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CONTRIBUTION TO THE RESEARCH OF ZIRCONS FROM GRANITOIDS OF THE ŠTIAVNICKÉ VRCHY MTS. AREA (CZECHOSLOVAKIA)

(7 Figs., 4 Tabs.)



Abstract: The paper presents results of studies of accessory minerals which occur in the principal rock types of the Hodruša-Stiavnica Intrusive Complex of Neogene age and Variscan Vyhne Fractured Granite. The authors have determined the accessory mineral assemblage characteristic of granitoids of the Hodruša-Štiavnica Intrusive Complex: magnetite-apatite-pyrite-zircon-epidote and that of the Vyhne Fractured Granite: pyrite (limonitized)-apatite-zircon-magnetite-garnet. A morphometric analysis of zircons from these rocks according to Pupin (1980) has been carried out, confirming that the genesis of the Hodruša-Štiavnica Intrusive Complex is different from that of the Vyhne Fractured Granite.

Резюме: В статье приводятся результаты изучения акцессорных минералов находящихся в главных типах пород годрушско-штявницкого интрузивного комплекса неогенного возраста и во варисцийском трещиноватом граните. Автори определили ассоциацию акцессорных минералов характеристическую для гранитоидов годрушско-штявницкого интрузивного комплекса: магнетит-апатит-пирит-циркон-эпидот; и для вигнянского трещиноватого гранита: пирит (лимонитизованный)-апатит-циркон-магнетит-гранат. Морфометрический анализ дирконов из этих пород по Пупину (Риріп, 1980) подтвердил что генезис годрушско-штявницкого комплекса отличается от генезиса вигнянского трещиноватого гранита.

Introduction

Accessory minerals are characteristic constituents of granitiod rocks, indicating whether these rocks are ore-bearing or not. Granitoids of the Hodruša-Štiavnica Intrusive Complex (HŠIC) and Vyhne Fractured Granite (VFG) have attracted attention for many years and therefore we attempt, on the basis of study of accessory mineral assemblages and morphometric research of zircons, to contribute to the solution of the complicated genesis of granitoids of the HŠIC and VFG.

Brief geological characteristics of the HSIC and VFG

The Hodruša-Štiavnica Intrusive Complex (Konečný — Lexa — Planderová, 1983) consists of intrusive rocks of diorite and granodiorite composition along with their porphyric varieties in the Banská Štiavnica - Hodruša - Hámre area. The central part of the area is built up of a bell-jar-type

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granodiorite intrusion (Miháliková—Konečný—Lexa, 1980), whereas its margins consist of several minor diorite bodies. The HŠIC situated amidst rocks of pre-volcanic basement is exposed on the surface in the Hodruša area, while in the Banská Štiavnica area it is overlain by a volcanic complex, and its existence was proved by drilling and mining works. The boundaries between the complex and surroundig rocks (Mesozoic and Paleozoic) are intrusive. The HŠIC has closer time relationship to the lower stratovolcanic structure and was formed in later stages of the development of the Lower Badenian stratovolcano.

The Vyhne Fractured Granite is part of the Paleozoic crystalline of Veporic development which constitutes deeper basement of the neovolcanics. Because of its geological position, it is not associated with the Hodruša Štiavnica Intrusive Complex, but with the Veporic (Paleozoic) crystalline underlying the territory (Š a l á t — R o z l o ž n í k, 1975).

The granite was designated by earlier authors as "gneiss", due to its plane-parallel structure similar to that of gneisses. The assemblage and development of its accessory minerals are similar to those of granitoid rocks of the core mountains.

Study methods

Our work was aimed at the study of accessory minerals, their assemblages and morphometric development of zircons in the principal rock types of the HŠIC and VFG.

For this reason we have collected three samples representing the HŠIC and VFG:

- 1. ZRŠ-1: coarse-grained Vyhne Fractured Granite of gray and brown colour with parallel structure, with quartz, K-feldspar and biotite phenocrysts. Locality: north of Spálený vrch Mt. (763 m above sea level) at the end of the community of Vyhne.
- 2. GRŠ-3: mafic granodiorite with basic inclusions of mafic minerals. Locality: right confluence of the brook in Kohútovo village, some 100 m upstream, under Hrb Mt. (760 m above sea level).
- 3. DRŠ-5: dicrite. Locality: Šobov, 200 m NE of the elevation point 888 m above sea level.

As most attention was paid to the determination of qualitative and quantitative differences in distribution of individual accessory minerals, the material collected was crushed, concentrated, separated and evaluated in a way commonly used by the preparation and study of "artifical panned concentrates" (Veselský— \mathbf{Z} abka, 1976).

Results of study of accessory minerals

Accessory minerals are present in the studied rocks in variable and fairly small amounts (Rajnoha, 1987).

Two main mineral assemblages have been distinguished on the basis of comparison of qualitative and quantitative presence of accessory minerals:

 $$T\,a\,b\,l\,e\,$\ 1$$ Quantitative presence of accessory minerals in VFG and HŠIC (in g/t)

Sample Mineral	ZRŠ-1	GR Š- 3	DRŠ-5
zircon apatite apatite (limonitized) pyrite pyrite (limonitized) limonite tourmaline titanite leucoxene barite garnets epidote actinolite magnetite spherical bodies carbonates chlorite arsenopyrite monazite ilmenite hematite	18 172 18 <0.5 180 <0.5 — <0.5 <0.5 — 4 — 7 2 — 46 — <0.5 <0.5 <0.5 <0.5 <0.5 <0.5	99 307 8 37 <0.5 <0.5 <0.5 <0.5 <0.5	15 61 5 115 <0.5 1 <0.5 0.8 <0.5 <0.5 <0.5 5 996 <0.5 <0.5
rutile malacon	<0.5	< 0.5 —	_

1. for granitoids of the Hodruša-Štiavnica Intrusive Complex: magnetite-apatite-pyrite-zircon-epidote and 2. for the Vyhne Fractured Granite: pyrite (limonitized)-apatite-zircon magnetite-garnet.

The table indicates that there exist some, often striking, differences in quantitative presence of the individual accessory minerals in granitoids of the HŠIC and VFG. Granitoid rocks of the HŠIC contain fairly abundant magnetite, whereas in the VFG, magnetite is only sporadic. In contrast, pyrite, which is scarce in the HŠIC, is the main accessory mineral of the VFG. We may state that the total amount of accessory minerals is higher in the HŠIC than in the VFG, except for garnets which are fairly abundant in the VFG, but in granitoids of the HŠIC there occur only exceptional garnet grains. This fact suggests not only different chemical composition of the rocks (Tab. 2), but also different character of the original magnetic melts. Garnets in the VFG differ from those found in granodiorite of the HŠIC in diverse types of morphological development and in colour. Unlike the above-mentioned minerals, apatite content in granitoids of the HŠIC is only slightly higher than in the VFG. In addition to the above accessory minerals, also sporadic grains of tourmaline, titanite, ilmenite, rutile, leucoxene, limonite, arsenopyrite and monazite have been identified. Interesting was the discovery of fairly abundant (2g/t) small spherical bodies in the VFG. These were glassy, white, obscured, but commonly transparent. The spherical bodies

Table 2

Chemical and normative analyses of rocks from which investigated zircons were separated

Chemical analyses			Normative analyses (CIPW)				
	ZRŠ-1	GRŠ-3	DRŠ-5		ZRŠ-1	GRŠ-3	DRŠ-5
SiO_2	73.21	59.43	59.38	Qz	35.39	0.12	17.10
$Al_2\tilde{O}_3$	14.28	15.07	16.96	Or	31.47	21.06	11.71
Fe_2O_3	1.47	1.85	1.60	Ab	22.73	46.91	19.52
FeO	0.54	3.19	3.78	An	2.04	5.49	30.01
CaO	0.41	5.95	6.91	Cpx	0.00	19.36	3.47
MgO	0.63	3.10	3.56	Opx	1.58	1.23	11.77
MnO	0.05	0.13	0.14	Mt	1.15	2.69	2.32
TiO_2	0.26	0.77	0.80	Ilm	0.49	1.46	1.52
$\mathbf{K}_2\mathbf{O}$	5.32	3.56	1.98	Ht	0.68	0.00	0.00
Na_2O	2.69	5.55	2.31				
$\mathbf{H}_2\ddot{\mathbf{O}}^{\perp}$	0.29	0.43	0.29				
$H_2^{-}O^+$	0.97	0.73	2.18				
Total	100.12	99.76	99.89	! 			

Results of X-ray fluorescent analysis carried out on apparatus of firm Philips.

contain abundant gas inclusions. The origin of these spherical bodies is unclear for the time being, but their shape and gas inclusions might suggest possible extraterrestrial origin (G belský, 1977).

Morphometric analysis of zircons

The fairly abundant presence of zircon populations in the studied granitoid samples made it possible to investigate this mineral in more details.

The studied zircons from granitoids of the HŠIC are fresh, uncorroded, with no manifestations of older cores, nor visible zoning. They most commonly occur in the form of idiomorphic crystals of short-prismatic habit, with length//width ratio of 1.8—2. Colour of the zircons studied, predominantly light-yellow, light-pink and yellow-brown, varies even within a single sample. Colour of zircons depends upon the chemical composition of magma - volatile components and upon thermal regime of the crystallization process (L y a k hovich, 1973). Inclusions, identified as apatite and zircon of the first generation, have frequently been observed in the zircons.

Morphology of the zircons from the HŠIC granitoids has been statistically evaluated using the classification of Pupin—Turco (1972). Results of the morphometric analysis are given in Figs. 1, 2 and 3. The analysis indicates that S_{18} -type zircons in granodiorite and S_{19} - and S_{14} -type zircons in diorite of the HŠIC belong among significant types, with the morphometric centres of gravity of these two populations falling into the S_{18} -field for the HŠIC granodiorite and into the S_{14} -field for the HŠIC diorite. As regards their dominant types (S_{18} , S_{19} , S_{14} , S_{17} , S_{20} and P_4) there is a conspicuous correlation between these two zircon populations and therefore also their centres

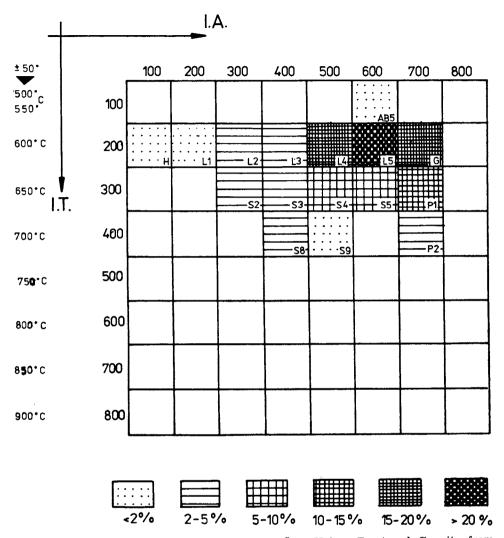


Fig. 1. Typogram of zircons from sample ZRŠ-1: Vyhne Fractured Granite from under Spálený vrch Mt. (after Pupin-Turco, 1972). Shaded area - percentage of individual morphological types of zircons, S_5 , P_1 , $L_3\ldots$ morphological types of zircons after Pupin-Turco (1972).

of gravity lie relatively close to each other. According to Pupin (1980) zircon assemblages of this area are characteristic of granitoids formed of mantle as well as crustal materials and fall into the field of calc-alkaline granitoids.

Studying morphology of zircons from granitoid rocks of the Hodruša-Štiavnica Intrusive Complex, the authors Rozložník-Timčák-Jakab-ská (1982, 1985) and Jakabská (1983) came to the conclusion that these zircons crystallized at a temperature of some 850 °C. They also assume the

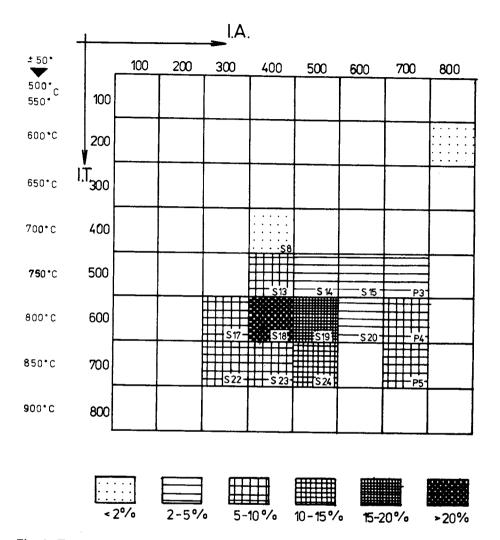


Fig. 2. Typogram of zircons from sample GRŠ-3: granodiorite from vicinity of Kohútovo (after Pupin—Turco, 1972). Shaded area - percentage of individual morphological types of zircons; S₁₃, S₈, P₅... morphological types of zircons after Pupin—Turco (1972).

existence of various types of the magmatic unit, which explains the differentiation among granodiorites, granodiorite porphyries and quartz-diorite porphyries discovered earlier. These conclusions are based on morphometric parametres of the studied zircon populations and vector directions of their evolution trends.

On the basis of Pupin—Turco's (1972) classification, which systematically classifies variations in the development of prismatic and pyramidal

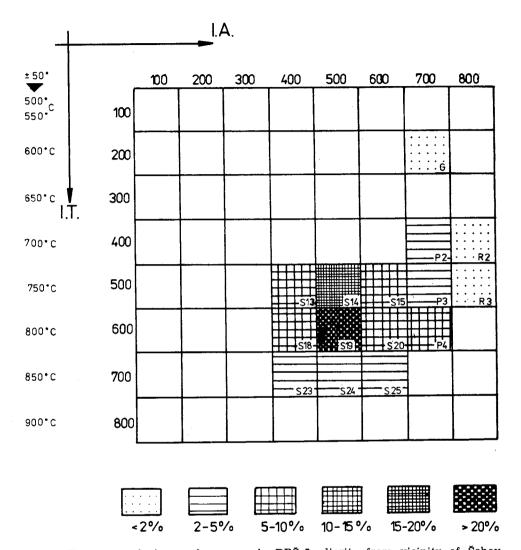


Fig. 3. Typogram of zircons from sample DRS-5: diorite from vicinity of Sobov (after Pupin — Turco, 1972). Shaded area - percentage of individual morphological types of zircons; S_{18} , R_3 , P_2 ... morphological types of zircons after Pupin — Turco (1972).

shapes, the crystallization temperatures of zircons from the sample GRŠ-3 have been determined at approximately 830 °C and of those from DRŠ-5 at 780 °C (Figs. 2, 3).

In the sample ZRŠ-1 we observed not only fresh isomorphic zircon crystals, transparent or light-pink to light-yellow-brown, but also zircons with visible zoning, resorbed, with relics of older cores and dark-brown colour. Gray-white, obscure to dark, opaque strongly metamictized zircons (malacon) occur-

red frequently. The relationship of darker colour of zircons to manifestations of their metamictization has been studied by several authors (Hovorka, 1968; Gbelský, 1977; Veselský, 1978; Lyakhovich, 1973 and others). The metamictization of zircons depends upon the chemical composition of zircons as well as content of radioactive microcomponents which isomorphically substitute for Zr and Hf (Tab. 3).

The character and occurrence of metamict zircons in granitoids and pegmatites in the Malé Karpaty Mts. have been studied by Veselský-Gbelský (1978). The two authors mention that zircons from pegmatites are larger-sized, clearly dominated by dark-brown, intransparent crystals of simple forms which crystallized at lower temperature than those coming from granitoids. As the metamict zircons occur exclusively in the Vyhne Fractured Granite, it may be assumed that the thermal regime during the VFG crystallization was somewhat lower than the crystallization temperature of granodiorite and diorite of the Hodruša-Štiavnica Intrusive Complex.

On the basis of the detailed study of zircons and found differences, we assume that the investigated zircons belong two populations. The first generation comprises zircons of dark-brown colour, partly opaque to obscure. Into the second, younger generation we assign light-pink, light-yellow to colourless zircons which differ from the foregoing generation also morphologically. The older generation of darker zircons is represented mainly by the types G_1 , P_1 to P_4 , whereas the light-coloured pink zircons of the second generation belong into the types S and L (Fig. 1).

In graphic presentation, where the projected points are defined by means of coordinates I.A. (pyramidal planes) and I.T. (prismatic planes), the morphometric centre of gravity of these two populations falls into the field L₅. According to Pupin (1980), zircon assemblages from these areas are characteristic of granitoid rocks formed under conditions close to anatectic ones.

Based on the I.A.—I.T. diagram, theoretical crystallization temperature of zircons of the VFG has been determined. The zircons began to crystallize at about 600—650 °C, but their crystallization culminated at approximately 550 °C.

Chemical composition of zircons

Zircon populations from granitoids of the HŠIV and VFG have been evaluated by semiquantitative analysis by means of electron microprobe by the method of energy dispersion and by quantitative microprobe analysis by the method of wave-length dispersion at the Electron Microanalysis Laboratory, Geological Institute of Dionýz Štúr, Bratislava by a team of workers supervised by J. Határ. Results of the analyses are given in Tab. 3.

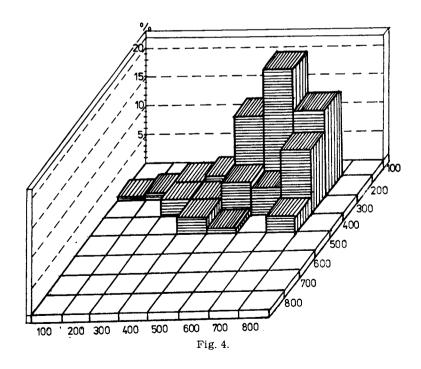
In addition to the main elements (Zr, Si, Hf), the semiquantitative analysis proved also the presence of trace elements (Fe, Ca, Al and Mg) and REE (La, Ce, Er). Inclusions in zircons from the HŠIC granitoids consisted only of apatite, whereas those from the VFG were constituted by K-Mg-Al silicates, probably garnets. Zoning, except for zircons from the VFG, has not been found.

Margins and centre of the investigated zircon grain have been quantitatively analysed by means of microprobe. Al, Mg, Fe and Ca contents were always

Table 3
Microprobe analyses of investigated zircons

Oxides	ZRŠ-1		GRŠ-3		DRŠ-5	
	centre	margin	centre	margin	centre	margin
Al_2O_3	0.0000	0.0000	0.0000	0.0111	0.0000	0.0000
ZrO_{2}	64.5972	65.5194	66.7371	65.9252	65.7291	66.7152
HfO_2	1.6307	1.6135	1.1867	1.2879	1.2988	1.4286
La_2O_3	0.0119	0.0000	0.0045	0.0000	0.0062	0.0049
La₂O₃ MgO	0.0000	0.0074	0.0000	0.0000	0.0000	0.0000
Ce ₂ O ₃	0.0000	0.0000	0.0021	0.0001	0.0011	0.0000
$\mathbf{Y}_{2}\mathbf{O}_{3}$	0.0000	0.0270	0.0610	0.1376	0.2756	0.5657
FeO	0.0000	0.6155	0.0328	0.0000	0.0000	0.0110
SiO ₂	32.8706	32.7734	32,9724	32.8878	33.1298	32.5285
CaO	0.0000	0.0076	0.0072	0.0000	0.0009	0.0121
${ m ThO}_2$	0.0041	0.0635	0.0000	0.0020	0.0428	0.0757
Total	99.1145	100.0273	101.0017	100.2496	100.4836	101.3416
Zr/Hf	39.29	40.36	56.27	51.03	50.41	46.59

very low, often below the sensitivity threshold of the apparatus used. REE contents (La, Ce) in the investigated zircons are markedly variable. Zircons from the VFG are almost devoid of rare earths (only La has been found in the centre of an investigated grain). REE content in zircons from the HŠIC gra-



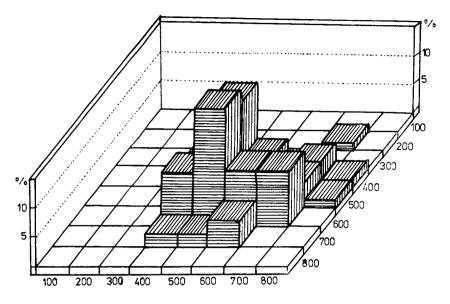
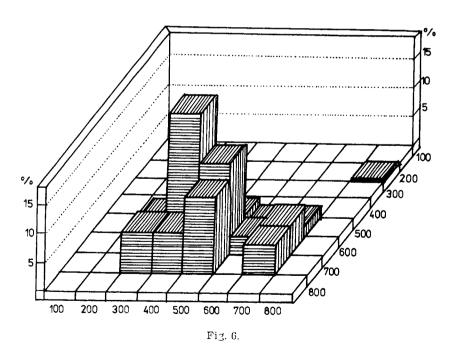


Fig. 5.



Figs. 4, 5, 6: Graphs of abundance of morphological zircon types from samples ZRŠ-1, GRŠ-3 and DRŠ-5.

	ZI	ZRŠ-1		GRŠ-3		DRŠ-5	
	centre	margin	centre	margin	centre	margin	
Si	1.014	1.005	1.001	1.005	1.009	0.990	
Αl	0.000	0.000	0.000	0.000	0.000	0.000	
Fe ²⁺	0.000	0.001	0.001	0.000	0.000	0.000	
Mg	0.000	0.000	0.000	0.000	0.000	0.000	
Ca	0.000	0.000	0.000	0.000	0.000	0.000	
Ce	0.000	0.000	0.000	0.000	0.000	0.000	
Hf	0.014	0.014	0.010	0.011	0.011	0.012	
La	0.000	0.000	0.000	0.000	0.000	0.000	
Th	0.000	0.000	0.000	0.000	0.000	0.001	
Y	0.000	0.000	1.001	0.002	0.005	0.009	
Źr	0.972	0.980	0.988	0.982	0.976	0.990	

Table 4
Formula, calculation to 4 oxygens

nitoids is somewhat higher, decreasing from the core towards the margins, each of these phases being zoned. Accessory minerals (monazite, titanite, alanite and xenotime) - concentrators of REE are very scarce in the VFG and HŠIC granitoids, which suggests that the dominant part is concentrated in zircons and apatite, possibly in other (non-accessory minerals) (G r o m e t -Silver, 1983, Fourcade—Allegre, 1981). Compared to REE, Th content in the investigated zircons behaves in a different way. It increases from the centre towards the margins, the trend being most distinct in the VFG zircons, which resulted also in the formation of metamict grains. Y, which can be better correlated with La than with Ce, tends to behave in a manner similar to Th (Rozložník et al., 1985). The presence of Th in zircons is usually related to the isostructural character of xenotime and zircon (Dennen - Shields, 1956). Hf content in the investigated VFG zircons falls from the margins towards the centre, whereas in zircons from the HŠIC granitoids the trend is reverse. In general, Hf contents in zircons depend upon isomorphic substitution of zirconium (Zr4+) by hafnium (Hf4+) due to diverse crystallization conditions in magmatic melt. The relations between Zr and Hf well reflect their mutual relationship. The Zr/Hf ratio in zircons reflects also metamorphic grade of rocks in which they crystallized. In zircons from metamorphosed rocks, the Zr/Hf ratio drops with the increasing share of acid minerals in the rock. The ratio in zircons from gabbro and diorite is 60-70, from calc-alkaline granites 30-40, from alkaline granites 20-30, and finally the ratio in zircons from nephelinic syenites amounts to 60-150 (Rozložník et al., 1985). Tab. 3 indicates that the compositions of zircons from the HŠIC granitoids are mutually very similar (including their almost identical Hf contents and Zr/Hf ratios). The Zr/Hf ratio in zircon from the granodiorite varies (from the margins towards the centre) from 51 to 56, and in zircon from diorite it ranges from 47 to 51, which confirms the fact that these zircons are autochthonous, fresh, derived from an alkali-lime development of magma. The Zr/Hf ratio in the VFG zircons varies from 40 to 39, which corresponds to the highest values determined for zircons from calc-alkaline granites. It is noteworthy that the average Zr/Hf ratio in zircons from the HŠIC granodiorite is higher

than that in zircons from the HŠIC diorite, which may be due to different PT conditions during their crystallization from melt.

Research of chemical composition of the zircons by means of electron microanalysis provided us with sufficient data on the chemical composition of the zircons studied, though it will be necessary to analyse more elements for the purpose of classification. This allowed us to distinguish zircons from the VFG and HŠIC, in both groups it proved the absence of areas enriched in Ce and Y and in the VFG zircons the presence of zonal pattern as well as older cores.

Conclusions

Study of accessory minerals from the HŠIC granitoids and from the VFG as well as morphometric analysis of zircons from these rocks carried out by Pupin's (1980) method confirmed the different genesis of the HŠIC and VFG.

The quantitative presence and study of the accessory mineral assemblage have shown that the accessory mineral composition of the rock is simple and the content of the rock is simple and the content of the accessories is low. The chemical composition and morphometric analysis of zircons suggest that the genesis of the VFG was probably close to anatectic conditions. The crystallization of the zircons began at $600-650\,^{\circ}\mathrm{C}$ and culminated at approximately 550 °C. The assemblage as well as quantitative and qualitative presence of accessory minerals in the VFG are similar to those of granitoid rocks in the Tatra-Vepor area.

On the other hand, study of accessory minerals, their assemblage and morphometric analysis of zircons from the HŠIC granitoids have confirmed views of Rozložník et al. (1985) and Rajnoha (1987) on the genesis of these

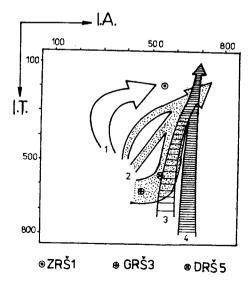


Fig. 7. Graph to show projection points of individual zircon populations (after Pupin, 1980).

Explanations: 1 — granitoid rocks of crustal and/or dominatly crustal origin; 2 — granitoids of crustal and mantle origin, hybrid; 3 — subalkaline granitoid series; 4 — granitoids of mantle and/or predominantly mantle origin.

rocks. The HŠIC granodiorites and diorites are of mantle-crustal origin, have a more distinct alkali trend with mantle material prevailing over crustal one. Some difference has been observed between the HŠIC granodiorit and granite:

a) in crystallization temperature of zircons (granodiorite 830 °C, diorite 780 °C) determined according to Pupin's (1980) diagram;

b) in Zr/Hf ratios in zircons from these rocks. The ratio in zircons from the granodiorite (51-56) is higher than that in zircon from the diorite (47-50), which may be due to different PT conditions during their crystallization from melt:

c) in a more alkaline trend of the diorite relative to the granodiorite.

Study of accessory minerals, their assemblages and their quantitative comparison make it probably possible to place the granitoid rocks of the studied HŠIC area, in the sense of Lyakhovich—Ovchinikov (1970), to granitoids of gabbroid formation (Rajnoha, 1987).

The assemblage, character and amount of individual accessory minerals in samples of the studied rocks indicate that postmagmatic (hydrothermal) processes were significantly involved, substantially affecting also the formation of the HSIC and VFG.

To make the interpretation of the development of the studied rocks more complex, more attention should be paid, in the future, to the study and distribution of trace elements in the individual accessory minerals.

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