KATARÍNA JAKABSKÁ, GEJZA M. TIMČÁK, EMÍLIA FIAČANOVÁ, MARGITA ČINČÁROVÁ*

THE RELATION OF MICROHARDNESS TO THE PHYSICAL AND CHEMICAL PROPERTIES OF GARNETS FROM VOLCANIC ROCKS OF THE WEST CARPATHIANS

(Fig. 1—10)

Abstract: The paper investigates the possible relations between microhardness, chemical composition, unit cell edge length, specific gravity and refractive index of Slovakian garnets from andesites, rhyolites, rhyodacites and mica schists. The microhardness of these garnets varies from ~ 1000 to ~ 1300 kg/mm^2. It was found that with the increase of the n, a_0 or γ values, the microhardness of the garnets under study decreased. The andraditic component had a positive effect on the microhardness. The quantitative relation between the elements present in the garnets and their microhardness is shown in fig. 4a—4c and Tab. 2, 5.

Резюме: В статье подается суммаризация результатов измерения микротвердости, индекса преломления, элементарной ячейки и уделного веса некоторых гранатов Западных Карпат. Влияние редких элементов на микротвердость не проявляется выразительно, влияние главных окислов более выразительное. С повышением данных n, a_0, γ микротвердость падает. Результаты показывают существенное значение альмадинового состава в анализируемых гранатах. Влияние части альмадина на микротвердость положительное. Количественное соотношение отдельных элементов в гранатах и микротвердость приводится на фиг. 4a—c и таб. 2, 5.

Introduction

This paper deals with the relation between the chemical composition, unit cell edge length, refractive index, specific gravity and microhardness of garnets from andesites, rhyolites, rhyodacites, micaschists from Burzovo, Brezina, Pomjaslo, Šariš, Šiatoroš, Tisovec, Záhradné; Beňatiná, Lesné, Kyslinky and Hnúšťa as well as of garnets from mineral concentrates (from Dukovce, Giraltovce, Poľana and Rikynčice; cf. Fig. 1).

The texture of the investigated garnets, as shown in Figs. 10a—10d, is to a great extent a product of grinding and polishing procedure. The proportion of disintegrated grains in the garnet concentrate depends on their history and on the used microseparation technique. In the concentrates many grains were found to be physically integrated (eg. Fig. 10e). For microhardness measurement disintegrated grains (mounted in a synthetic resin) offer a more random population of section surfaces than the integrated ones.

The relation of the chemical composition of garnets and that of their parent rocks are not detailed as they are treated in another paper by J. Šalát et al (1973) and R. Brousse et al (1972).

Separation of garnets

As polished rock section usually did not provide a sufficient number of grains for statistically correct microhardness measurements, and as we had to determine their

* Ing. M. Jakabská, Ing. G. M. Timčák, Ing. E. Fiačanová, Ing. M. Činčárová, Mineral Research Laboratory of the Košice Technical University, Švermova 5c, Košice.

chemical and physical properties, too, the garnets had to be separated from their parent rocks. For separation 50 kp samples were used. The samples were comminuted and the 0.1—0.2 mm fraction was used for separation on riffles, dry (isodynamic) magnetic separators and in heavy liquids. The garnet concentrate was semimanually after-cleaned (G. M. T i m č á k 1968) to ensure maximum purity (cf. Fig. 2). Trace amounts of dark inclusions present in some grains could not be separated.

Fig. 1. Sample sites location. 1 — Záhradné, 2 — Brezina, 3 — Šiatoroš, 4 — Tisovec, 5 — Šariš, 6 — Burzovo, 7 — Pomjaslo, 8 — Lesné, 9 — Beňatiná, 10 — Kyslinky, 11 — Hnúšťa, 12 — Rikyněice, 13 — Dukovce, 14 — Giraltovce, 15 — Poprad, 16 — Poľana.

Microhardness testing

For all the tests the PMT-3 microhardness tester (Tab. 1.) was used (S. I. L e b e d e v a 1963, K. H o r m u t h 1963). The garnet grains were embedded in „Dentakryl" synthetic resin. Part of the measurements was performed on polished rock sections. The spatial orientation of the investigated garnets did not show any preferred orientation and was therefore considered to be random. On every garnet population up to 50 measurements were taken (cf. S. I. R i b a l k o 1965). Only uncracked individuals (or areas) were tested.

The test results were statistically treated according to the method given by F. Z á b r a n s k ý and J. D r a b a n t (1970). The character of the microhardness frequency distribution for the investigated garnet types before and after statistical treatment is

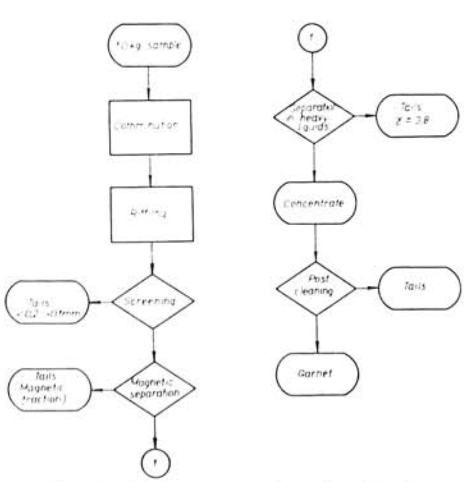


Fig. 2. Garnet separation flowsheet.

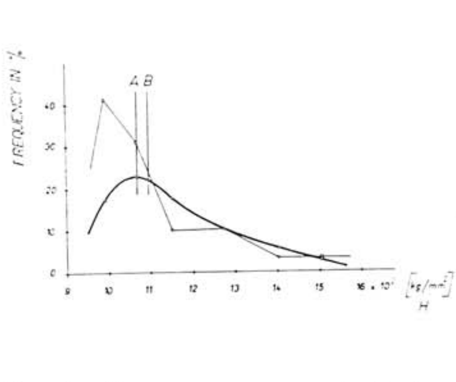


Fig. 3. Frequency versus microhardness plot for garnets from Poľana. Heavy line — values after the statistical treatment of the measured data. A — mode, B — mean.

shown in Fig. 3. The frequency curves showed a tendency for negative skewness, but in the central area they could be approximated to normal distribution. All the distribution curves were unimodal. For further investigations the modal microhardness values were used. All the microhardness values, both modal and mean, are given in Tab. 2. They cover a range from ~ 1000 to ~ 1300 kg/mm². This is in accordance with data given by S. I. Lebedeva (1963) and F. Zábranský and J. Drabant (1970).

Chemical analysis of garnets

The separated garnets were used for wet chemical and qualitative spectrochemical analysis (cf. Tab. 3,5). The chemical composition of garnets is given in Tab. 3. The wet chemical analysis data of parent rocks were taken from J. Šalát et al (1973).

The relation between the SiO_2, CaO, MgO, TiO_2, Al_2O_3, FeO, MnO, $(Na_2O + K_2O)$ and P_2O_5 content an the microhardness is given in Figs. 4a—4c. The graphical evaluation shows that the increase of CaO, FeO, $(Na_2O + K_2O)$, as well as SiO_2, TiO_2 and P_2O_5 contents tends to have a positive effect on microhardness, whereas an

Table 1. The specification of the used microhardness tester and the test conditions

Instrument type	PMT-3
Manufacturer	Optical Laboratories, USSR
Indenter	diamond
Indenter form	$\frac{1}{2}$ octaeder ∢ 136°
Weight	100 g
Indentation time	5 sec.

Table 2. The measured microhardness data after statistical treatment

No.	Site	The number of analysed samples	Number of measurements	Modal microhardness (read from the smoothed frequency curve)	Mean values of microhardness kg/mm²
1	Záhradné	4	40	1270,00	1303,5
2	Brezina	2	40	1150,00	1209,1
3	Šiatoroš	3	40	1300,00	1325,3
4	Tisovec	4	40	1305,00	1295,8
5	V. Šariš	4	50	1255,00	1301,7
6	Burzovo	3	39	1200,00	1254,7
7	Pomjaslo	4	40	1240,00	1283,0
8	Lesné	2	40	1265,00	1285,7
9	Beňatina	3	40	1230,00	1258,9
10	Kyslinky	4	40	1170,00	1247,1
11	Hnúšťa	4	45	1200,00	1247,4
12	Rikynčice	1	31	1045,00	1080,03
16	Poľana	1	29	1070,00	1097,31

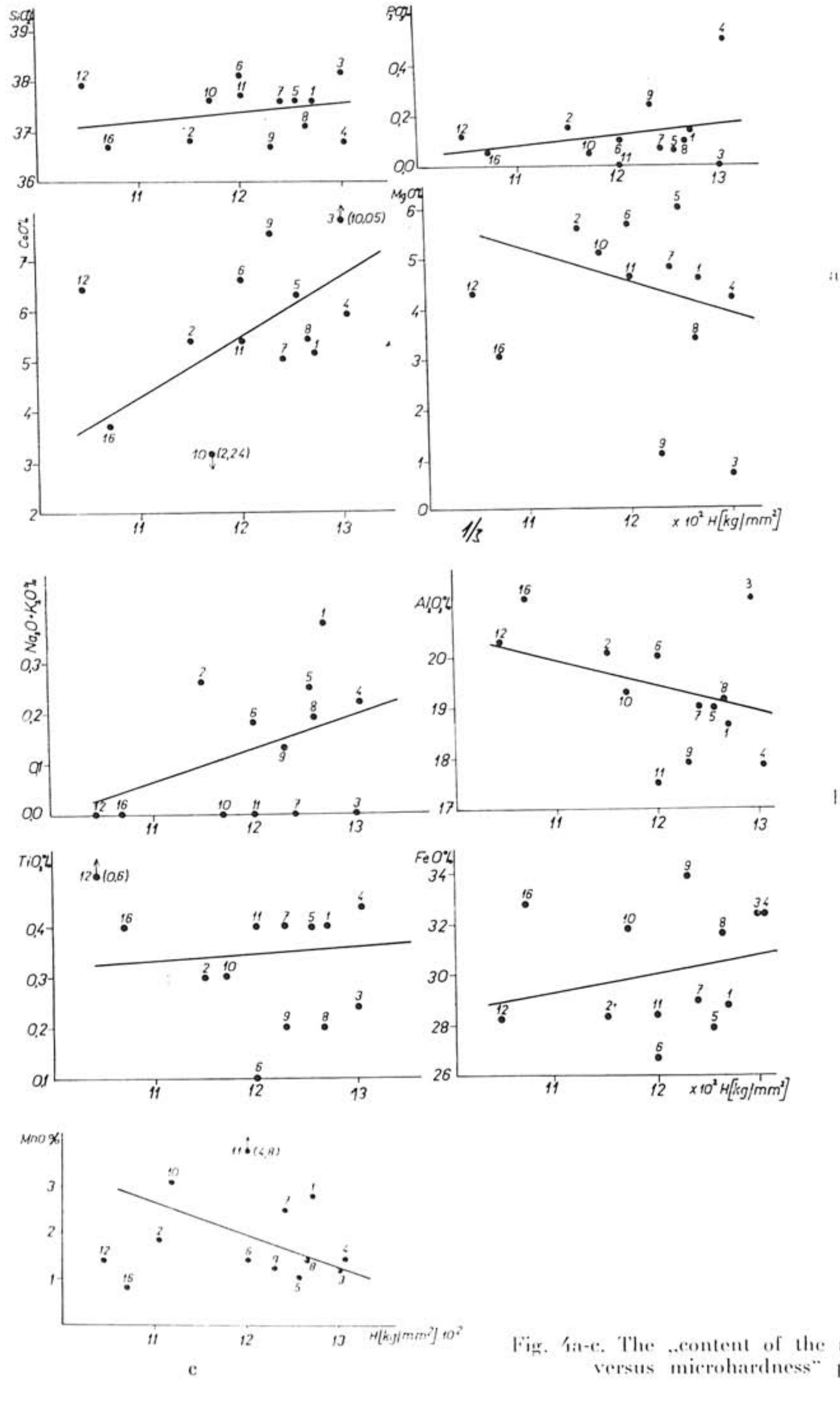


Fig. 4a-c. The „content of the major oxides versus microhardness" plots.

Table 3. Wet chemical analysis data of the investigated garnets (in WPC)

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Code No.	9/68	10/68	12/68	13/68	47/68	48/68	51/68	8/68	11/68	49/68	50/68	23/69	24/69	25/69	26/69	27/69
SiO_2	37,60	36,80	38,13	36,84	37,60	38,12	37,56	37,10	36,66	37,60	37,74	37,90	37,40	37,08	37,10	36,70
TiO_2	0,40	0,30	0,24	0,44	0,40	tr.	0,40	0,20	0,20	0,30	0,40	0,60	0,60	0,40	0,60	0,40
Al_2O_3	18,66	20,50	21,25	17,85	19,02	20,00	19,07	19,17	17,90	19,33	17,47	20,30	17,96	19,83	19,73	21,07
Fe_2O_3	6,46	4,20	2,47	7,20	6,76	2,52	3,82	6,43	5,70	3,76	5,36	1,32	4,36	3,26	2,55	4,81
FeO	22,96	24,40	26,12	24,32	21,84	24,40	25,57	25,84	28,73	28,44	23,57	27,00	27,60	28,42	29,65	28,43
MnO	2,80	1,84	1,20	1,68	1,06	1,40	2,52	1,40	1,24	3,12	4,80	1,40	2,84	2,53	2,53	0,85
MgO	4,60	5,50	0,74	4,22	6,00	5,66	4,76	3,36	1,08	5,12	4,64	4,28	4,56	4,16	4,08	3,04
CaO	6,17	6,40	10,05	6,92	7,30	7,64	6,06	6,43	8,52	2,24	6,38	7,40	5,04	4,48	4,16	4,70
Na_2O	0,23	0,16	—	0,12	0,18	—	—	0,10	0,08	—	—	—	—	—	—	—
K_2O	0,15	0,10	—	0,10	0,07	0,18	—	0,08	0,05	—	—	—	—	—	—	—
P_2O_5	0,14	0,15	—	0,50	0,06	0,10	0,07	0,10	0,24	0,05	—	0,12	0,02	0,02	0,02	0,05
CO_2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
S	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H_2O^+	—	—	—	—	—	0,25	—	—	—	—	—	—	—	—	—	—
H_2O^-	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Σ	100,17	100,35	100,20	100,19	100,29	100,27	99,83	100,21	100,40	99,96	100,36	100,32	100,38	100,18	100,42	100,15

Table 4. The end member molecule calculation of the investigated garnets

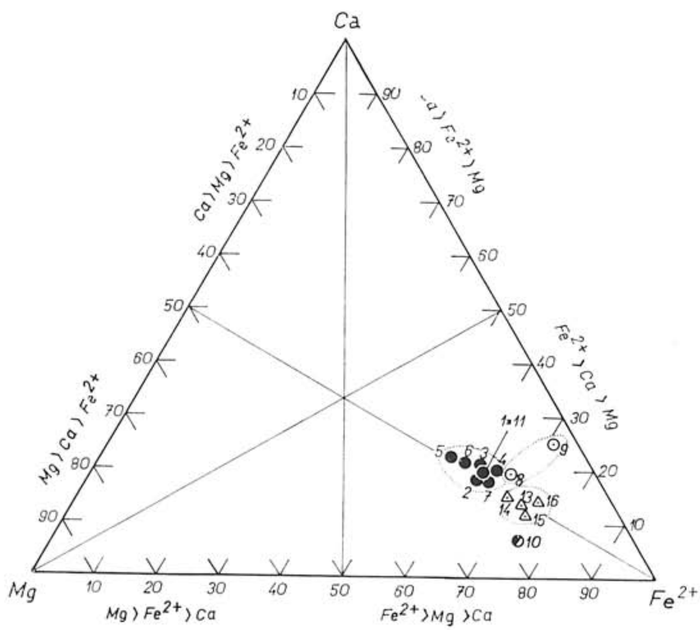
No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Site	Záhradné	Brezina	Šiatoroš	Tisovec	V. Šariš	Burzovo	Pomjaslo	Lesné	Beňatina	Kyslinky	Hnúšťa	Rikynčice	Dukovce	Giraltovce	Poprad	Poľana
Code No.	9/68	10/68	12/68	13/68	47/68	48/68	51/68	8/68	11/68	49/68	50/68	23/69	24/69	25/69	26/69	27/69
Garnets from	Andensite							Rhyolite	Rhyolite	Rhyodacite	Mica schist	Mineral concentrates				
Al	57,94	55,20	58,46	59,32	53,48	54,72	58,28	64,86	67,95	66,43	52,48	59,28	61,28	64,72	66,15	72,17
P	18,20	22,08	17,27	16,90	23,56	22,58	18,84	13,46	4,34	20,17	18,44	16,77	18,05	16,68	16,25	12,22
Sp	6,30	4,20	5,01	3,84	2,40	3,24	5,64	3,18	2,84	7,07	10,90	3,15	6,35	5,75	5,70	1,95
An	9,10	1,26	12,46	15,03	10,64	7,72	8,61	9,20	13,73	6,33	15,42	3,87	13,21	8,72	7,70	2,92
G	8,46	17,26	6,80	4,91	9,92	11,74	8,63	9,30	11,14	—	2,76	16,93	1,11	4,13	4,20	10,74
Σ	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

Table 5. The results of quantitative spectrochemical analysis of the investigated garnets

NO	CODE	SITE	QUALITATIVE SPECTROCHEMICAL ANALYSIS																							
			Al	Fe	Si	Ca	Mg	Mn	Ti	Sc	Y	Zn	V	Co	Cr	Bi	Cu	Ga	Pb	B	Yb	Na	Ba	Tl	Zr	Ni
8	M1/67	LESNÉ	●	●	●	⊙	⊙	⊙	⊕	Φ	Φ	Φ	O		O	O	O	O	O		O					
9	M4/67	BEŇATINÁ	●	●	●	⊙	⊙	⊙	⊕	O		Φ	O	O	O		O	O	O		O	O				
3	M1/68	ŠIATOROŠ	●	●	●	⊙	⊙	⊙	⊕	O		Φ	O		O		O	O			O	O				
4	M2/68	TISOVEC	●	●	●	⊙	⊙	⊙	⊕	Φ	Φ	Φ	Φ	O	O		O	O			O	O	O			
2	M3/68	BREZINA	●	●	●	⊙	⊙	⊙	⊕			Φ	O		O		O	O			O	O				
7	M4/68	POMJASLO	●	●	●	⊙	⊙	⊙	⊕			Φ	O		O		O	O			O	O				
5	M5/68	ŠARIŠ	●	●	●	⊙	⊙	⊙	⊕	Φ	Φ	Φ	O	O	O		O	O			O	O				
15	M7/68	POPRAD	●	●	●	⊕	⊕	⊙	⊕	Φ	Φ	Φ			O		O	O				O				
6	M8/68	BURZOVO	●	●	●	⊙	⊙	⊙	⊕				O				O				O	O				
10	M9/68	KYSLINKY	●	●	●	⊙	⊙	⊙	⊕		Φ	Φ	O		O			O	O		O	O			Φ	
11	M10/68	HNÚŠŤA	●	●	●	⊙	⊙	⊙	⊕	Φ		Φ	O		Φ		O		O		O	O		O		O

● 100 – 10 %   ⊙ 10 – 1 %   ⊕ 1 – 0,1 %   Φ 0,1 – 0,01 %

O 0,01 – 0,001 %



● Andesite   ⊙ Rhyolite   ◑ Rhyodacite   ▲ Mica schist

△ Mineral concentrates

Fig. 5. The Ca-Mg-Fe diagram of the investigated garnets.

increase of the MgO, Al_2O_3 and MnO content has a negative effect. Thus it can be concluded that the andraditic component significantly contributes to the increase of garnet microhardness. These experimental results are in accordance with the results obtained through the (normalised) end member calculation (using the wet chemical analysis data), given in Tab. 4 (C. Burri and I. Parga-Pondal 1936, P. C. Rickwood 1966).

It was found that in the Mg-Ca-Fe diagram (K. Smulikowski 1965) garnets from andesites fall along the Fe > Ca > Mg and Fe > Mg > Ca border line; garnets from rhyolites are shifted towards the Fe > Ca > Mg area and garnets from rhyodacite fall close to the Fe > Mg > Ca area (Fig. 5). The correlation of the chemical composition of parent rocks and the garnets (cf. P. C. Rickwood et al 1968, J. Šalát et al 1973, A. Sriramadas 1957) is given in Fig. 6, where the corresponding pairs of values are joined by lines. A correlation between these two types of parameters exists, is comparatively well defined and is a subject of our further investigation.

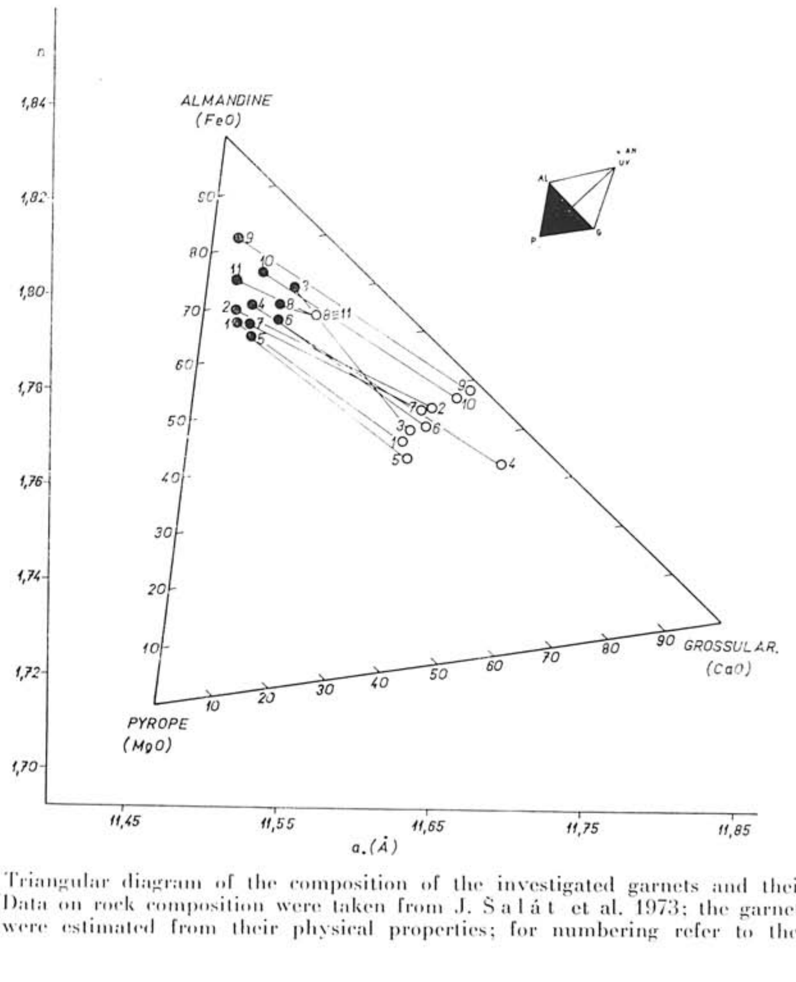


Fig. 6. Triangular diagram of the composition of the investigated garnets and their parent rocks. (Data on rock composition were taken from J. Šalát et al. 1973; the garnet compositions were estimated from their physical properties; for numbering refer to the tables.)

To establish the effect of trace elements on microhardness, the garnets were spectrochemically analysed (Tab. 5). The possible effect of Pb, Sc, Y and Co was investigated. The presence of Pb seems to have a positive effect on microhardness and the presence of Y a negative one. The other elements did not show any well defined effect.

Measurement of specific gravity, unit cell edge length and refractive index

The specific gravity of garnets was determined pycnometrically. The measured data are shown in Tab. 6. The refractive index was established using the minimum deviation method (in methylene iodide and West's solution) (R. Rost 1956).

The unit cell edge length was determined by X-ray powder photography (V. Radzo 1964, K. I. Sztrókay et al 1970), using a MIKROMETA I (type instrument Chirana, Czechoslovakia). The technical details are listed in Tab. 7. The films were measured by 3 operators independently on a Chirana measuring rule. The films and

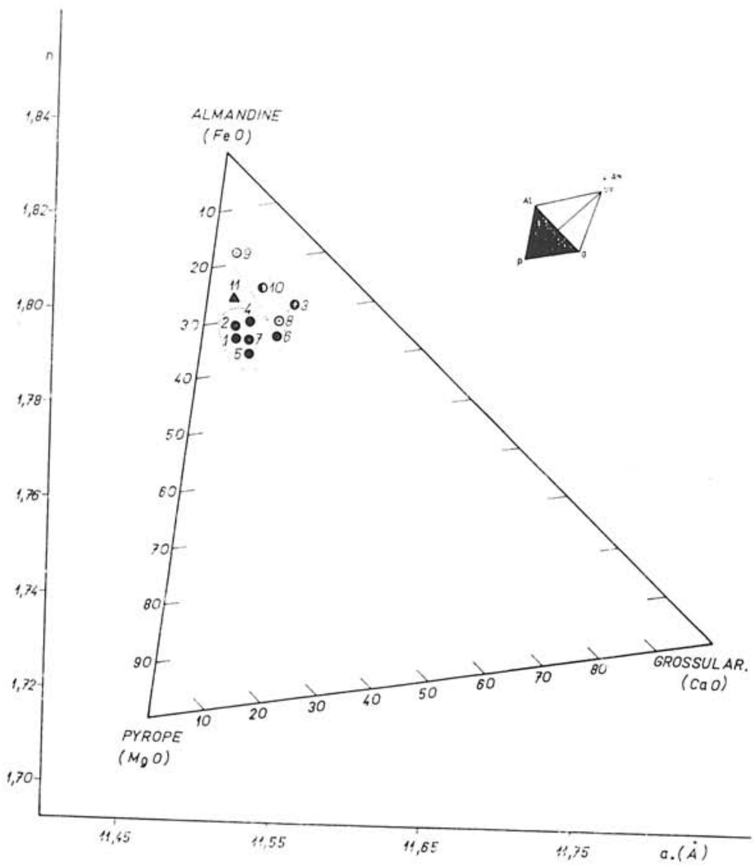


Fig. 7. Graph of refractive index (n) versus unit cell edge length (a_0) of the investigated garnets.

records have been permanently stored in Mineral Research Laboratory of the Košice Technical University. The theoretical unit cell edge lengths were calculated from the wet chemical analysis data. The experimentally determined and calculated values were not identical. This results — to a great extent — from the simplifications necessary for

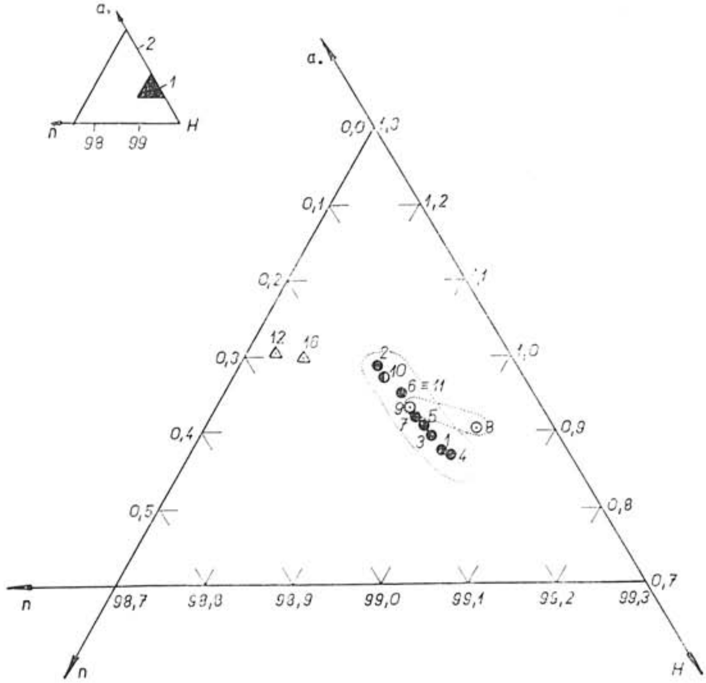


Fig. 8. The n-a_o-H triongle of the investigated garnets. Garnets from each rock type are located in well defined regions.

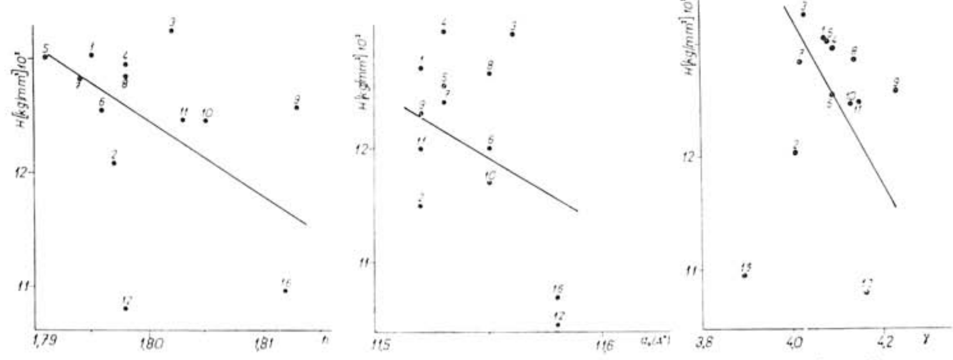


Fig. 9a-b. Graphic presentation of the relations between the physical properties of garnets (n, a_o, γ) and their microhardness.

the theoretical calculation (P. C. R i c k v o o d 1968, P. C. R i c k w o o d et al 1968, E. T r ö g e r 1959, N. V. S o b o l e v 1964). For further considerations we used the experimentally measured data.

The refractive index and unit cell edge length values were plotted in a modified

Fig. 10. Microphotographs of typical garnets (polar //, magnif. 75 ×). Photo J. O r č í k.

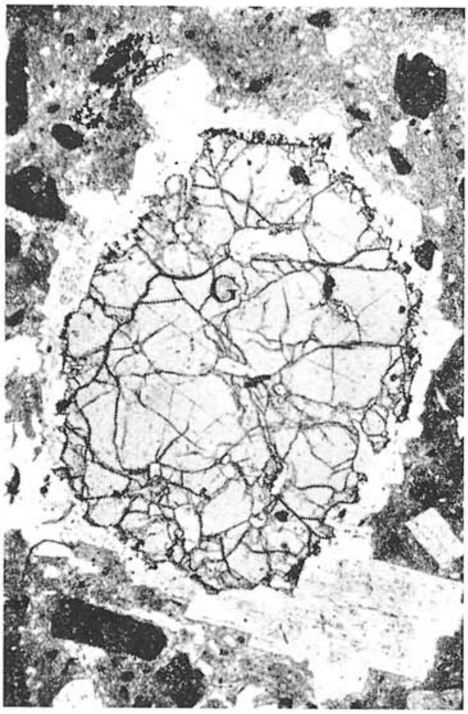


Fig. 10a. Garnet in andesite from Brezina.

Fig. 10b. Garnet in rhyolite from Lesné.

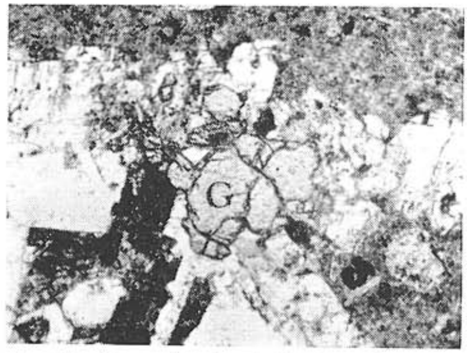


Fig. 10c. Garnet in rhyodacite from Kyslinky.

Fig. 10d. Garnet in mica schist from Hnúšťa.

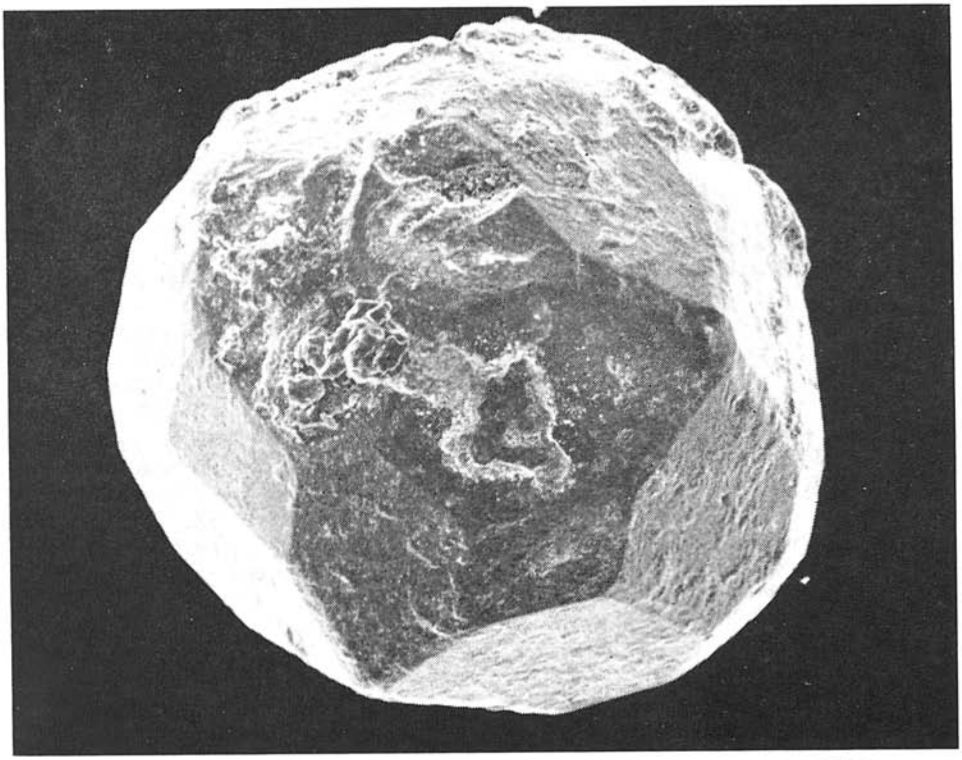


Fig. 10e. Garnet from rhyolite. SEM image, JXA 50 A, 300 ×. Photo: JEOL.

T a b l e 6. Physical properties of the investigated garnets

No	Code No	Site	Garnets from	Specific gravity	Refractive index	Unit cell edge length	
						Calculated	Measured
1	9/68	Záhradné	andesite	4,0782	1,795	11,62	11,52
2	10/68	Brezina	andesite	4,0111	1,797	11,61	11,52
3	12/68	Štiatoroš	andesite	4,0296	1,802	11,63	11,56
4	13/68	Tisovec	andesite	4,0891	1,798	11,64	11,53
5	47/68	V. Šariš	andesite	4,0807	1,791	12,62	11,53
6	48/68	Burzovo	andesite	4,0899	1,716	11,67	11,55
7	51/68	Pomjaslo	andesite	4,0226	1,794	11,62	11,53
8	8/68	Lesné	rhyolite	4,1452	1,798	11,63	11,55
9	11/68	Beňatina	rhyolite	4,2341	1,813	11,67	11,52
10	49/68	Kyslinky	rhyodacite	4,1360	1,805	11,58	11,55
11	50/68	Hnúšťa	mica schist	4,1493	1,803	11,63	11,52
12	23/69	Rikyněice	mineral conc.	4,1650	1,798	11,62	11,58
13	24/69	Dukovce	mineral conc.	4,2193	1,795	11,62	11,57
14	25/69	Giraltovce	mineral conc.	4,4720	1,809	11,61	11,55
15	26/69	Poprad	mineral conc.	4,0266	1,791	11,60	11,58
16	27/69	Poľana	mineral conc.	3,8993	1,812	11,61	11,58

Table 7. X-ray powder photography conditions

Film	ORWO 17° DIN
X-ray generator	Mikrometa 1 (camera radius R = 64 mm)
Tube	Co target run at 28kV and 18mA
Exposure time	Co (Fe filter) — 6 hours
Development	ORWO-R 09 (1 : 50) at 18° ± 1 °C
Drying	Air dried

A. Sriramadas — H. Winchell diagram (A. Sriramadas 1957, H. Winchell 1958, P. C. Rickwood et al 1968). The results (Fig. 7) indicate a high almandine content. This corresponds with the results given in Tab. 4.

The relation between refractive index, unit cell edge length and microhardness is shown in Fig. 8, where garnets from the particular types of parent rocks occupy well defined areas.

A more detailed analysis of the relation between refractive index, unit cell edge length, specific gravity and microhardness is given in Fig. 9a—9b. With increasing refractive index, unit cell edge length and specific gravity the microhardness of the investigated garnets decreased.

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