MORPHOLOGICAL AND MICROCHEMICAL ASSESSMENT OF ZIRCONS IN GRANITE SPECIMENS FROM THE ČIERNA HORA MTS. (WESTERN CARPATHIANS)

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Abstract: This paper outlines the application of the magmatic phase determination and related techniques of zircon research in the investigation of 9 zircon specimens separated from Variscan granites from the Cierna Hora Mts. (Western Carpathians). Three types of data originating from zircon study lead to a more precise determination and discussion of the genesis of granitic rocks: morphological data, geochemistry of trace elements and internal structure of zircon crystals. The morphometrical properties of specimens from the Miklušovce Complex indicate the pronounced peraluminous character of the melt. The zircon data from specimens TI, TII and SK, SP seem to reflect two series of events in the development of the Bujanová Complex. In the case of the Lodina Complex the analysed data indicate anatectic conditions.

Key words: microchemistry, REE, magmatic phase, biotite, zircon morphometry.

Introduction

The investigation of zircon morphometry began in the thirties, and it has intensified since the early seventies. Since the late seventies the new morphometrical approach was also applied to the study of Slovak magmatic rocks of the Hodruša Intrusive Complex, Malé Karpaty Mts., Považský Inovec Mts., Malá Fatra Mts., Tribeč Mts. and the Spišsko-Gemerské Rudohorie Mts. (cf. Petrík et al. 1994). The magmatic phase sensitive methods of zircon analysis were first used during the investigation of the geology of the French Central Massif, Corsica, Eastern Alps and the Nepal part of the Himalayan range (Pupin 1992). In this paper a further analysis of zircon data from the Čierna Hora Mts. granitoids (Western Carpathians) is given.

The Čierna Hora Mts. (Fig. 1a) belong to the Veporic tectonic unit. The Crystalline Complex of the Čierna Hora Mts. has been divided into 3 lithostratigraphic units: the Lodina, Miklušovce and Bujanová Complexes (Jacko 1985, 1992). All three are the product of a repeatedly refolded, polymetamorphic, probably Early Paleozoic volcano-sedimentary sequence penetrated by Variscan plutonites. The Čierna Hora Mts. Crystalline Complex was reworked by Alpine, polyphase tectonometamorphosis. The Bujanová Complex is formed by migmatites. Variscan granitoids, restites of gneisses, and rarely of amphibolites, aplite and pegmatite veins, extensive zones of phyllonites and mylonitized granites. The Lodina Complex is formed by Variscan metamorphites, diaphtoritised metamorphites, diaphtoritised gneisses and rarely by aplitic granite. The Miklušovce Complex is formed mainly by fine-grained mylonites and aplitic granites. Granitoid rocks occupy a significant part of the Cierna Hora Crystalline Complex. Granitoids of four types were described there: contaminated granodiorites and tonalites, biotitic granodiorites, granites, aplite and pegmatitic granites. An important part of the aplitic granitoid bodies is developed in the Miklušovce Complex (Jacko 1985; Jacko & Petrík 1987; Jacko 1992).

Zircons were separated from granitoids from all the three complexes. Zircons from 9 specimens were analysed. Their characterisation is given in Tab. 1, their position in the QAP diagram in Fig. 1b. The exact location of the specimens is given in Fig. 1a (cf. Jablonská 1993).

The mean points and typological evolution trends - TET1, TET2 and TET3 were calculated using the PUP1 program (Timčák & Hroncová 1992). The optimised magmatic phase fields in the Y_2O_3/HfO_2 and ThO_2/UO_2 diagrams are given using the data for zircons from aplitic granite (Miklušovce). The data were complemented by REE data from the parent rocks, the Ce and La contents of zircons and the chemistry of biotites from the same localities which were used for co-assessing the magmatic development of the parent rocks.

A note on the separation and observation of zircons

During the separation, to obtain the most complete material for the estimation of the development of magma, the 0.050-0.1 and the 0.16-0.24 mm fraction had to be separated. Cleaned zircons were embedded in Canada balsam on a glass slip covered by an other glass slip and observed under a polarising microscope. The new alternative for viewing embedded polished zircon grains - the confocal microscope that enables "optical sectioning" of the grains (the Petráň type of confocal microscope - Confocal 2002) - was also successfully used for the typological assessment of zircon inclusions.



Fig. 1a. A structural-geological sketch of the Čierna Hora Mts. (Jacko 1990). 1 - Neogene mollase sediments; 2 - sediments of the Central Carpathian Paleogene; 3 - amphibole-pyroxene diorite (Upper Cretaceous); 4 - Mesozoic envelope. 5 - Late Paleozoic (mainly Permian) envelope; 6-12 - the Čierna Hora Crystalline Complex; 6-7 - the Miklušovce Complex; 6 - stromatite-nebulite and ophtalmite migmatites; 7 - aplite granite; 8 - diaphtoritic paragneisses, mica schists, amphibolites and phylonites of the Lodina Complex; 9-12 - the Bujanová Complex; 9 - gneisses, amphibolites and migmatites; 10 - biotite granodiorites; 11 - autometamorphosed granite; 12 - mela-granodiorites and tonalites; 13 - gneisses, amphibolites, migmatites and granitoides of the Branisko Mts.; 14 - Carboniferous and Permian of the Gemeric Unit; 15 - sole of the Gemeric Unit Nappe; 16 - regionally significant overthrust zones; 17 - overthrust zones of lower order; 18 - faults; 19 - localisation of the analysed specimens; 20 - distribution of metamorphic zones in the Čierna Hora Crystalline Complex.

Extension of the zircon morphometry data interpretation

Pupin (1976) defined the typological distribution mean points and typological evolution trends (TET1, TET2, TETM). The TET1 reflects the statistical evolutionary trend of zircons in a non-linear and coded way, because the tangent function allows - under the given conditions - only a variation between 0 and 90 degrees, and because the weight of the IA values is higher than those of the IT values. In cases of a large spread of IA values and narrow spread of IT values the change of alpha is large. In reverse cases the change of alpha is much smaller. Thus it is a relatively good measure of changes in the aluminium/alkali antagonism of the melt, but not so good a measure of the temperature changes in the melt. The TET2 - a polygon connecting the points of weighted arithmetical means calculated for rows of typogram data - avoids these problems, but does not use the IT-wise statistical information. Fig. 2 shows the uncertainty of the alpha and TET1 due to the departure of the projected typological frequency data distributions from a normal-shaped distribution (Timčák et al. 1990; Timčák & Hroncová 1992). A TET3 was also developed (Timčák 1990; Timčák et al. 1991), which connects the points in three-dimensional typograms which follow the minimum slope anticlinal path, i.e. the path of the most persistent morphometrical types. The TET3 usually resembles the TET2, but takes into consideration wider contexts in the typogram (it has a look-round logic). As the

| Locality | Specimen code | Rock type | Affiliation |
|------------------|------------------|--|-----------------------|
| Ťahanovce I | Π | medium grained biotitic granodiorite | Bujanová Complex |
| Ťahanovce II | TII | biotitic granodiorite with porphyric feldspars | Bujanová Complex |
| Sokoľ | SK | tonalite | Bujanová Complex |
| Sopotnica | SP | tonalite | Bujanová Complex |
| Košické Hámre | КН | medium grained biotitic to muscovitic autometamorphosed granite | Miklušovce Complex |
| Miklušovce | MK | aplitic granite | Miklušovce Complex |
| Vyšná Dolina | AG | aplitic granit c | Mikhišovce Complex |
| Predná Dolina | HAG | hybrid two-mica aplitic granite | Miklušovce Complex |
| Šibená Hora | Н | aplitic granite | Lodina Complex |

Table 1: Description of rock samples from which zircons were separated.

course of TET3 in our case did not follow a trace that would alter the position of the TET in the typological evolution fields (Pupin 1988), only 1 TET3 example was given (Fig. 2).

The typological frequency data for the various IT classes were tried as indicators of changes in water pressure that affect the zircon crystallization timing (Pupin 1988; cf. Fig. 3).

Special electron microprobe analysis of zircon grains was used to enable the detection of the magmatic phases. The grains are best analysed at points determined on the basis of the zoning pattern observed by cathodoluminiscence (cf. e.g. Broska 1986). In order to be able to correlate zircon morphometry with intragranular micro-chemistry it was necessary to analyse grains selected according to morphometric criteria, with analytical points primarily selected on the basis of their zoning patterns. This approach enables the detection of evolutionary phases of the rock from which the zircons were separated. At present, phases 1 (1a,1b), 2 (2a, 2b) and 3, could be defined, the primal definition of which are given below (Pupin 1992, 1994).

For the Cierna Hora Mts. granitoids, the microprobe analysis data were obtained mainly at the facilities of the Montpellier University (the program for data processing was made by J. Merlet (cf. Merlet & Bodinier 1990), using a CAMEBAX electron microprobe. Tab. 2 shows an example of microprobe data, which are suitable for magmatic phase determination for specimen TI. They were taken from our GeoGIS information system.

Zircon assessment taking into consideration the intragranular zoning

The present frontiers of zircon data interpretation lie mainly around understanding the genetic significance of zircon zonality – intragranular spatial variations of the micro-chemical composition – of grains with specified typological properties. Thus in this part, using electron microprobe data on HfO₂, ThO₂, Y_2O_3 and UO₂ content at properly selected analytical points



Fig. 1b. Position of the investigated rock specimens in the QAP diagram (1 - TI; 2 - TII-Ťahanovce; 3 - SK-Sokoľ; 4 - SP-Sopotnica; 5 -KH-Košická Belá; 6 - ŠH-Šibená Hora; 7 - AG-Vyšná Dolina Valley; 8 - HAG-Predná Dolina Valley; 9 - MK-Miklušovce). The modal data were calculated from chemical ones according to the CIPW norm. 2 alkali granite, 3 - granite, 3a - syenogranite, 3b - monzogranite, 4 granodiorite, 5 - tonalite.



Fig. 2. Typograms of specimen MK (Miklušovce) showing TET1, TET2 and TET3. Hatched zones show the uncertainty of the direction of TET1 due to the departure of the projected typological frequency distributions from ideal distribution shapes.

within the zircon grains, the essential features of the zircon crystallization phase determination can be shown. The analytical points have been selected on the basis of cathodoluminiscence images, but it has to be noted that the magmatic phases may (Fig. 4) or may not (Fig. 5) be fully identical with the zoning apparent through cathodoluminiscence.

Fig. 4. Zoning and crystallization phases of a zircon grain of type S1 from aplitic granite MK – Miklušovce. Phases 1b, 2 and 3 are visible. The grain section sketch shows the crystallization phases on its left half and zoning on its right half. The points show the locations of microprobe analyses. The photomicrographs of Figures 4-5 were taken on a polarising microscope. The shown scale (I-V) reflects the shades of grey observed on the cathodoluminiscence image. The same scale is valid for Fig. 5. Magnification 328×.

Fig. 5. Crystallization phases and zoning of a type S2-3 zircon grain section, separated from granodiorite TII - Tahanovce. There is a well observable overgrowth of phase 3 on phase 2b. The right half of the grain section shows the zoning of the analysed grain. For analogous data on the other specimens, see Jablonská (1992, 1993). Magnifica-

tion 280×.



The chemical composition (including the REE content) changes from grain to grain, but the dispersion of data is genetically restricted.

Knowledge of the magmatic phases discernible in the zircon grains is also very important in zircon age determination. Zircon age obtained by isotope analysis of morphologically unsorted zircons can be discordant or controversial (cf. Rozložník et al. 1985, 1991). As the quantity of assorted zircon grains would be too small for conventional analysis, ion microprobe analytical techniques are being developed for that purpose. At present, the application of ion microprobe (Compston et al. 1982;



2





Table 2: Typical microprobe data for the magmatic phase analysis of zircon grains from the analysed specimens. The table shows chemical data for magmatic phases 1 (1a, 1b), 2 (2a, 2b) and 3. Detailed analytical data for the specimens are given in Jablonská (1992, 1993). For magmatic phase determination within one zircon grain usually 3 to 15 point analyses are needed. For data interpretation strategy see Pupin (1992, 1994). Analytical conditions: CAMEBAX microprobe, 25 kV, 100 mA, integration time: 30-140 s.

| Localities and specimen codes | Type of the analysed zircon grain | Serial number of the analysis | Detected phase | SiO2 [%] | ZrO2 [%] | HfO2 [%] | ThO2 [%] | UO2 [%] | Y ₂ O ₃ [%] | Total [%] |
|-------------------------------------|---|-------------------------------------|-------------------|-------------|-------------|--------------|-------------|------------|--------------------------------------|--------------|
| Ťahanovce | \$7 | 93 | 2a | 32.73 | 65.56 | 0.97 | 0.09 | 0.03 | 0.42 | 100.06 |
| π | | 94 | 2b | 32.77 | 65.79 | 1.62 | 0.06 | 0.02 | 0 | 100.61 |
| | | 96 | 2b | 32.52 | 65.41 | 1.57 | 0 | 0.02 | 0.07 | 100.01 |
| | | 97 | 3 | 32.19 | 64.80 | 1.77 | 0.02 | 0.35 | 0.25 | 99.81 |
| Ťahanovce | S 1 | 65 | 2a | 32.33 | 65.77 | 0.96 | 0.54 | 0.83 | 1.87 | 99.66 |
| TII | | 67 | 2b | 32.51 | 65.46 | 1.60 | 0 | 0.36 | 0 | 99.87 |
| | | 70 | 3 | 32.55 | 65.59 | 1.56 | 0 | 0.23 | 0 | 99.93 |
| Sokol | S11-12 | 138 | 2a | 31.62 | 65.95 | 1.10 | 1.70 | 0.06 | 0.42 | 99.63 |
| SK | | 141 | 2b | 31.68 | 66.23 | 1.40 | 0.06 | 0.08 | 0.13 | 99.81 |
| | | 142 | 2b | 31.63 | 66.88 | 1.32 | 0.02 | 0 | 0.02 | 100.06 |
| Sopotnica | S ₁₁₋₁₆ | 129 | 2a | 32.90 | 65.49 | 1.54 | 1.73 | 0.53 | 0.56 | 100.39 |
| SP | | 130 | 2b | 33.13 | 65.58 | 1.48 | 2.32 | 0.05 | 0.08 | 100.62 |
| | | 131 | 2b | 33.02 | 65.51 | 1.45 | 0.38 | 0.49 | 0.9 | 100.36 |
| Košická Belá | S 1 | 12 | 1 | 32.52 | 64.76 | 1.24 | 0 | 1.20 | 0 | 98.68 |
| КН | | 15 | 2 | 32.82 | 64.11 | 1.62 | 0.13 | 0.20 | 0 | 98.72 |
| | | 18 | 2 | 32.30 | 64.90 | 1.60 | 0.20 | 0 | 0 | 99.03 |
| | | 19 | 3 | 31.77 | 63.31 | 1.60 | 0.21 | 2.60 | 4.40 | 97.92 |
| Šibená Hora | G 1 | 214 | 3 | 31.03 | 64.37 | 2.60 | 0 | 3.70 | 0.50 | 98.75 |
| ŠH | | 215 | 3 | 30.54 | 64.16 | 2.46 | 0.07 | 5.91 | 2.28 | 98.49 |
| | | 216 | 3 | 30.92 | 64.78 | 2.15 | 0.15 | 2.73 | 1.00 | 98.66 |
| Vyšná Dolina | S7 | 104 | 1 | 32.62 | 66.39 | 1.14 | 0.20 | 0 | 2.01 | 100.63 |
| AG | | 105 | 2 | 32.96 | 66.09 | 1.22 | 0.85 | 0 | 0.02 | 100.60 |
| | | 106 | 3 | 32.10 | 64.85 | 1.73 | 0.04 | 0.96 | 3.94 | 99.82 |
| Predná Dolina | \$2 | 366 | 1 | 31.70 | 64.07 | 1.15 | 1.18 | 0.70 | 2.68 | 97.56 |
| HAG | | 367 | 2 | 31.76 | 63.91 | 1.52 | 0.20 | 0.43 | 3.53 | 98.14 |
| | | 369 | 3 | 31.57 | 62.74 | 2.44 | 0.30 | 2.64 | 0.91 | 97.48 |
| Mikłušovce | S ₁₁ | 274 | 1a | 32.69 | 63.50 | 1.16 | 0.79 | 0.80 | 3.15 | 98.24 |
| MK | | 276 | 2 | 31.86 | 63.77 | 1.98 | 0 | 2.40 | 0.52 | 98.72 |
| | | 278 | 1b | 32.58 | 64.83 | 1.32 | 0.15 | 0 | 0.29 | 99.06 |
| | | 280 | 3 | 31.11 | 62.18 | 1. 69 | 0.06 | 5.68 | 4.14 | 97.24 |

Kröner 1987) for the determination of magmatic phases is technically still complex and tends to suffer from the large primary ion beam spot size (typically 30 μ m). A one grain dating, however, is now possible.

Description of the zircon development phases

As it was mentioned earlier, 3 phases of zircon development can be described at present (Pupin 1992). Phase 1 represents the inherited phase. The 1st phase is thus built by older, inherited zircons. This phase manifests a structural discordance with the later phase of crystallization and also a geochemical discordance. The latter discordance is such, that it cannot be otherwise explained for the considered zircon population and for the given parent rock. If the analytical points of the inherited phase show the lowest HfO_2 content below 1.15–1.30 per cents, this is considered as a diagnostic feature for phase 1. As mentioned, the structural discordance is best observable by cathodoluminiscence.

Structural and geochemical aspects taken together can help to determine the protolith. In cases where the nuclei show a homogeneity both in structure and geochemistry that corresponds to a model zircon population from a given type of magmatic rock, then it can be induced that the protolith is a type of rock close to that from which the model population was taken. In cases where, from both structural and geochemical points of view, the nuclei show great heterogeneity, the protolith is more probably polygenic.

| Specimen | TI | TII | SK. | SP | KH | MK | AG | HAG | ŠН |
|---|--------------------------|----------------------|---------------------------|---------------------------|--|------------------------------|---------------------------|---------------------------|-----------------------------------|
| Rock names based on modal composition | biotitic granodiorite | granodiorite | granodiorite/ tonalite | granodiorite/ tonalite | autometam. granite | migmatitic aplite/granite | aplitic granite | aplitic granite | aplitic granite |
| Rock name in the QAP diagr. | granodiorite | granodiorite | tonalite | tonalite | granodiorite | granodiorite | granite with K-felspar | granite with K-felspar | granodiorite |
| Rock name in the La Roche diagram | granodiorite | granodiorite | tonalite | tonalite | granite | granite | granite | granite | granite |
| TET2/3 evolution trend field | GPCO | GPCO | GPCO | GPCO | GPCO | GPCO | GPCO | GPCO | GPCO |
| Mean point evolution trend field | IAM | IAM | IAM | IAM | autochthonous monzogranite/ granodiorite/ IAM | IAM | IAM | IAM | Aluminous leucogranite/ IAM |
| Y ₂ O ₃ /HfO ₂ based magmatic phase and type | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 2:CA | 2:CA | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 3:AN |
| UO2/ThO2 based magmatic phase and type | 1:CA 2:CA 3:AN | 1:AN 2:CA 3:AN | 2:CA | 2:CA | 1:AN 2:CA 3:AN | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 1:CA 2:AN 3:AN | 3:AN |

Table 3: Summary of the data derived from typological and microchemical measurements (TI, TII - Ťahanovce; SK - Sokol; SP - Sopotnica; KH - Košická Belá; MK - Miklušovce; AG - Vyšná Dolina; HAG - Predná Dolina; ŠH - Šibená Hora).

Explanations: GPCO: granites of predominantly crustal origin. IAM: intrusive aluminous monzogranite, CA - calc-alkaline field, AN - anatectic field, M - migmatite field. Numbers 1 to 3 indicate the magmatic phases.

Table 4: Microprobe analysis of biotite grains from the investigated specimens (cf. Jablonská 1992). The Fe values were recalculated to FeO. For specimen description see Tab. 3.

| | Specimen code | | | | | | | | | |
|--------------------------------|---------------|-------|-------|-------|-------------|-------|--|--|--|--|
| Analysed oxides (wt.%) | Π | TII | SK | SP | КН | HAG | | | | |
| SiO ₂ | 34.55 | 35.13 | 35.65 | 36.70 | 33.65 | 34.09 | | | | |
| TiO ₂ | 3.91 | 3.66 | 3.48 | 2.86 | 2.58 | 2.02 | | | | |
| Al ₂ O ₃ | 17.29 | 17.42 | 15.98 | 16.40 | 17.83 | 18.39 | | | | |
| FeO | 22.27 | 21.91 | 18.91 | 18.69 | 22.02 | 25.84 | | | | |
| MnO | 0.23 | 0.23 | 0.39 | 0.35 | 0.41 | 0.21 | | | | |
| MgO | 8.01 | 8.11 | 10.04 | 11.11 | 10.32 | 4.53 | | | | |
| CaO | 0.01 | 0.02 | 0.17 | 0.02 | 0.03 | 0.02 | | | | |
| Na ₂ 0 | 0.05 | 0.05 | 0.08 | 0.06 | 0.07 | 0.05 | | | | |
| K ₂ O | 9.08 | 9.14 | 9.26 | 8.99 | 6.68 | 9.46 | | | | |
| Total | 95.4 | 95.67 | 93.96 | 95.18 | 93.59 | 94.61 | | | | |

In assessing the structural discordance one can assume that if [101] is strongly predominant in the nucleus, it belongs to the alkaline development. If [101]+[211] or [211] are predominant, calc-alkaline development is to be assumed.

The inherited phases are often broken or rounded, in contrast to the central zones, which are often termed as cores, but are innate constituents of the grain. These innate cores belong to the second magmatic phase. In cases where the structural and geochemical properties of the inherited phase permit it, phase 1 can be subdivided into phase 1a and 1b (Fig. 4).

Zircon cores are sometimes also visible optically, but their proper determination is possible only under electron microprobe or analytical SEM.

Phase 2 represents the magmatic phase. Within it, it is sometimes possible to recognise subphase 2a - the early subphase, usually termed as central zone and 2b - the later or standard magmatic phase (Fig. 5). Phase 2 in zircons crystallised during anatectic processes and has HFO_2 values greater than 1.15-1.30 per cents.

Phase 3 represents the late magmatic phase and new overgrowths. It is formed by overgrowing parts of the grain as shown in Figs. 4 and 5, or often as young zircon types (such as L_1 to L_3 or G_1), belonging to the upper parts of the typogram. The young zircons are often enriched in REE.

Discrimination diagrams employing the obtained magmatic phase-related analytical data

The microprobe data can also be plotted into the Y_2O_3 -HfO₂ and ThO₂-UO₂ diagrams, which are used for the discrimination of the magmas originating mainly in the mantle (tholeiitic, alkaline, calc-alkaline) from crustal magmas (anatectic melts that always have the lowest observable HfO₂ content greater than

| | Specimen code | | | | | | | | |
|------------------|---------------|--------|--------|--------|--------|--------|--------|--------|--------------|
| Element [ppm] | TI | TII | SK | SP | КН | ŠН | AG | HAG | МК |
| La | 98.09 | 94.00 | 137.60 | 167.57 | 47.68 | 4.22 | 16.62 | 20.71 | 20.44 |
| Ce | 101.36 | 94.57 | 125.39 | 149.42 | 44.93 | 5.33 | 16.72 | 20.58 | 20.27 |
| Pr | 262.77 | 259.12 | 299.27 | 291.97 | 262.77 | 288.32 | 291.97 | 262.77 | 321.17 |
| Nd | 59 .07 | 54.15 | 72.43 | 74.54 | 24.89 | 3.80 | 9.00 | 12.94 | 9.56 |
| Sm | 25.97 | 28.14 | 26.41 | 30.74 | 12.77 | 2.60 | 8.23 | 10.39 | 8 .01 |
| Eu | 12.64 | 12.07 | 16.09 | 18.96 | 7.47 | 2.43 | 2.74 | 2.60 | 4.60 |
| Gd | 19.28 | 15.36 | 11.11 | 16.34 | 7.84 | 1.63 | 8.01 | 9.15 | 6.64 |
| Ть | 3.61 | 3.99 | 2.66 | 3.10 | 2.47 | 1.14 | 2.72 | 3.10 | 2.09 |
| Но | 4.94 | 4.94 | 5.17 | 5.76 | 4.58 | 4.82 | 6.23 | 4.70 | 6.70 |
| Tm | 7.89 | 7.67 | 5.03 | 6.57 | 7.98 | 5.17 | 7.36 | 18.82 | 11.52 |
| ΥЪ | 3.55 | 4.64 | 2.62 | 4.64 | 3.71 | 3.95 | 7.26 | 8.06 | 5.24 |
| Lu | 3.65 | 3.44 | 1.31 | 4.70 | 4.33 | 3.31 | 9.45 | 7.64 | 4.70 |
| Σ | 602.82 | 582.09 | 705.09 | 774.31 | 431.42 | 326.72 | 386.31 | 381.46 | 420.94 |

Table 5a: REE content of granitoid rocks from the Čierna Hora Mts. The INNA analyses were made at the UP Stráž pod Ralskem laboratories. The data were chondrite-normalised.

(Localities: TI, TII – Ťahanovce, SK – Sokoľ, SP – Sopotnica, KH – Košická Belá, ŠH – Šibená Hora, AG – Vyšná Dolina, HAG – Predná Dolina, MK – Miklušovce).

Table 5b: Average La₂O₃ and Ce₂O₃ content of zircon grains from the studied localities. For specimen codes, see Tab. 5a. The analyses were made at CLEM GÚDS Bratislava. Analytical conditions: JEOL SU-PERPROBE, 15 kV, 4×10^{-8} A, integration time 50-200 s. Analyst: F. Caňo.

| Locality/specimen code | La2O3 [ppm] | Ce2O ₃ [ppm] |
|------------------------|-------------|-------------------------|
| ТІ | 53 | 288 |
| TII | 35 | 205 |
| SK | 18 | 266 |
| SP | 38 | 208 |
| КН | 41 | 244 |
| AG | 186 | 258 |
| HAG | 99 | 233 |
| MK | 62 | 239 |
| ŠН | 261 | 281 |

1.15-1.30 per cent). In these diagrams the distribution of the values for the magmatic and late magmatic phases are important. The data fields for the analysed specimens were obtained by joining the outermost data points characterising the phases/sub-phases in question (Figs. 6, 7).

By the above outlined type of processing of the microprobe point analysis data and the other diagnostic tools mentioned above, it is possible to assess the changes in the crystallization conditions as well as the type of recrystallization or resorption processes that evoked these changes.

Tab. 3 contains the assessment of the magmatic phase- and related data for the analysed specimens. The data were derived from the proposed Y_2O_5 vs. HfO₂ and the ThO₂ vs. UO₂ diagram and from results given in Jablonská (1992).



Fig. 6. The Y_2O_3 vs. HfO₂ plot for microprobe data of zircon grains separated from aplitic granite (MK - Miklušovce). The spread and location of subphases 1a, 1b (inherited phases), 2 (magmatic phase) and 3 (tardimagmatic phase) indicate the magmatic succession and the accompanying geochemical changes of the parent rock. For data on other specimens, see Jablonská (1993). TH - Oceanic tholeiitic albitites; CA - calc-alkaline and K-calc-alkaline field; HA - alkaline-hypersolvus; AN - anatectic granites; SA - alkaline subsolvus; MI migmatites (see Pupin 1992).

Correlation of zircon morphometry data with whole rock trace element-, zircon Ce, La- content and biotite chemistry

The morphometric T index was correlated with whole rock REE content (Tab. 5a) and the Ce and La content of the analysed zircons discussed (Tab. 5b). In the modified Nockolds plot, biotite chemistry data (Tab. 4) were correlated with the plot of mean IA and IT values in the Pupin (1988) petrogenetic field diagram.



Fig. 7. The ThO₂ vs. UO₂ plot for microprobe data of zircon grains separated from aplitic granite (MK – Miklušovce). These data are complementary to those from the Y_2O_3 vs. HfO₂ plot. The numbers below the field names (cf. Fig. 6) indicate the magmatic phase type to which the field applies. The diagonal shows the region where the Th/U ratio in zircons is equal to one (cf. Pupin 1992).



Fig. 8a. The whole rock Ce content vs. mean IT plot of the investigated specimens. The specimens belonging to the Bujanová (TI, TII, SP, SK), Miklušovce (KH, HAG, AG, MK) and Lodiná Complex (ŠH) form separate fields.

Correlation of trace element content in rocks, Ce, La content in zircon grains and of the mean IT values

Pupin (1985, 1990) has shown that the mean IT values of zircon populations correlate well with the trace element content of parent rocks. Figs. 8 and 9 show the correlation of these values for the specimens from the Čierna Hora Mts. Here we can see that with decreasing crystallization temperature (and mean IT value) the content of REE manifest a concordant ten-



Fig. 8b. The whole rock La content vs. mean IT plot of the investigated specimens (see Fig. 8a). An analogous relationship to that shown in Fig. 10a can be seen.

dency, supporting the Pupin (1985) findings. An analogous relationship between the IT and REE content was also observed in the case of granitoid rocks from the Tribeč Mts. (Broska et al. 1990). Furthermore, the specimens from Bujanová - (TI, TII, SP, SK), Miklušovce- (KH, HAG, AG, MK) and from the Lodina Complexes (ŠH) form well discernible groups in the diagram, which thus could be used as a classification tool. The average Ce content of zircons from the Miklušovce (243 ppm), Bujanová (242 ppm) and Lodina Complex (281 ppm) and the observed La content pattern (Tab. 5b) may indicate a REE enrichment in zircons from specimen ŠH.

Correlation of biotite analysis data with the results of morphometrical assessment of zircons

Chevremont et al. (1988), Amenzou (1988) and Pupin (1990) have shown that under certain conditions it is possible to correlate the microprobe analysis data of unaltered biotites with the morphometric data from zircons. Fig. 10 shows the biotite analysis data projection of specimens TI, TII, KH, HAG, SP and SK (cf. Tab. 4) in the FeO-Al₂O₃-MgO diagram. The diagram shows that biotite from specimen HAG fell into field 1 (Aluminous leucogranite stock) and specimens KH and TII fell into field 2-3 (sub-autochthonous monzogranite and intrusive aluminous monzogranite-granodiorite stock). Biotite specimen TI is on the boundary of the 2-3 field. In the Pupin (1985) classification of granites, on the basis on zircon data, these specimens fall into group A (granites derived from crustal melting due to regional anatexis and/or induced melting by rising granitic or more basic melts). Biotites from specimens SP and SK fell into field 4 (calcalkaline and K-calc-alkaline series granites). This position corresponds to group B (hybrid granites) of the zircon based classification. In the FeO/MgO diagram (Macek 1992) the biotites from specimen TI and TII fell into the leucogranite field, biotite from specimen KH and SK into the granite/granodiorite field, and from SP into the metamorphite/tonalite field.



Fig. 9. The whole rock REE content vs. mean IT plot of the investigated specimens (see Fig. 8a). The correlation is well defined and the specimens form analogous groups to those observed on Figs. 8a-b.



Fig. 10. The FeO-Al₂O₃-MgO plot of analytical data (cf. Tab. 1) for unaltered biotites for specimens TI, TII, KH, HAG, SP and SK. Their distribution in the petrogenetic fields defined by Pupin (1985) and shown as encircled numbers, correlates with that based on zircon typological mean point distribution of the investigated zircon populations in the standard diagrams of typological evolution rends (cf. Pupin 1990).

Discussion

Three groups of data originating from zircon study lead to a more precise determination and a discussion of the genesis of granitic rocks (Pupin 1992): 1. Morphological data; 2. Geochemistry of trace elements, and 3. Internal structure of zircon crystals, notably the presence of inherited cores (nuclei). The structure and geochemistry of these nuclei aid the derivation of their source by narrowing down the range of possibilities (Pupin 1992, 1994).

The petrogenetic interpretation of the morphometric mean points of the analysed specimens were given in Jablonská (1993).

The TET2 and TET3 plots show that TI, TII, KH as well as AG, HAG, MK belong to crustal granitoids. The TET of specimens SP, SK also indicate a crystallization under peraluminous conditions, but their tonalitic composition forbids use of the TET diagram proposed for granitic rocks (Pupin 1988). Nevertheless these TET are coherent with the trends obtained for low or normal K calc-alkaline andesitic series (Giraud et al. 1980). The TET2/3 of specimen SH – as there is a discontinuity in its typological distribution - may at its final stage of development show a more pronounced change in the aluminium/alkali antagonism (late precipitation of Zr in zircon together with other incompatible trace elements during the crystallization of the residual melt at low temperature, cf. Fig. 3). There are differences in the chemical and temperature development pattern indicated by the TET2/3 of the analysed specimens that characterise the variations in the crystallization conditions (Jablonská 1993). The most pronounced changes in the aluminium/alkali antagonism can be observed in specimens MK, KH, TII and SH. The estimated crystallization temperature range - based on zircon morphometry - is the shortest in case of SK and SP i.e. $800-750 \text{ °C} \pm 50 \text{ °C}$. These two specimens – in contrast to the other ones - end their crystallization at higher temperatures (by approximately 100 °C). This would usually indicate crystallization under relatively drier conditions (see, however Petrík & Broska 1994). The other samples correspond to estimated crystallization temperature range mainly around 750-650 °C ± 50 °C, due to the possible influence of inherited relictual nuclei on the morphological character of the new anatectic growth (Pupin 1994). We can note that the magmatic phase pattern of specimens TI and TII indicate similar conditions. The above crystallization temperature range estimates were given as they accord with the geothermometric data derived from phase relations in the Qz-Ab-An-Or diagram (Jacko 1987).

As regards the zoning of zircons, Tab. 3 contains the relevant data. Thus phase 1 was detected (through both the Y2O3/HfO2 and UO₂/ThO₂ diagram and the internal structure of zircon crystals) in specimens KH, AG, HAG and MK which are from the Miklušovce Complex. In the Y₂O₂/HfO₂ diagram, in the case of specimens MK and AG subphases 1a and 1b could be distinguished. The micro-chemistry of phase 1 and of the later phases differed substantially, indicating that the nuclei were inherited from the rocks that formed the pre-granitoid structure. A more detailed study of phase 1 of zircons from the Miklušovce Complex granitoids could thus be of use in the reconstruction of the pre-granitoid structure of the Crystalline Complex. The zircon data indicate that phase 1 in case of specimen KH, MK, AG and HAG - according to Y₂O₂/HfO₂ and UO2/ThO2 diagrams - crystallised under calc-alkaline conditions. For phase 2 and 3, the same diagrams indicate anatectic processes, mainly based on the absence of low hafnium contents in zircons (HfO₂ always over 1.2 per cents for phase 2) and a U/Th ratio greater than 1 (Pupin 1992, 1994).

Some inherited nuclei could also be observed in the TI and TII granitoids, whereas these are very rarely found in zircons from specimens SP, SK – in agreement with the results obtained on some other tonalitic rocks (e.g. tonalites from the Adamello Massif, Pupin, unpublished data). The absence of phase 3 (late overgrowths) on zircons in these tonalitic samples indicate an earlier crystallization under drier conditions of the melt, as com-



Fig. 11. Magmatic phase mean point trend vectors derived from the Y_2O_3 vs. HfO₂ diagram showing two different development trends for specimens from the Bujanová and Miklušovce Complexes.

pared to specimens TI and TII, where phase 3 is present together with the geochemical characteristics normally encountered in late overgrowths developed in anatectic melts. The estimated temperature of zircon crystallization of SP, SK (800-750 °C \pm 50 °C) and TI, TII (750-650 °C \pm 50 °C) correlate with the values given in Jacko et al. (1990). The zircon data from specimens TI, TII and SK, SP seem to reflect two events in the development of the magmatic history of the Bujanová Complex.

In case of the Lodina Complex more data is needed. In specimen $\check{S}H$ only phase 3 was present, - and both the Y₂O₃/HfO₂ and UO₂/ThO₂ data indicate anatectic conditions.

The MOP AM03 image analyser was used for the determination of magmatic phase field centres of gravity. Their trend vectors in the Y_2O_3/HO_2 diagram (Fig. 11) indicate different development trends of the granitoids from the Miklušovce and Bujanová Complexes.

According to the biotite chemistry based classification, specimen TI is projected on the boundary of fields of the calc-alkaline series granites (4) and of (sub)autochthonous monzogranites-granodiorites/intrusive aluminous monzogranites-granodiorite stock (2–3), specimens TII into field 2–3, specimens SP and SK into field 4, specimen KH into field 2–3 and specimen HAG into the field aluminous leucogranites (cf. Fig. 10).

The high REE content of the granitoids of the Čierna Hora Mts. is discussed by Jacko (1992). Fig. 9 shows that the REE content (cf. Tab. 5a) is the highest in the granitoids from the Bujanová Complex. Figs. 8a, b show that an identical relationship exists for La and Ce. The average Ce content of zircons from the specimen from the Lodina Complex is the highest, and of the specimens from the Miklušovce Complex the lowest. The average La content of zircons from the Bujanová Complex is the lowest and from the Lodiná Complex the highest (Tab. 5b; cf. Jablonská 1992).

The data on zircon morphology and micro-chemistry support the conclusions on the position of the Miklušovce and other granitoids of the Čierna Hora Mts. Crystalline Complex determined on structural and petrographic grounds as given by Jacko (1992). The investigation of specimens from other areas of the Veporic Crystalline Complex will enable a more complex analysis.

Conclusions

The TET2 and TET3 plots show that specimens TI, TII, KH as well as AG, HAG, MK belong to crustal granitoids. The TET of specimens SP, SK also indicate a crystallization under peraluminous conditions. The TET2/3 of specimen ŠH may at its final stage of development show a more pronounced change in the aluminium/alkali antagonism. The most pronounced changes in the aluminium/alkali antagonism can be observed in specimens MK, KH, TII and ŠH. The zircon crystallization temperature range estimated through zircon typology suggested in the case of specimens SK and SP is 800–750 °C ± 50 °C. The zircons from other samples could have crystallised around 750–650 °C ± 50 °C.

The zircon data indicate that magmatic phase 1 crystallised under calc-alkaline conditions in case of specimen KH, MK, AG and HAG. Phase 2 and 3 of the same specimens are considered to have been formed through anatectic processes.

Some inherited nuclei could also be observed in the TI and TII granitoids. These are very rarely found in zircons from specimens SP, SK. The absence of phase 3 in zircons in these specimens indicate an earlier crystallization that could have occurred under drier conditions of the melt than in the case of specimens TI and TII. The zircon data from specimens TI, TII and SK, SP appear to reflect two series of events in the development of the Bujanová Complex.

The data on zircon morphology and micro-chemistry support the conclusions on the position of the Miklušovce- and other granitoids of the Čierna Hora Mts. Crystalline Complex determined on structural and petrographic grounds.

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