same mineral) arbitrary value from some interval as a consequence of various factors. This mainly depends on physical-chemical, crystallo-chemical as also mechanical factors (type of the crystal structure of the mineral, chemical binding, valency, coordination number, elasticity, brittleness and plasticity, solidity etc.). The results of microhardness measuring are to a certain degree also influenced by subjective factor.

With mass measuring of microhardness of one mineral the average value of microhardness most probable is obtained by calculation of mean arithmetic average or most frequently by graphic interpretation in the form of variation curves (S. L. L e b e d e v a 1963). Regarding to the variability of measured microhardness values it is necessary to equalize them frequently so that the resulting curve should render prominent the character of division of microhardness values. Equalization is performed by the method

Table 1. Division of Microhardness Values of Flogopite (Železná Hora — Number of Measurements 40)

Number of interv.	Interval H in kg mm²	Frequency in %	Equalization I.	Equalization II.
1	31,5	5,0	9,1	7,7
2	42,3	22,5	14,1	13,6
3	49,1	15,0	17,5	15,5
4	55,5	15,0	15,0	15,2
5	62,0	15,0	13,3	13,0
6	70,1	10,0	10,8	10,5
7	78,0	7,5	7,5	8,0
8	84,0	5,0	5,8	5,5
9	97,5	5,0	3,3	3,0

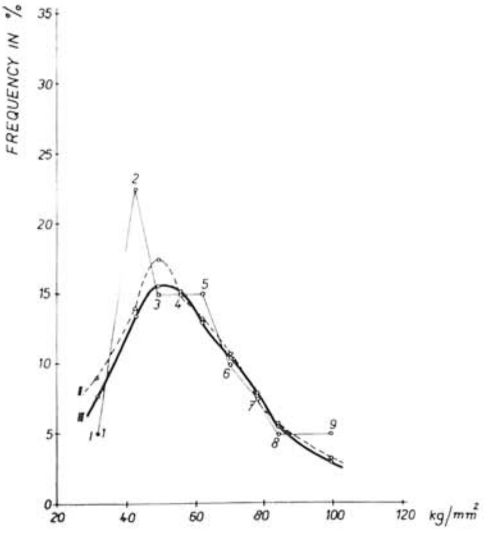

Fig. 2. Variation curve of microhardness of flogopite and its equalization.

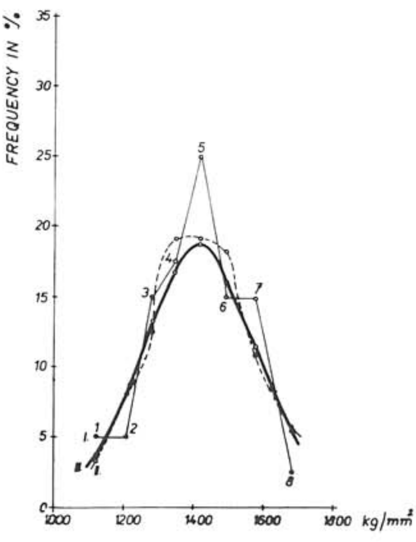

Fig. 3. Variation curve of olivine.

of averaging of three values of relative per cent frequencies following one after another. The calculated average is related to the mean value. The mentioned procedure of equalization may be repeated several times until optimum fluency of the variation curve is reached. We are presenting the way of equalization on the example of flogopite (tab. 1, fig. 2). In fig. 3, 4, 5 are equalized variation curves of olivine, calcite and sphalerite.

Mathematic-Statistical Evaluation of the Results of Microhardness Measurement of Minerals

The aim of mathematic-statistical treating of results of microardness measurement is determination of the most important numerical characterization of accidental variable, which includes:

1. mean value $\bar{x}$
2. mean quadratic deviation σ, or variation coefficient v
3. interval of reliability for unknown, real mean microhardness value of the mineral $\triangle$.

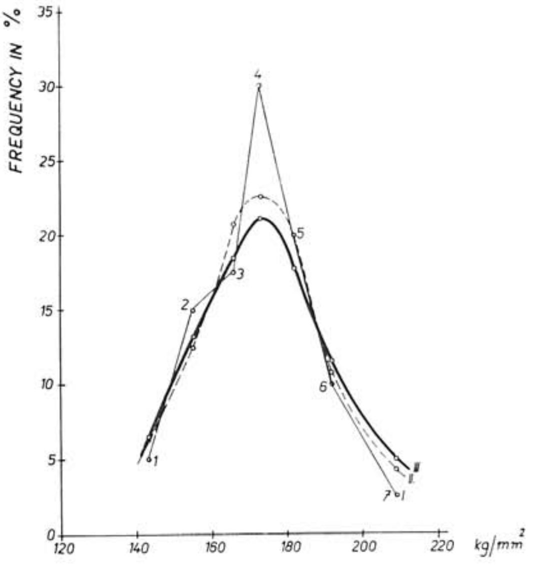

Fig. 4. Variation curve of calcite.

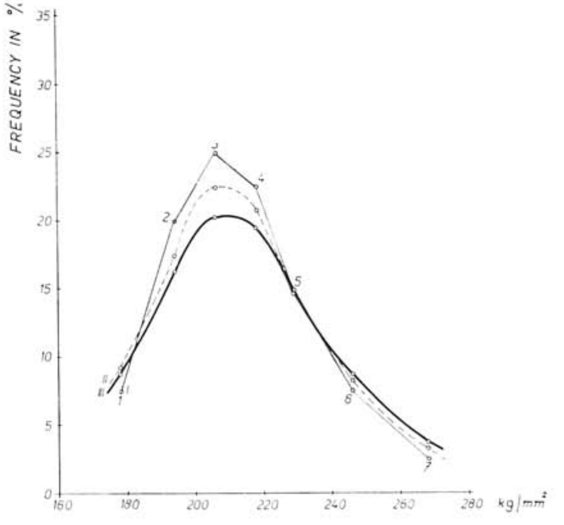

Fig. 5. Variation curve of sphalerite.

4. optimum number of measurements, guaranteeing required accuracy of estimation of unknown, real mean value.

For numerical characterization or so called estimation of unknown mean value of accidental variable the arithmetic average $\bar{x}$ is used, which does not depend on the function of division of accidental variable and with increasing number of measurements one approaches the real mean value of accidental variable. This approachig is getting greater the more empiric division of accidental variable is nearer to normal division.

For characterization of the degrees of dispersion or concentration of all value around the mean value mean quadratic deviation is applied (standard, standard deviation) σ or variation coefficient v.

For calculation of the mentioned numerical characterizations of microhardness of minerals the following relations were used:

arithmetic average: $$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad (1)$$

mean quadratic deviation: $$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}} \quad (2)$$

variation coefficent: $$v = \frac{\sigma}{\bar{x}} \cdot 100\,\% \quad (3)$$

where x_i — measured microhardness values.

These numerical characterizations for individual minerals are mentioned summarized in tab. 2. Tab. 2 shows relatively most variable microhardness values to be reached

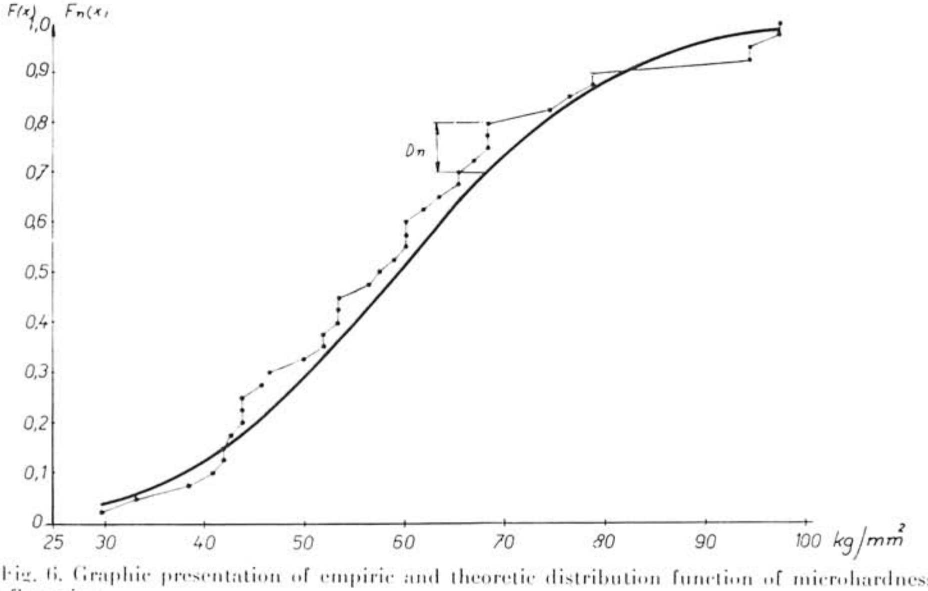

Fig. 6. Graphic presentation of empiric and theoretic distribution function of microhardness of flogopite.

Table 2. Results of Mathematic-Statistical Evaluation of Microhardness of Minerals

No.	Mineral locality	Weight in gr	Number of Samples	Number of Measuremenst	Mean value $\bar{x}$	Mean quadratic deviation σ	Variation coefficient V	D_n	$D_n(\alpha)$ $\alpha = 5\%$	Hypothesis of normal distribution at 5% level	Reliability interval at 5% level $\bar{x} \pm \triangle$	$\frac{\triangle}{\sigma}$
1	2	3	4	5	6	7	8	9	10	11	12	13
1	Brown garnet (grossularite) Treibole	100	3	50	1122,0	125,8	11,2	0,1482	0,1884	valid	1122,0±34,9	0,277
2	Brown garnet (andradite) Karlík	100	3	45	1072,0	100,1	9,3	0,1988	0,1984	not valid	1072,0±29,2	0,291
3	Reddish-grown garnet (grossularite) Treibole	100	5	50	1093,7	81,1	7,4	0,1918	0,1884	not valid	1093,7±22,5	0,277
4	Yellow garnet (andradite) Treibole	100	4	60	1067,8	112,9	10,6	0,1490	0,1723	valid	1067,8±28,6	0,253
5	Epidote Železná Hora	100	2	40	1009,4	92,0	9,2	0,1200	0,2101	valid	1009,4±28,0	0,309
6	Fassaite Kohútovo	100	6	30	950,0	64,0	6,7	0,1839	0,2417	valid	950,0±23,0	0,359
7	Olivine Železná Hora	100	4	40	1398,5	128,2	9,2	0,1272	0,2101	valid	1398,5±39,7	0,309
8	Flogopite Železná Hora	20	3	40	59,6	17,0	28,6	0,0981	0,2101	valid	59,6± 5,3	0,309
9	Flogopite Kohútovo	20	4	34	69,3	12,0	17,9	0,1030	0,2274	valid	69,3± 4,2	0,338

10	Pleonaste Kohútovo	200	2	40	1391,2	84,6	6,1	0,1744	0,2101	valid	1391,2±26,2	0,309
11	Pleonaste Železná Hora	200	2	40	1451,6	106,5	7,3	0,2255	0,2101	not valid	1451,5±33,0	0,309
12	Hematite (specular hematite) Treibole	100	3	46	1012,5	60,2	6,0	0,1572	0,1962	valid	1012,5±17,4	0,289
13	Chalcopyrite Treibole	50	2	40	211,5	11,0	5,2	0,1255	0,2101	valid	211,5± 3,4	0,309
14	Chalcopyrite Treibole	50	3	40	213,0	26,0	12,2	0,1596	0,2101	valid	213,0± 8,0	0,309
15	Sphalerite Treibole	50	4	40	212,5	19,7	9,3	0,0983	0,2101	valid	212,5± 6,1	0,309
16	Galenite Treibole	20	3	56	100,9	7,6	7,6	0,1376	0,1782	valid	100,9± 2,0	0,263
17	Calcite Treibole	50	4	40	172,5	14,0	8,1	0,0982	0,2101	valid	172,5± 4,3	0,309
18	Sphalerite Treibole	50	4	32	215,5	18,1	8,4	0,1406	0,2342	valid	215,5± 6,3	0,348
19	Pyrite Alžbeta	150	5	40	1170,0	131,1	11,2	0,1453	0,2101	valid	1170,0±40,6	0,309
20	Pyrite deposit Rozália VI horizont	150	4	50	1283,4	145,2	11,3	0,0996	0,1884	valid	1283,4±40,3	0,277
21	Pyrite Železná Hora	150	4	40	1289,4	155,0	12,0	0,1714	0,2101	valid	1289,4±48,0	0,309
22	Pyrite Treibole	150	6	42	1294,0	176,3	13,6	0,1666	0,2052	valid	1294,0±53,3	0,302

No.	Mineral locality	Weight in gr	Number of Samples	Number of Measurement	Mean value $\bar{x}$	Mean quadratic deviation σ	Variation coefficient v	D_n	$D_n(\alpha)$ $\alpha = 5\,\%$	Hypothesis of normal distribution at $5\,\%$ level	Reliability interval at $5\,\%$ level $\bar{x} \pm \triangle$	$\frac{\triangle}{\sigma}$
1	2	3	4	5	6	7	8	9	10	11	12	13
23	Pyrite Karlík	150	3	40	1321,7	134,9	10,2	0,1450	0,2101	valid	$1321{,}7 \pm 41{,}8$	0,309
24	Pyrite Rumplovská	150	3	40	1386,0	143,0	10,3	0,2078	0,2101	valid	$1386{,}0 \pm 44{,}3$	0,309
25	Magnetite Železná Hora	100	2	40	577,6	30,2	5,2	0,1474	0,2101	valid	$577{,}6 \pm 9{,}4$	0,310
26	Magnetite Karlík	100	7	70	582,7	33,4	5,7	0,2051	0,1597	not valid	$582{,}7 \pm 7{,}8$	0,233
27	Magnetite Rozália VI horizon	100	4	40	584,4	36,7	6,3	0,1449	0,2101	valid	$584{,}4 \pm 11{,}4$	0,310
28	Magnetite Rumplovská	100	4	50	587,4	37,3	6,3	0,1559	0,1880	valid	$587{,}4 \pm 10{,}3$	0,276
29	Magnetite Čelín West	100	2	35	601,0	43,1	7,2	0,2203	0,2242	valid	$601{,}0 \pm 14{,}3$	0,332
30	Magnetite Treibole	100	2	35	611,8	38,8	6,3	0,1152	0,2242	valid	$611{,}8 \pm 12{,}9$	0,332
31	Magnetite Alžbeta	100	3	36	622,2	48,8	7,8	0,1706	0,2212	valid	$622{,}2 \pm 15{,}8$	0,326
32	Magnetite Čelín East	100	4	40	628,9	45,3	7,2	0,2030	0,2101	valid	$628{,}9 \pm 14{,}0$	0,309

Table 3. Calculation of the Supremum of the Deviation of Distribution Functions

No.	x_i kg/mm²	$x_i-\bar{x}$	$(x_i-\bar{x})^2$	$t=\frac{x_i-\bar{x}}{\sigma}$	F(t)	$F_n(x)$	D_n
1	2	3	4	5	6	7	8
1	29,8	−29,8	888,04	−1,74	0,04093	0,0250	0,01593
2	33,3	−26,3	691,69	−1,53	0,06301	0,0500	0,01301
3	38,6	−21,0	441,00	−1,23	0,1094	0,0750	0,0344
4	41,0	−18,6	345,96	−1,09	0,1379	0,1000	0,0379
5	41,9	−17,7	313,29	−1,03	0,1515	0,1250	0,0265
6	41,9	−17,7	313,29	−1,03	0,1515	0,1500	0,0015
7	42,7	−16,9	285,61	−0,99	0,1611	0,1750	0,0139
8	43,8	−15,8	249,64	−0,92	0,1788	0,2000	0,0212
9	43,8	−15,8	249,64	−0,92	0,1788	0,2250	0,0462
10	43,8	−15,8	249,64	−0,92	0,1788	0,2500	0,0712
11	45,7	−13,9	193,21	−0,81	0,2090	0,2750	0,0660
12	46,6	−13,0	169,00	−0,76	0,2236	0,3000	0,0764
13	49,9	−9,7	94,09	−0,57	0,2843	0,3250	0,0407
14	52,2	−7,4	54,76	−0,43	0,3336	0,3500	0,0164
15	52,2	−7,4	54,76	−0,43	0,3336	0,3750	0,0414
16	53,4	−6,2	38,44	−0,36	0,3594	0,4000	0,0406
17	53,4	−6,2	38,44	−0,36	0,3594	0,4250	0,0656
18	53,4	−6,2	38,44	−0,36	0,3594	0,4500	0,0906
19	56,6	−3,0	9,00	−0,18	0,4286	0,4750	0,0464
20	57,5	−2,1	4,41	−0,12	0,4522	0,5000	0,0478
21	58,9	−0,7	0,49	−0,04	0,4801	0,5250	0,0449
22	60,3	0,7	0,49	0,04	0,5160	0,5500	0,0340
23	60,3	0,7	0,49	0,04	0,5160	0,5750	0,0590
24	60,3	0,7	0,49	0,04	0,5160	0,6000	0,0840
25	62,0	2,4	5,76	0,14	0,5557	0,6250	0,0693
26	63,6	4,0	16,00	0,23	0,5910	0,6500	0,0590
27	65,7	6,1	37,21	0,36	0,6406	0,6750	0,0344
28	65,7	6,1	37,21	0,36	0,6406	0,7000	0,0594
29	66,9	7,3	53,29	0,43	0,6664	0,7250	0,0586
30	68,6	9,0	81,00	0,53	0,7019	0,7500	0,0481
31	68,6	9,0	81,00	0,53	0,7019	0,7750	0,0731
32	68,6	9,0	81,00	0,53	0,7019	0,8000	0,0981
33	74,6	15,0	225,00	0,88	0,8106	0,8250	0,0144
34	76,6	17,0	289,00	1,00	0,8413	0,8500	0,0087
35	78,8	19,2	368,64	1,12	0,8686	0,8750	0,0064
36	78,8	19,2	368,64	1,12	0,8686	0,9000	0,0314
37	94,6	35,0	1225,00	2,05	0,9798	0,9250	0,0548
38	94,6	35,0	1225,00	2,05	0,9798	0,9500	0,0298
39	97,5	37,9	1436,41	2,22	0,9868	0,9750	0,0118
40	97,5	37,9	1436,41	2,22	0,9868	1,0000	0,0132
	2384,0	0,0	11690,88				

$$\bar{x}=\frac{2384}{40}=59{,}6; \qquad \sigma=\sqrt{\frac{11\,690{,}88}{40}}=17{,}09$$

at flogopite, chalcopyrite and pyrite. It is, however, remarkable that the average variation coefficient of all studied minerals is 10 %, what is an evidence of careful measuring and keeping equal conditions in measuring.

For determination of the reliability interval for the unknown, real mean value of microhardness of minerals it is necessery to verify the hypothesis that accidental choices were selected from normal fundamental set or what also signifies to prove that microhardness of the followed minerals is controlled by normal division. In the given case for verification of this hypothesis tets are most suitable to be applied, which are based on distribution functions (J. Janko 1958, J. Drabant 1967). The citerion of these tests, according to which acceptance or refusal of the hypothesis will be decided, is the supremum of deviation of distribution function of the choice from the hypothetic distribution function of the fundamental set.

In our case we suppose microhardness of minerals to be controlled by normal division with distribution function

$$F(t) = \frac{1}{\sqrt[2]{2\pi}} \int_{-\infty}^{t} \exp\left(-\frac{t^2}{2}\right) dt \qquad (4)$$

tabulated for the values of the argument

$$t = \frac{x - \mu}{\sigma} \qquad (5)$$

where μ — mean value
σ — mean quadratic deviation

and may be found in handbooks of mathematic statistics.

We designate the distribution function of the choice $x_1, x_2, \ldots\ldots\ldots\ldots x_n$, the extent n from the fundamental set with distribution function $F(t)$ as $Fn(x)$ and calculate it as follows:

$$Fn(x) = \begin{cases} o & \text{for} \quad x < x_1 \\ \frac{k}{n} & \text{for} \quad x_k \leqq x < x_{k+1},\ k = 1, 2, \ldots\ldots n\text{-}1 \\ 1 & \text{for} \quad x \geqq x_n \end{cases} \qquad (6)$$

where $x_1, x_2, \ldots\ldots x_n$ are measured values, ordered according to the magnitude from the smallest to the largest.

From observation of distribution functions (4) and (6) we determine the value of supremum

$$Dn = \sup\,[Fn(x) = F(t)] \qquad (7)$$

and from the tables (J. Janko 1958, J. Drabant 1967) we are finding the critical values $Dn(\alpha)$., for which is valid

$$P\,\{\sup\,[Fn(x) - F(t)] > Dn(\alpha)\ \} = \alpha, \qquad (8)$$

or the probability of that supremum of deviation of distribution functions which exceeds critical value equals α.

For clarification of using the mentioned test we present calculation of the criterion for microhardness of flogopite in tab. 3. The mentioned table shows, that the supremum of deviation of distribution functions

$$Dn = 0.0981 \text{ for the value } x_i = 68.6.$$

The critical value $Dn(\alpha)$ for $n = 40$ and $\alpha = 5\,\%$ — level of significance is 0.2101. Regarding to that $Dn = 0.0981 > Dn(\alpha) = 0.2101$, we accept the hypothesis of normal division of microhardness of flogopite.

Graphic interpretation of the applied test is presented in fig. 6. In a similar way also the results of other followed minerals were tested and the results of the tests are mentioned in tab. 2, which makes evident that the hypothesis of normal division of microhardness at the level of 5 % is rejected in 4 cases only : 2, 3, 11, 26 but whith using, for instance, 2 % level of significance the hypothesis is also confirmed in these cases.

As a consequence of that it is possible to use for determination of reliability interval, which will cover the real, unknown mean microhardness value of the studied minerals, the known relation (J. J a n k o 1958, J. D r a b a n t 1967):

$$\left((\bar{x} \pm t \,.\, \frac{\sigma}{\sqrt[3]{n}} \right) \tag{9}$$

where $t = 1.96$ at 5 % level of significance from the table of values of the twofold value of the function of Laplace determining the probability of the occurence of accidental variable in the interval $\pm$ t. Calculation of the reliability interval according to (9) was carried out for all studied intervals and is mentioned in tab. 2.

Relation (9) may be used for determination of necessary number of measurements, when required accuracy of determination of mean value of the fundamental set or the difference between the real, mean value and selectional arithmetic average is established in advance. If we thus designate

$$\triangle = (\bar{x} - \mu)$$

then it is evident, that

$$\triangle = t \,.\, \frac{\sigma}{\sqrt[3]{n}}$$

or at 95 % probability

$$\triangle = \frac{1.96 \,.\, \sigma}{\sqrt[3]{n}}$$

from what

$$n = (\left(\frac{1.96 \,.\, \sigma}{\triangle} \right)^2 \tag{10}$$

If we divide the numerator and denominator (10) by the mean value $\bar{x}$ then

$$n = (\left(\frac{1.96 \,.\, v}{\gamma} \right)^2 \tag{11}$$

where $\gamma = \frac{\triangle}{\bar{x}}$ expresses the limit error of estimation μ in units $\bar{x}$. If we divide the numerator and denominator of equation (10) σ, then

$$n = (\left(\frac{1.96}{q} \right)^2 \tag{12}$$

where $q = \frac{\triangle}{\sigma}$ expresses limit error of estimation μ in units σ.

Each of the relations (10), (11), (12) may be applied for establishing of the number of measurements n of microhardness of minerals, guaranteeing required accuracy. Relation (10) may be applied when it is possible to estimate parametre σ from the range of variation of measured values, for instance:

$$\sigma = \frac{(x_{max} - x_{min})}{dn}$$

where dn is coefficient dependig on the number of measurements (N. V. Smirnov, J. Dunin, J. V. Barkovskij 1959).

Relation (11) may be applied when the coefficient of variation of a larger number of measurements is known or from several sets of measurements.

The most suitable is however, relation (12) because it does not require neither determination of σ nor of v, but it is sufficient to choose limit error of estimation of the unknown, real value with regard to σ. On empiric material limiting relative values of $\frac{\triangle}{\sigma}$ were studied, which varied within the limits from 0.253 to 0.359, the mean value of the quotient was 0.30 or 30 % of the mean quadratic deviation (tab. 2).

Regarding to the mentioned relative values of $\frac{\triangle}{\sigma}$ and on the basis of the attained values of the mentioned quotient and relation (12) a table for determination of the number of measurements may be compiled — guaranteeing required accuracy (tab. 4).

Table 4

q	0,25	0,30	0,35	0,40	0,45	0,50
n	61	42	31	24	19	15

If we compare the number of measurements, from which numerical characterization of tab. 2 with tab. 4 were calculated and required relative accuracy of estimation μ q = 0,30, then it is evident that numbers with n ≧ 40 are suitable for the mentioned requirement of accuracy but all n < 40 do not fulfil the mentioned requirement. The question of required accuracy of estimation can be discussed. If accuracy of estimation were lowered e. g. to the value q = 0,40, than the sufficient number of microhardness measurements would be n = 24.

Conclusion

In the presented contribution we summarize the results of microhardness measurement of minerals taking part in composition of skarn deposits in he area of the Štiavnica „island". For the purpose of obtaining the most probable values of microhardness of individual minerals we examined the results of microhardness measurement by mathematic-statistical evaluation.

This study makes possible some conclusions for practical application in microhardness measurement of minerals in current mineralogical practice. Especially the problem of finding out the most probable value of microhardness for the considered mineral is concerned under conditions, when no oriented sections of the mineral are available but the aggregate of minerals, frequently consisting of allotriomorphic grains. Under these conditions we carried out measuring of microhardness of minerals mentioned in tab. 2 by the method of larger number of measurements of the same mineral, as mentioned in tab. 2. In order to obtain the most probable average microhardness value we calculated average value of microhardness by calculation of the mean arithmetic average and also graphic interpretation in the form of variation curves, which show very well variability and dispersion of microhardness values. These, however, have to be frequently equalized in the way mentioned in tab. 1 regarding to the variability of microhardness values in order to obtain optimum fluency of the curve, which after such modification clearly demonstrates the character of distribution of microhardness values. For the obtained microhardness value of the mineral characterized by certain chemical, crystallo-chemical, structural and mechanical properties to be reliably applied for diagnostic purpose it is necessary to know the law of distribution of microhardness as well as the degree of dispersion in the given mineral. Therefore the hypothesis of normal distribution of microhardness in the studied minerals was tested by aid of the supremum of the deviation of empiric and theoretical distributional function. The results of the test have confirmed good accordance of empiric and theoretic division. The degree of variability of the measured microhardness values of minerals is suitable to be considered by calculation of the mean quadratic devation and variation coefficient. In current mineralogical practice, obtaining microhardness values, we are always concerned with certain limited number of measurements, from which we determine the most probable value by calculation of the mean arithmetic average. This, however, can be different from the theoretical mean microhardness value of the mineral and therefore it is suitable to find out the interval of reliability, which with probability near to one (with probability 0.95 in our case) will cover the unknown theoretic mean value. For considered accuracy of establishing the mean value of microhardness of minerals to be attained certain optimum number of measurements is necessary, which can be found out from the reliability interval (see tab. 4).

Particular attention has to be paid to evaluation of microhardness mentioned in tab. 2 from mineralogical standpoint. A more detailed analysis of the attained values of microhardness of minerals can be carried out in our case only in the situation when values of several measurements of the same mineral are available. To this requirement pyrites, magnetites and partly also garnets suit. Other minerals, of which 13—32 measurements are available to us, may be only compared with data mentioned in literature.

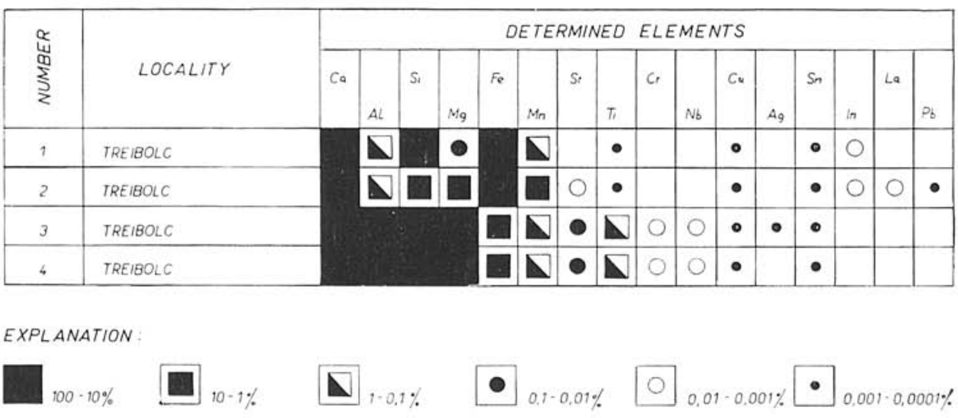

Fig. 7. Qualitative spectral analyses of garnets.

Garnets taking part in the composition of skarn deposits of the Štiavnica „island" (F. Z á b r a n s k ý 1968) are characterized by essential representation of andradite and grossularite constituent, other fundamental garnet constituents take only slightly part in their composition. According to the predominating constituent garnet no. 1 (tab. 2) may be ranged to grossularite as well garnet no. 3. Garnets 2 and 4 may be ranged to andradite. The mentioned character of garnets is also indicated by the dimensions of structural lattice: garnet 1 $a_0 = 11.828$ Å, garnet 2 $a_0 = 11.986$ Å, garnet 3 $a_0 = 11.839$ Å, garnet 4 $a_0 = 11.978$ Å. The picture of representation of macro- and microelements of garnets is provided by the results of qualitative spectral analysis (fig. 7). The microhardness of the studied garnets varies within the interval of 1067.8—1122 kg/mm², garnets with predominating andradite constituent show lower microhardness values (1067.8—1072 kg/mm²) in contrast to garnets with predominating grossularite constituent (1093.7—1122 kg/mm²). Microhardness values of garnets with predominating constituent of spessartite, almandine and pyrope show higher values than the garnets measured by us. For instance, S. I. L e b e d e v a (1963) mentioned for almandine the microhardness in the interval 1228—1290 kg/mm². Generally it is thus valid for garnets that with diminishing of the dimensions of structural lattice (from andradite $a_0 = 12.048$ Å to pyrope $a_0 = 11.459$ Å — according to W. E. T r ö g e r 1967) the value of microhardness will increase. This relation could be applied in determination of garnets on the basis of microhardness, but this problem requires more detailed analysis.

Pyrites in the skarn deposits of the Štiavnica „island" are represented in the hydrothermal stage of quartz-calcite-sulphides of the development of deposits in several periods (F. Z á b r a n s k ý 1968). There is mainly the pyrite-chalcopyrite period, in which with pyrite and chalcopyrite as non-metalliferous minerals calcite and quartz are present. From this period microhardnesses of pyrites 19, 20 and 23 were measured (tab. 2). The predominating ore mineral is pyrite also in the polymethallic period, in which together with pyrite also chalcopyrite, sphalerite, galenite and from non-metalliferous minerals calcite, quartz and chlorite are found. From this period microhardness of pyrite 22 was measured. Pyrite is also very much represented in ore mineralization, which is at some localities (Rumlovská, Alžbeta and Rozália) spatially connected with skarn mineralization, but genetically belongs to younger hydrothermal mineralization of subvolcanic vein deposits of the Štiavnica-Hodruša ore district. From this mineral filling, where together with pyrite mainly calcite and quartz are present, was measured pyrite 24. In Mg skarns (F. Z á b r a n s k ý 1968) pyrite forms together with chalcopyrite, calcite, quartz and chlorite the youngest mineral association. From it microhardness of pyrite 21 was measured.

Pyrite belongs among minerals characterized by wide dispersion of microhardness values, which depends on many factors (geochemical, physical, crystallographical, mechanical etc.). Pyrites in which microhardness was measured, are characterized by quite varied association of microelements, but to stable microelements belong Ni and Co, according to B. C a m b e l and J. J a r k o v s k ý (1967) the ratio of Co : Ni is 1 : 0.01. According to the mentioned authors is the ratio Co : Ni also similar at subvolcanic deposits of the West Carpathians.

In spite of expectation, regarding to known wide dispersion of microhardness values of pyrites, microhardness of pyrites from skarn deposits of various periods does not show wide dispersion of values. If we do not take into consideration the relatively low value of microhardness of pyrite 19 (1170 kg/mm²), probably caused by more considerable overgrowing of pyrites with chalcopyrites and microhardness of pyrite

24 (1368 kg/mm^2), belonging to the mineral association, genetically connected with hydrothermal subvolcanic mineralization, the values of pyrites vary within the interval 1283.4—1321.7 kg/mm^2. This fact can be used in solving genesis of skarn deposits on the basis of determined microhardness values, similarly as mentioned by M. H á b e r (1965) also for other genetic types of deposits. This question is necessary to examine also at other skarn deposits, taking into regard the factors influencing microhardness.

Magnetite at skarn deposits of the Štiavnica „island" is the most wide spread ore mineral. It is present in Ca skarns (prevailingly garnet, more rarely garnet-pyroxene ones) as well as in Mg skarns. In Ca skarns it is mostly found as small veins of various density frequently, however, forms layers of almost compact aggregate. In Mg skarns it is mostly present in the form of scattered idiomorphic and hypidiomorphic grains, more rarely it forms network of small veins. Magnetites from individual localities show relatively uniform character of the content of microelements. The invariable content of Ti, Sn, Mn, Co, Zn and Cu and in magnetites of Mg skarns also of Cr and vice versa the absence of Mo, B, V and Ni (F. Z á b r a n s k ý 1968) is typical. Microhardness of magnetites from the skarn deposits of the Štiavnica „island" varies within the intervals of 577.6—628.9 kg/mm^2 and is in good accordance with microhardness values mentioned by various authors [F. M. N a k h l a (1956) 882, E. P ä r n a m a s a (1963) 480—585, S. B o w i e, K. T a y l o r (1958) 530—599, B. B. Y o u n g, A. P. M i l l m a n n (1964) 490—660, S. J. L e b e d e v a (1963) 535—695 kg/mm^2]. Higher microhardness values were found out in magnetites present as isolated grains in silicate Mg skarn and that in magnetites no. 31 (622.2 kg/mm^2) and no. 32 (628.9 kg/mm^2) while magnetites in veinlets and compact coarse-grained aggregate show relatively stable values (577,6—611,8 kg/mm^2). This fact probably is not connected with different representation of microelements, but with slight martitization of isolated grains at their rims.

Microhardness values of minerals as hematite, chalcopyrite, sphalerite, galenite and calcite are in good accordance with the values mentioned in literature and do not show any differences.

At flogopite we also find good accordance with data known from literature. Because of the lack of data in literature, however, it is not possible to compare minerals as epidote, fassaite, olivine and pleonaste. Quite for orientation it is possible to compare microhardness of pleonaste 1391.2 kg/mm^2 (no. 10 in tab. 2) and 1451.6 kg/mm^2 (no. 11) with that of chromspinel (S. I. L e b e d e v a 1963—1317—1366 kg/mm^2), even when such comparison is problematic as well comparison of microhardness of fassaite (no. 6) 950 kg/mm^2 with spodumene (S. I. L e b e d e v a) 948—1176 kg/mm^2 and aegirine 764—824 (S. I. L e b e d e v a 1963).

Translation by J. P e v n ý.

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Review by B. C a m b e l.