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CHEMICAL COMPOSITION OF ORTHOPYROXENES IN SOME ANDESITES OF CENTRAL SLOVAKIA

(Fig. 1—5)

Abstract. Orthopyroxenes in andesite rock types of central Slovakia are very wide-spread and usually in paragenesis of several femic minerals. Commonly the Mg-constituent predominates in them, which is markedly the highest in leucoandesites, whilst in association with clinopyroxenes, amphiboles, biotites or garnets they contain a distinctly less frequent Mg-constituent. The Ca-constituent of orthopyroxenes is insignificantly higher than in other types in one andesite type only.

Резюме: Ортопироксены в разных типах андезитовых пород в средней Словакии очень распространенны и обыкновенно находятся в парагенезисе нескольких фемических минералов. Как правило в них часто повышенное содержание магнезия, выразительное количество, которое появляется в лейкоандезитах, пока что в ассоциации с клинопироксенами, роговой обманкой, биотитами или гранатами содержание магнезия ясно низкое. Ca-часть ортопироксенов исключительно только в одном случае в андезите выше чем у остальных пород.

Very wide-spread femic minerals, occurring mostly in the form of more or less well-developed idiomorphic phenocrysts in many rocks of andesite composition in central Slovakia, are orthopyroxenes. In some rocks they are represented only as a single femic porphyric phenocryst, however, usually they are a member of the association of several femic prophyric phenocrysts as e. g. of clinopyroxenes, amphiboles, biotites and garnets. Orthopyroxenes and, as naturally, also other femic minerals are present, beside phenocrysts, also as smaller individuals, often in the shape of microlites.

The modal content of orthopyroxenes is not equal in all varieties of andesite rocks. For instance, some two-pyroxene andesites contain about 10 % orthopyroxenes, 3-4 % clinopyroxenes; amphibole-pyroxenic andesites have about 3-5 % orthopyroxenes; about 1-2 % clinopyroxenes; leucocratic andesites are characterized by an abnormally low content of femic phenocrysts, orthopyroxenes together around 1 %. In andesite tuffs and ignimbrites orthopyroxenes also form variable modal contents.

According to the chemical composition of the investigated orthopyroxenes there are predominantly hypersthenes and in two cases also bronzites. In one case a pyroxene very close to the rhombical pyroxene is concerned, which, however, according to H. Hess (1951) is already found in the field of clinopyroxenes-pigeonites.

The chemical composition of orthopyroxenes results from complete silicate analyses of minerals separated under the binocular microscope or from analyses of minerals by the electron microprobe. (Tab. 1.) They are from the following rocks:

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	1		2		3		4		5	
Locality: Analyst: Method:	Bukovinka Andesite Amf-Bi-Hy-Gr Zd. Kotrba microprobe		Podzámčok Andesite Amf-Hy E. Sůrová separated grains		Babiná Andesite Amf-Hy E. Sůrová separated grains		Dekýš Andesite Amf-Hy Jakeš separated		Kozelník Andesite Amf-Bi-Hy Jakeš separated	
SiO_2	53,85		41,85		46,05		49,21		49,03	
TiO_2	—		1,10		0,75		0,68		0,43	
Al_2O_3	0,59		5,96		4,89		1,38		1,25	
Fe_2O_3	—		11,73	36,32	9,39	33,06	1,83	28,17	5,71	31,83
FeO	22,52		12,86		14,28		24,51		20,41	
MnO	—		0,68		0,54		0,84		0,96	
MgO	19,27		20,14		20,80		18,91		18,79	
CaO	0,95		2,44		1,11		1,09		2,12	
Na_2O	—		0,20		0,50		st.		st.	
K_2O			0,19		0,20		st.		0,08	
P_2O_5	—		2,01		0,10		st.		0,26	
H_2O			2,01		1,60					
	97,18		99,66		100,21		98,45		99,04	
Si	2,053	2,05	1,610	2,00	1,749	1,96	1,911	1,97	1,890	1,94
Al	—		0,390		0,219		0,063		0,057	
Al	0,028		0,195		—		—		—	
Ti	—		0,032		0,020		0,020		0,013	
Fe^{3+}	—		0,340		0,269		0,054		0,166	
Fe^{2+}	0,715	1,97	0,414		0,454		0,796		0,658	
Mn	—		0,023	1,90	0,016	2,03	0,027	2,03	0,031	2,04
Mg	1,197		0,753		1,177		1,094		1,080	
Ca	0,039		0,102		0,046		0,045		0,088	
Na	—		0,014		0,036		—		—	
K	—		0,009		0,009		—		0,004	
P	—		0,018		0,005		—		—	
Fe	36,65		46,86		37,15		45,50		41,31	
Mg	61,35		46,80		60,48		52,37		54,25	
Ca	2,—		6,34		2,36		2,13		4,42	
	63,63		53,86		41,34		47,05		44,56	
values of andesite										
SiO_2	59,97 %		56,10 %		54,06 %		59,16 %		59,08 %	
FeO / MgO + FeO	+ 100 = 64		47		49		56		54	
Basicity of plagioclases	An_{50}		An_{50}		An_{60}		An_{50}		An_{45}	

6 7 8 9 10 11 12

Obyce Ignimbrite Amf-Bi-Hy-Aug J. Krištin microprobe		Ignimbrite Amf-Bi-Hy J. Krištin microprobe	Čajkov Tuff Amf-Bi-Hy J. Krištin microprobe		LEK 2 Leucocratic Andesite Hy-Aug. J. Krištin microprobe	
1	2		1	2	1	2
50,67	50,88	49,47	50,52	49,79	53,06	50,51
—	—	0,12	0,14	0,12	0,36	0,30
1,20	0,96	1,46	0,98	0,55	1,46	1,19
26,83	27,80	28,55	21,98	20,04	19,09	13,62
0,56	0,64	0,09	0,54	0,66	st.	st.
19,47	17,94	16,38	18,25	19,12	24,55	26,86
1,55	0,98	1,13	1,01	1,04	1,53	1,37
0,12	1,20	—	—	—	—	—
0,08	0,08	—	—	—	—	—
		—	—	—	—	—
100,43	100,48	97,20	93,42	91,32	100,25	93,85
1,929 } 1,95	1,973 } 2,00	1,980 } 2,00	2,018 } 2,01	2,024 } 2,02	1,949 } 2,00	1,937 } 1,99
0,028	0,028	0,020	—		0,051	0,055
—	—	—	0,048	0,027	0,011	—
—						
		0,016	0,005	0,002	0,011	0,099
0,853	0,899	0,954	0,734	0,681	0,584	0,435
0,018 } 2,04	0,021 } 2,04	0,002 } 1,99	0,017 } 1,93	0,022 } 1,93	— } 2,00	— } 2,12
1,104	1,035	0,976	1,088	1,157	1,344	1,534
0,062	0,042	0,048	0,043	0,047	0,059	0,056
0,004	0,044	—	—	—	—	—
0,002	0,003	—	—	—	—	—
—	—	—	—	—	—	—
42,25	45,50	48,23	39,35	36,13	29,99	21,48
54,68	52,88	49,34	58,34	61,38	67,04	75,75
3,07	2,12	2,43	2,31	2,49	2,97	2,77
42,80	47,06	49,48	41,00	37,86	30,69	22,45
61,60 %			62,83 %		54—57 %	
48			70		74 48	
An_{50}		An_{50}			An_{70}	

1. Hypersthene-amphibolic andesite with garnet and subordinate biotite; quarry Bukovinka in the Karanč-Šiatov massif, south of Fiľakovo, Cerová vrchovina hilly country (E. Karolusová 1972);

2. Hypersthene-amphibolic andesite; borehohe HŠ-1, Neresnica valley near Podzámčok (E. Karolusová 1971);

3. Amphibole-pyroxenic andesite; quarry near Babiná, western foothill of the Javorie Mts.;

4. Amphibole-pyroxenic andesite; quarry south of the community Dekýš, Štiavnické pohorie Mts.;

5. Amphibole-biotitic andesite with pyroxene; railroad cut near Kozelník, Štiavnické pohorie Mts.;

6.—7. Ignimbrite of andesite composition with amphibole, biotite, hypersthene and augite; quarry near the community Obyce, western foothill of the Pohronský Inovec Mts.;

8. Ignimbrite of andesite composition with amphibole, biotite and hypersthene; borehole NBK-15 at the eastern foothill of the Háj massif, eastern margin of the Pohronský Inovec Mts.;

9.—10. Pumice andesite tuff with amphibole, biotite and hypersthene; quarry near the community Čajkov, south-western foothill of the Štiavnické pohorie Mts.;

11.—12. Leucoandesite; borehole LEK-2 near Žemberovce, southern spurs of the Štiavnické pohorie Mts.;

The analyses of orthopyroxene from andesite near Bukovinka locality 1; Tab. 1, analyse 1, and from andesite of Podzámčok locality 2; Tab. 1, anal. 2, are adopted from literature (E. Karolusová 1971, 1972) and compared with orthopyroxenes from new localities.

Chemical composition of orthopyroxenes

The investigated orthopyroxenes have a variable chemical composition, on which also their mineralogical character in the isomorphous series depends (Tab. 1). Most conspicuously are varying in them the contents of SiO_2, mainly with low percentage in orthopyroxenes from andesite of Podzámčok (41.85 %) and from andesite of Babiná (46.05 %). In other analyses SiO_2 varies within the range 49.03—53.85 %. In analyses of orthopyroxenes with the lowest SiO_2 contents, on the contrary, the highest contents are of Al_2O_3 and from andesite of Podzámčok 5.95 % and of Babiná 4.89 % Al_2O_3. In other analyses essentially lower contents of Al_2O_3 are varying within the range 0.55 % — 1.46 %. Critical oxides of the elements Fe, Mg and partly also of Ca predominantly vary in dependence on mutual relations[1]. The highest FeO contents are in analyses from Podzámčok (36.32 %), Babiná (33.06 %) and Kozelník (31.83 %). In other andesite rocks with a polyfemic mineral association they vary within the range 2.04—28.55 %. In leucoandesites the range is 13.62—19.09 %. The MgO contents are in all rocks with polyfemic mineral composition scaled within the range 16.38—20.80 %, however, in leucoandesites they are markedly higher (24.55—

[1] In analyses 1, 5, 7, 8, 9, 10, 11, 12 FeO was established by the microprobe. In analyses 2, 3 4 are determined particularly Fe_2O_3 and FeO by silicate analysis. In further calculation Fe_2O_3 is recalculated to FeO.

26,86 %). CaO forms the lowermost contents, among which, however, the higher content in the analyses from Podzámčok (2.44 %) is prominent only. In other analyses they are varying within the range 0.95—2,12 %. In some analyses also other oxides (Na_2O, K_2O, P_2O_5 or H_2O), present in orthopyroxenes only as unessential elements, are established.

In Table 1 the analyses have been recalculated to 6 oxides.

As already mentioned in the introduction, on the basis of pyroxene classification the investigated orthopyroxenes are members of the isomorphous series hypersthene-bronzite and in one case on the basis of two constituents pigeonite composition is apparent (A. Poldewart — H. H. Hess 1951).

The series of hypersthenes includes the majority of analysed orthopyroxenes. In the classification of pyroxenes according to A. Poldewart — H. H. Hees (1951) for rhombical hypersthenes the quantitative range 30—50 mol. %, $FeSiO_3$ to 0—5 mol. %, $CaSiO_3$ is delimited in the triangle $MgSiO_3$ — $FeSiO_3$ — $CaSiO_3$ (Fig. 1). Included are here the analyses of andesite from Bukovinka (no. 1.), Babiná (no. 3.), Dekýš (no. 4.), Kozelník (no. 5.), two analyses from ignimbrite of Obyce (no. 6, 7) and two analyses of andesite pumice tuffs from Čajkov (no. 9, 10). The analyse of ignimbrite from borehole NBK-15 (no. 8) lies in its composition at the boundary of iron and magnesium in the triangle Fe — Mg — Ca at the boundary of hypersthene and ferrohypersthene (Fe 48,23 %, Mg 49,34 %, Ca 2,43 %). In all rocks (beside the later) hypersthenes are characterized by mol. % Fe within the range 45,50—36,65 %, Mg 61,38—52,37 %, Ca 4,42—2,0 %. On the whole, hypersthenes from the studied rocks are characterized by the relation Mg > Fe and in Ca content the range is objectively limited to 0,0—5,0 % only.

Orthopyroxenes of bronzite composition are resulting from analyses of leucoandesite (borehole LEK-2), indicated by a distinct higher content of MgO. In the classification triangle (Fig. 1, anal. 11 and 12) Mg attains 67,04—75,75 %, Fe 29,99—21,48 %, Ca 2,77—2,97 %, so markedly they are distinguished from hypersthenes due to higher Mg content although it should be stated that

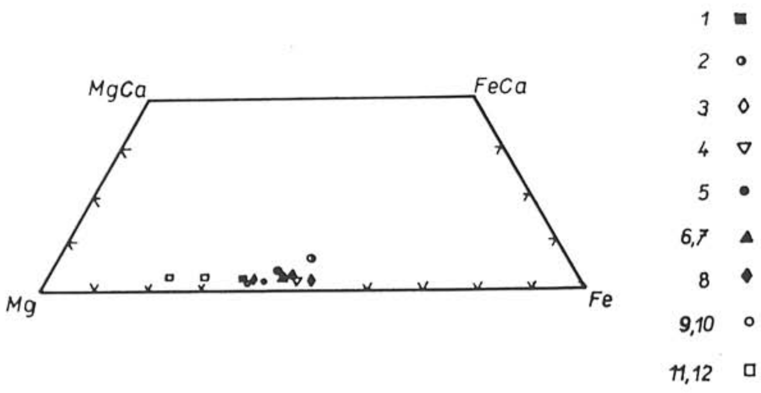

Fig. 1. Ca-Fe-Mg triangle of studied orthopyroxenes. 1 — andesite from Bukovinka; 2 — andesite from Podzámčok; 3 — andesite from Babiná; 4 — andesite from Dekýš; 5 — andesite from Kozelník; 6 and 7 — ignimbrite from Obyce; 8 — ignimbrite from borehole NBK-15 NE of Nová Baňa; 9 and 10 — andesite pumice tuffs from Čajkov; 11 and 12 — leucoandesite from borehole LEK-2 near Žemberovce.

analysis no. 11, according to the Mg content (29,99 %), almost lies at the boundary of bronzite and hypersthene.

Magnesium rhombical pyroxenes are characteristic of rocks of the early crystallization stages of any intrusive bodies (H. H. Hess 1941). They play also an important role in extrusive and effusive volcanics of various composition from basic to acid rocks (F. H. Hatch — A. K. Wells — M. K. Wells 1972). Mostly spread, however, they are in andesites. From the series of magnesium-ferrous orthopyroxenes are common in eruptive rocks enstatite, bronzite and hypersthene as in rapidly cooling rocks they represent the most stable crystalline phases. They crystallize in the process of sinking temperature from 1140 °C in transition from pigeonite, stable under high temperatures. In rapidly cooling lavas pigeonite becomes a metastable mineral.

Pyroxene, close to pigeonite composition (anal. 2), is situated in the classification triangle already in the field of pigeonites on the basis of Ca-constituent 6,34 % whilst Mg and Fe constituents are almost equal, 46,80—46,86 %. Higher Ca-contents in rhombical pyroxenes are also mentioned in literature. H. Kuno (1954) concludes that the content of Ca in rhombical pyroxenes is determined by the temperature, under which their crystallization took place. It has been proved that in rhombical pyroxenes from pyroxenic andesites of the volcano Hakone the number of Ca-atoms is (0,057—0,104) to 6 atoms of oxygen. It is higher than in dacites from the same region (0,045—0,053). L. Atlas (1952) has found the maximum amount of Ca-atoms to 6 oxygen atoms to be 0,115 at the temperature 1100 °C; 0,050 at 1000 °C and 0,030 at 700 °C. The results of the investigations of Schairer and Boyd (1957) also agree with these

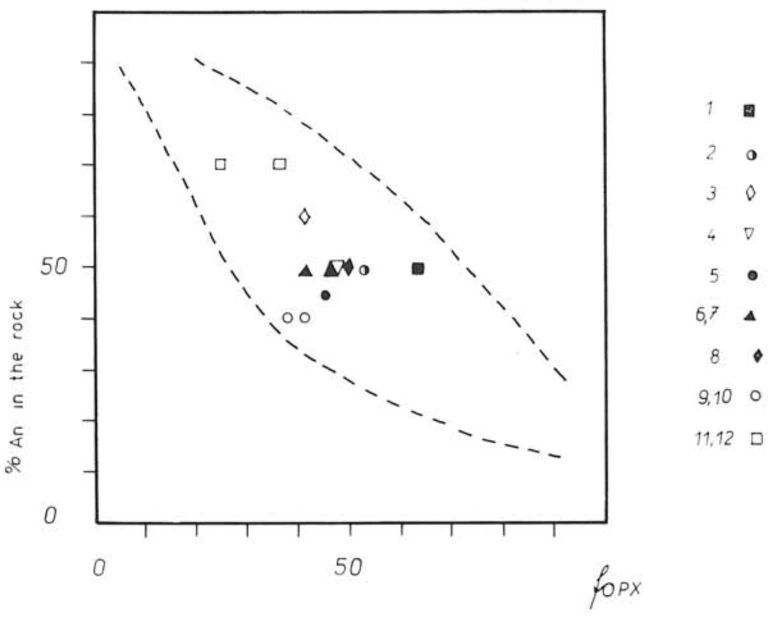

Fig. 2. Diagram of f-value in orthopyroxenes % An in mother rocks. 1 to 12 — see Fig. 1, Tab. 1.

data. H. H. Hess (1952) states that Ca enters the crystal lattice of hypersthenes under conditions of their rapid crystallization.

According to data from literature Ca is almost in hypersthenes of gradually cooling deep rocks.

From this aspect CaO-contents are varying within the range 0,95–2,44 % in the studied analyses of hypersthenes from central Slovakia. After recalculation to atomic amounts these are within the range 0,039–0,102. When compared with data from the volcano Hakone (H. Kuno 1954) only some hypersthenes from central Slovakia agree with those from pyroxenic-andesites in Japan; mostly they are up to the value of Japanese dacites or less.

When applying crystallization temperatures according to Ca-content of atoms in the sense of the above mentioned statements from literature, at the highest temperatures orthopyroxene in andesite from Podzámčok crystallized; other ones crystallized at lower temperatures, i. e. around 1000 °C.

In andesite from Podzámčok the crystallization of orthopyroxene under high temperatures is also confirmed by the high content of aluminum (5,96 % Al_2O_3). It is the highest content of Al_2O_3 in analyses of the investigated hypersthenes; it is objective to state that controlling analyses in the individual grains show differently increased Al_2O_3 contents, e. g. 4,21 %, 4,94 %, 5,44 %, 5,58 %, however, in some around 1,82–1,35 % only. In these ones are also increased CaO contents, around 1,29–0,84 %. They probably crystallized in later stages, at lower temperatures (E. Karolusová 1971).

Correlation of f-value of orthopyroxenes with mother rocks on the basis of its FeO share, character of plagioclase and SiO_2 content

1. $f = \frac{Fe}{Fe + Mg}$ is the value expressed in orthopyroxenes according to N. L. Dobrecov et al. (1971) by relation of the elements

$$\frac{(Fe^{+2} + Fe^{+3} + Mn + Cr + Ti)}{Fe^{+2} + Fe^{+3} + Mg + Mn + Cr + Ti} \cdot 100$$

From correlation of f-values of orthopyroxenes with the character of plagioclasses from rocks result conspicuous relations between mutual composition (Fig. 2). In rocks as leucoandesites with the most basical plagioclasses (An_{70}) orthopyroxenes-bronzites with very low f-values (22,45 and 30,69) are bound. The majority of rocks with An_{50} have variable f-values in orthopyroxenes, varying within the limits 42,08–63,63. Concerned are andesites from Bukovinka, Podzámčok with highest f; lower f-values are in ignimbrites, among which the andesite from Dekýš is situated. A more acid plagioclase and approximately an equal numerical f-value in orthopyroxene displays the andesite from Kozelník (An_{45}, f 44,56). The most acid plagioclasses and adequate low f-values in orthopyroxenes from 11 rocks are in Čajkov tuffs (An_{40}, f 37,83–41,0).

2. $\frac{FeO}{FeO + MgO} \cdot 100$ is the value (N. L. Dobrecov et al. 1971), which expressed the ferro-proportion in ferro-magnesium constituents of the competent rocks. Total dependence of f-values in orthopyroxenes and the ferro-

proportion in mother rocks (Fig. 3) sets out from conspicuous differences in the position of projection points in the diagram. In leucoandesites the ferro-proportion is bound to low f-values of bronzites in andesites. Quite a balanced position of both Čajkov tuffs is conditioned by f-values of orthopyroxenes close to the ferro-proportion of tuffs. f-values of orthopyroxenes with ferro-proportions of other mother rocks are lower, beside andesite from Bukovinka and Podzámčok. The magnitude of both data of the andesite of Bukovinka is almost identical (FeO-proportion 64, f-value 63,63). The ferro-value in andesite from Podzámčok is from all rocks the least (5,47), however, the f-value lies between orthopyroxenes of andesite from Bukovinka and all other rocks. From the mentioned almost for all mother rocks the relation results

$$f\,OPX < \frac{FeO}{FeO + MgO} . 100$$ in mother rocks whilst in andesite from Bukovinka and in andesite from Podzámčok is this relation

$$f\,OPX > \frac{FeO + MgO}{FeO} . 100$$

Beside the two last andesites all rocks are characterized by a higher Fe constituent in rocks than in their orthopyroxenes. Some dispersion exists between them there. In foreign literature on the example of mean values (N. L. Dobrecov et al. 1971) is also mentioned that Fe constituents in pyroxenes are different from mother rocks in dependence on their composition. For instance, in pyroxenes from ultrabasic rocks 10—15 %, from intermediate rocks 25—45 %, and acid rocks 40—45 %.

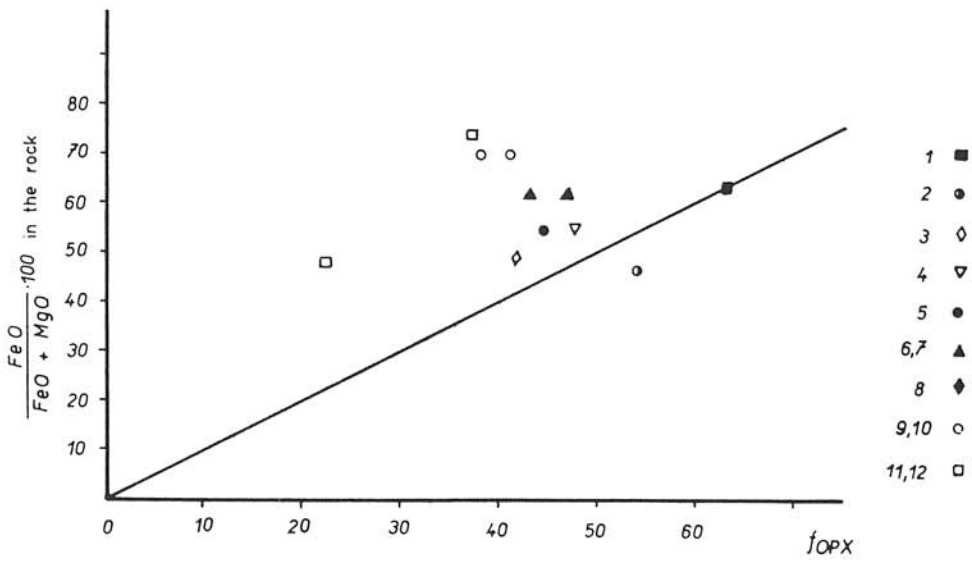

Fig. 3. Diagram of f-value in orthopyroxenes — $\frac{FeO}{Feo+MgO}$. 100 in mother rock. 1 to 12 — see Fig. 1, Tab. 1.

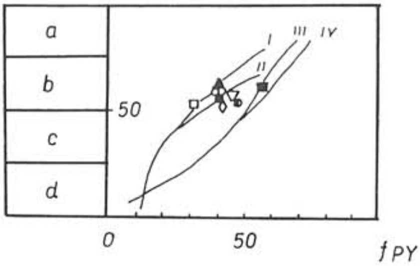

Fig. 4. Dependence of value f of orthopyroxenes on composition of rocks. a — quartzites; b — acid rocks; c — basic and intermediate rocks; d — hyperbasites. I — effusive rocks; II — intrusive rocks; III — high-temperature metamorphites; IV — low-temperature metamorphites. 1 to 12 — see Fig. 1, Tab. 1.

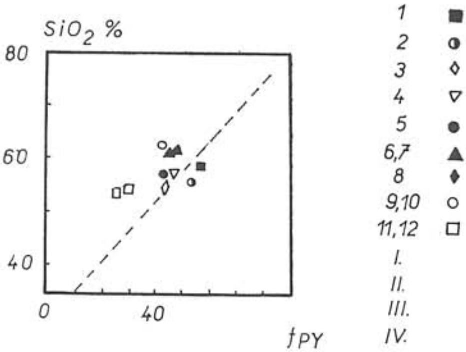

Fig. 5. Dependence of f-value of orthopyroxenes and weight % SiO_2 from mother rock. 1 to 12 — see Fig. 1, Tab. 1.

3. On the basis of this information the analysed orthopyroxenes from leucoandesites in borehole LEK-2 are projected on the curve of intermediate-basic eruptive rocks (Fig. 4). Orthopyroxenes from most rocks are projected on the curve corresponding to acid eruptives. Orthopyroxenes from andesite of Bukovinka are projected on the curve of high-thermal metamorphites. Among the curve of metamorphic and intrusive rocks also orthopyroxene from Podzámčok is projected. This position can be explained perhaps in a way that crystallization of orthopyroxenes of both andesites was under the influence of high pressures and temperatures. High pt conditions are also indicated by garnets present in the andesite from Bukovinka and alumo-hypersthenes in the andesite from Podzámčok.

Correlation of orthopyroxenes to mother rock may be also expressed by means of the ratio of % SiO_2 in mother rocks and f-values of rhombical pyroxenes (Fig. 5). The diagram shows that the analysed orthopyroxenes lie with their projections in the field of effusive and intrusive rocks, in which fact the manifestations of magmatic differentiation can be seen.

Translated by J. PEVNÝ

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Review by A. VARČEKOVÁ