

ZIRCON IN HERCYNIAN GRANITIC PEGMATITES OF THE WESTERN CARPATHIANS, SLOVAKIA

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Abstract: Zircon is an uncommon but widespread accessory mineral in Hercynian barren to beryl-columbite rare-element granitic pegmatites of the Central Western Carpathians, Slovakia. BSE images show either homogeneous composition, or irregular to oscillatory zoning, and locally also two-stage crystal growth. Electron-microprobe analysis reveals elevated Hf, locally also P, Y, REE, Al, Fe and Ca. Hafnium content and Zr/Hf ratio are proportional to the fractionation degree of the host pegmatite; zircon from the barren pegmatites attains 1 to 8 wt.% HfO₂ (average 3 wt.%), zircon from the beryl-columbite pegmatites contains 2 to 22 wt.% HfO₂ (average 7 wt.%). HfZr_{1-x}, Al³⁺P⁵⁺Si⁴⁺₂ and (Y,HREE,Fe)³⁺P⁵⁺(Zr,Hf)₁Si₁⁴⁺ are the possible substitution mechanisms. Calculation of the temperature of zircon saturation gave T_s ≈ 700 to 580 °C, which corresponds to a primary magmatic origin of the zircon.

Key words: Western Carpathians, geochemistry, temperature of crystallization, granitic pegmatite, zircon.

Introduction

Zircon is one of the most widespread accessory minerals in a great variety of igneous rocks, including the granitic pegmatites. Although the largest concentrations of zircon are affiliated with alkaline granites, syenites and their pegmatites, the peraluminous granitic pegmatites of the LCT-family (Černý 1991) usually contain a little zircon. Zircon is practically the only Zr-rich phase in non-alkaline igneous environments; baddeleyite ZrO₂, elpidite Na₂ZrSi₆O₁₅·3H₂O and other complex zirconosilicates occur only in highly alkaline suites.

Crystal morphology, internal texture and especially geochemistry of igneous zircon are useful indicators of conditions controlling the growth of zircon and consolidation of its host rock. The current understanding of zircon is based on the dependence between the pyramidal/prismatic ratio of zircon crystals and temperature or the genetic type of parent rock (Pupin 1980), on internal growth pattern detectable by BSE and cathodoluminescence (Vavra 1990), and on chemistry (mainly the Zr/Hf ratio and distribution of U, Th, Y and REE; Pupin 1992). The zircon-saturation experiments for felsic magmas facilitate calculation of reasonable crystallization temperatures of zircon (Watson & Harrison 1983).

Pegmatitic zircon regarded commonly as a product of true magmatic crystallization is also a potential petrological indicator of cooling history, fractionation level and temperature. Its chemistry is more complex than that of zircon from granites, as it shows large variations in Zr/Hf, P, Y, REE, U, Th, Ca and other elements, depending on the fractionation level of the pegmatite, and on local chemical environment (Černý et al. 1985; Kapustin 1985). However, the geochemical and petrological significance of pegmatite zircon is still rarely utilized, and only regional studies based on statistically adequate databases can reveal the correlations between the properties of zircon and the characteris-

tics of host pegmatites. This paper is an attempt to contribute to this line of study, using the example of zircon from 18 granitic pegmatites of the Western Carpathians (Fig. 1).

Parent granites and pegmatites

The West-Carpathian granitic pegmatites form dyke- to lens-like bodies emplaced in the parent granitic rocks or in adjacent amphibolite-facies lithologies, mainly metapelites-metapsammites and rarely metabasalts. The parent granitic rocks are Hercynian, mainly Lower Carboniferous biotite and two-mica (leuco)tonalites, granodiorites, granites to muscovite leucogranites, with orogenic calc-alkaline S- or I-type affinities (Petřík et al. 1994).

Hercynian granitic pegmatites can be subdivided into two principal genetic groups on the basis of the mineralogy and geochemistry of their parent granites and the pegmatites themselves (Uher 1994; Uher & Broska 1995):

(1) Pegmatites of S-type, monazite-bearing granites, Moravany-type (PMOG).

(2) Pegmatites of I-type, allanite-bearing granites, Prašivá-type (PAOG).

Some granite-pegmatite suites reveal mixed characteristics between (1) and (2), and it is still not clear whether they represent a third independent granite-pegmatite association, or only atypical members of (1) or (2). Only more precise geochemical and especially geochronological data could solve this problem in the future.

The following paragenetic zones have been described in West-Carpathian pegmatites (Dávidová 1978, 1981): (1) aplitic, (2) feldspar-quartz-mica, (3) graphic, (4) blocky microcline, (5) blocky quartz, (6) quartz-(plumose) muscovite and (7) albite; the first five zones are suggested primary magmatic, the zones (6) and (7) are believed to be autometasomat-

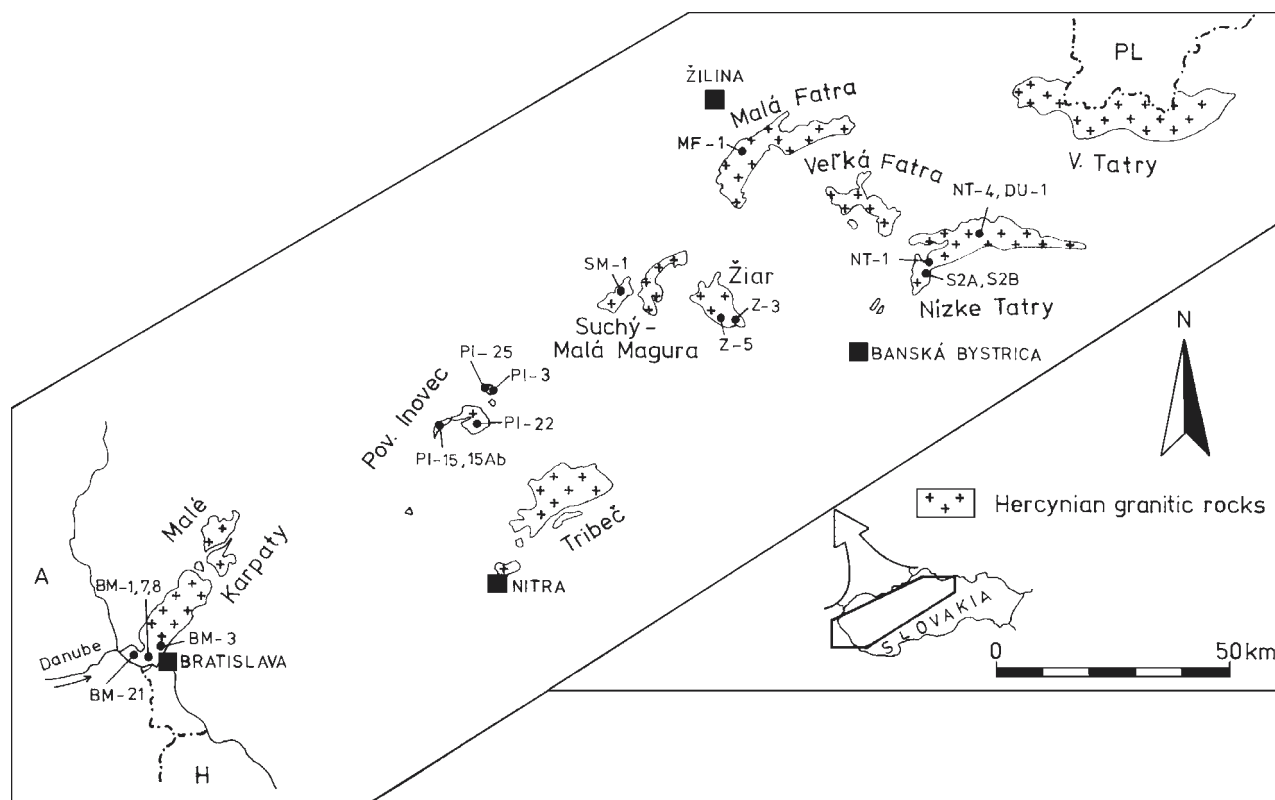


Fig. 1. Location of investigated pegmatites of the Western Carpathians. Locality abbreviations: see the Appendix.

ic (Dávidová, l.c.). The majority of pegmatites exhibit relatively simple zoning, from graphic borders through intermediate blocky K-feldspar and/or coarse-grained K+Na-feldspar-quartz-muscovite-(biotite) zone to quartz-(muscovite) core. Late-magmatic albite-rich units (albitic aplite or cleavelandite+quartz) replace in part the above zones; they occur only in the more fractionated pegmatites, e.g. the Moravany nad Váhom pegmatite (Uher 1991; Uher & Broska 1995). PMOG bodies are muscovite- and garnet-rich, while PAOG members are more primitive with both biotite and muscovite. The most widespread coarse-grained quartz+K-feldspar ± albite + muscovite ± biotite intermediate pegmatite zone or blocky K-feldspar rich zone (Kunerad pegmatite) was sampled for zircon. Other accessory minerals comprise almandine-spessartine, fluorapatite, monazite-(Ce), xenotime-(Y), uraninite, magnetite, gahnite, pyrite and arsenopyrite. Accessory beryl, columbite-tantalite and rarely ferrotapiolite, Nb, Ta-rich rutile, pyrochlore-group minerals and fersmite are formed only in the more fractionated pegmatites. These latter bodies belong to the beryl-columbite subtype of the beryl type, LCT-family, rare-element-class granitic pegmatites (cf. Černý 1991). On the basis of the pegmatite zonality and trace-element geochemistry of K-feldspar, the Tatric West-Carpathian granitic pegmatites could be subdivided into three groups: (1) simple feldspar-quartz-mica pegmatites of the abyssal (barren) class, (2) zonal (graphic-blocky-equigranular-core) feldspar-quartz-mica pegmatites, locally with metasomatic albite, of the muscovite class, and (3) zonal pegmatites with metasomatic albite and/or quartz-muscovite zones and accessory Be, Nb-Ta minerals of the beryl-columbite subtype of

rare-element class (Dávidová 1997). The chemical compositions of the studied barren and beryl-columbite granitic pegmatites are presented in Table 1A, B.

Methods

Zircon crystals were extracted from pegmatite samples by crushing, sieving and concentrating in a heavy liquid. Electron-microprobe analyses were carried out in the wavelength dispersion mode on a Cameca SX50 instrument at the Department of Geological Sciences, University of Manitoba. The beam diameter of 1–2 μm was used. An accelerating potential of 15 kV, beam current of 20 nA and counting time of 20 s were applied for P, Si, Zr, Hf, Al, Fe, Sc, Y, Ca, F and Cl, but 20 kV, 30 nA and 40 s, for Th, U, Ce, Sm, Tb, Dy, Er and Yb. The following standards were used: monazite (for P K α), zircon (Si K α , Zr L α), metallic Hf (Hf M α), kyanite (Al K α), almandine (Fe K α), NaScSiO₄ (Sc K α), YAG (Y L α), diopside (Ca K α), fluor-riebeckite (F K α), tugtupite (Cl K α), ThO₂ (Th M α), UO₂ (U M β), REE3 (Ce L α), REE2 (Sm L α , Y β L α), REE1 (Tb L α) and REE4 (Dy L β , Er L α). Data were reduced using the PAP routine (Pouchou & Pichoir 1985).

Some of the older data were obtained on the JEOL JXA-733 electron microprobe, at the Geological Survey of the Slovak Republic, Bratislava; for analytical conditions see Uher (1992).

The main elements of pegmatites and Rb, Sr, Ba (also Zr, Y, Ce and Nb of sample SM-1) were analysed by XRF (Universi-

Table 1A: Chemical composition of studied West-Carpathian barren granitic pegmatites (in wt.% — main elements, ppm — trace elements). Locality abbreviations: see the Appendix.

	BM-3	BM-7	PI-25	SM-1	Z-3	MF-1
SiO ₂	74.97	75.06	76.40	72.43	74.78	62.90
TiO ₂	0.04	0.02	0.07	0.02	0.02	0.21
Al ₂ O ₃	14.65	14.58	14.24	16.54	14.21	18.76
Fe ₂ O ₃	0.47	0.63	0.74	0.47	0.51	1.51
MnO	0.01	0.22	0.03	0.03	0.05	0.03
MgO	0.10	0.06	0.22	0.10	0.06	0.49
CaO	0.25	0.28	0.65	0.67	0.23	1.66
Na ₂ O	2.89	5.38	2.01	6.12	3.42	5.96
K ₂ O	5.73	2.82	2.94	1.53	5.58	6.18
P ₂ O ₅	0.10	0.13	0.10	0.11	0.15	0.93
LOI	0.50	0.50	1.60	0.90	0.60	0.70
TOTAL	99.71	99.68	99.00	98.92	99.61	99.33
Rb	75	188	89	72	191	87
Be	3.0	4.5	3.9	n.a.	3.1	2.1
Sr	103	8	61	67	60	379
Ba	202	38	302	118	50	2892
B	4.2	3.0	4.4	n.a.	3.8	5.4
Ga	16.0	19.0	n.a.	n.a.	20.2	18.4
Y	7.44	3.47	6.57	2.00	2.40	14.50
Ce	5.16	2.34	15.83	4.00	3.21	23.62
Zr	12.85	21.11	28.19	19.00	9.33	12.81
Hf	0.48	1.22	1.32	n.a.	0.44	0.46
Sn	3.5	6.5	9.6	n.a.	1.9	<3.0
Nb	2.14	6.94	9.26	10.0	6.44	3.09
Ta	0.55	1.70	2.09	n.a.	1.16	0.35

Table 1B: Chemical composition of studied West-Carpathian beryl-columbite granitic pegmatites (in wt.% — main elements, ppm — trace elements). Locality abbreviations: see the Appendix.

	BM-8	BM-21	PI-15	Z-5	NT-1	DU-1
SiO ₂	79.15	76.37	79.06	71.65	74.89	70.27
TiO ₂	0.02	0.03	0.02	0.01	0.06	0.03
Al ₂ O ₃	12.53	13.75	12.29	16.20	14.25	15.68
Fe ₂ O ₃	0.36	0.50	0.82	0.58	0.66	0.76
MnO	0.02	0.13	0.17	0.11	0.08	0.08
MgO	0.11	0.09	0.06	0.07	0.16	0.17
CaO	0.19	0.40	0.16	0.60	0.29	0.81
Na ₂ O	3.92	3.81	2.96	6.59	4.07	6.23
K ₂ O	2.48	3.84	2.34	2.39	4.44	3.88
P ₂ O ₅	0.10	0.06	0.06	0.52	0.13	0.68
LOI	1.00	0.90	0.90	0.80	0.80	0.30
TOTAL	99.88	99.88	98.84	99.52	99.83	98.89
Rb	202	184	485	146	249	281
Be	n.a.	6.8	41.0	11.0	n.a.	12.6
Sr	6	50	12	50	39	142
Ba	35	125	39	283	98	101
B	n.a.	8.1	13.2	5.3	n.a.	7.0
Ga	n.a.	20.0	18.6	30.0	n.a.	43.0
Y	1.13	21.79	0.69	7.00	2.01	5.97
Ce	1.68	8.03	0.92	3.42	4.01	7.49
Zr	9.01	19.90	5.71	23.07	11.12	41.90
Hf	0.80	0.97	0.61	2.26	0.70	4.09
Sn	n.a.	5.5	41	4.2	n.a.	<3.0
Nb	0.77	7.07	45.48	17.55	25.55	13.06
Ta	0.19	0.93	11.75	4.66	4.72	6.77

ty of Ottawa, Canada); Y, Ce, Zr, Hf, Nb and Ta by ICP-MS (Memorial University of Newfoundland, St. John's, Canada) and Be, B, Ga and Sn by OES (Geological Institute of the Slovak Academy of Sciences, Bratislava, Slovakia).

Results

Morphology and internal zoning

Zircon forms usually short prismatic crystals of the G₁-subtype, rarely prismatic-pyramidal G₂ to pure dipyramidal A-type, or locally also L-S₁₋₅ (Fig. 2), according to the classification of Pupin (1980). The size of crystals is usually 0.1–0.5 mm, their colour is pale grey, pink to red, or brownish. Three basic zoning and textural patterns of zircon could be recognized:

(1) metamict unzoned to irregularly zoned grains with abundant uraninite inclusions (at most of the localities, Fig. 3A, B),

(2) grains with metamict, unzoned, or irregularly zoned central parts, locally with inclusions of uraninite, xenotime-(Y) or monazite-(Ce), overgrown by a single or several non-metamict zones with oscillatory compositional variations (Fig. 3C–E),

(3) semi-transparent to transparent, non-metamict crystals, with oscillatory and locally sector zoning (Fig. 3F).

Chemistry

Representative compositions of zircon are shown in Table 2A, B. The most distinctive geochemical feature is the rela-

tively high abundance of hafnium as indicated by the content of wt. % HfO₂, weight Zr/Hf and atomic 100Hf/(Hf+Zr) ratios. Some zircon crystals are relatively homogeneous but others show a very broad variability in Hf contents. The Hf concentration may also vary among crystals from a single hand specimen. Generally, zircon from the barren pegmatites has a lower Hf content than zircon from the beryl-columbite bodies: 1.5 to 8.4 wt. % HfO₂ (average 2.98, Table 2A), versus 3.6 to 22.3 wt. % HfO₂ (average 6.93; Table 2B), respectively. The HfO₂ content and atomic 100Hf/(Hf+Zr) ratio could be (1) relatively constant across a single crystal, (2) irregularly variable, or (3) increasing from the centre to the rim. The Kamzik pegmatite zircon is an example of a very rapid Hf-increase and two-stage growth: from ca. 3.5 to 8 wt. % HfO₂ and 100Hf/(Hf+Zr) = 3.2–7.5 in the metamict centre to 22 wt. % HfO₂ and 100Hf/(Hf+Zr) = 22.1 in the oscillatory zoned rim (Fig. 3C, D; □ Table 2B).

Locally, high P and Y+HREE abundances (up to 0.22 P and 0.18 Y+Dy+Er+Yb apfu) are introduced by heterovalent substitution (Y,HREE)³⁺P⁵⁺Zr⁴⁺Si⁴⁺₁, based on the isostructural relationship between xenotime-(Y) and zircon. In rare cases elevated contents of Al (≤3.53 wt. % Al₂O₃, 0.13 Al apfu), Fe (≤5.69 wt. % Fe₂O₃, 0.14 Fe apfu), U (≤2.72 wt. % UO₂, 0.02 U apfu) and Ca (2.10 wt. % CaO, 0.08 Ca apfu) are observed. The fluorine content of zircon is usually close to the analytical detection limit (ca. 0.15 wt. % F); however, some compositions from the beryl-columbite pegmatites contain 0.20–0.33 wt. % F, up to 0.03 apfu. The chlorine content is also below or near microprobe detection limit (0.00–0.05 wt. % Cl), and only exceptionally reaches 0.15 wt. % Cl (DU-1). In some places the higher F and Cl contents are connected with low total compositions (Σ = 89–97 wt. %) and metamict parts of zircon,

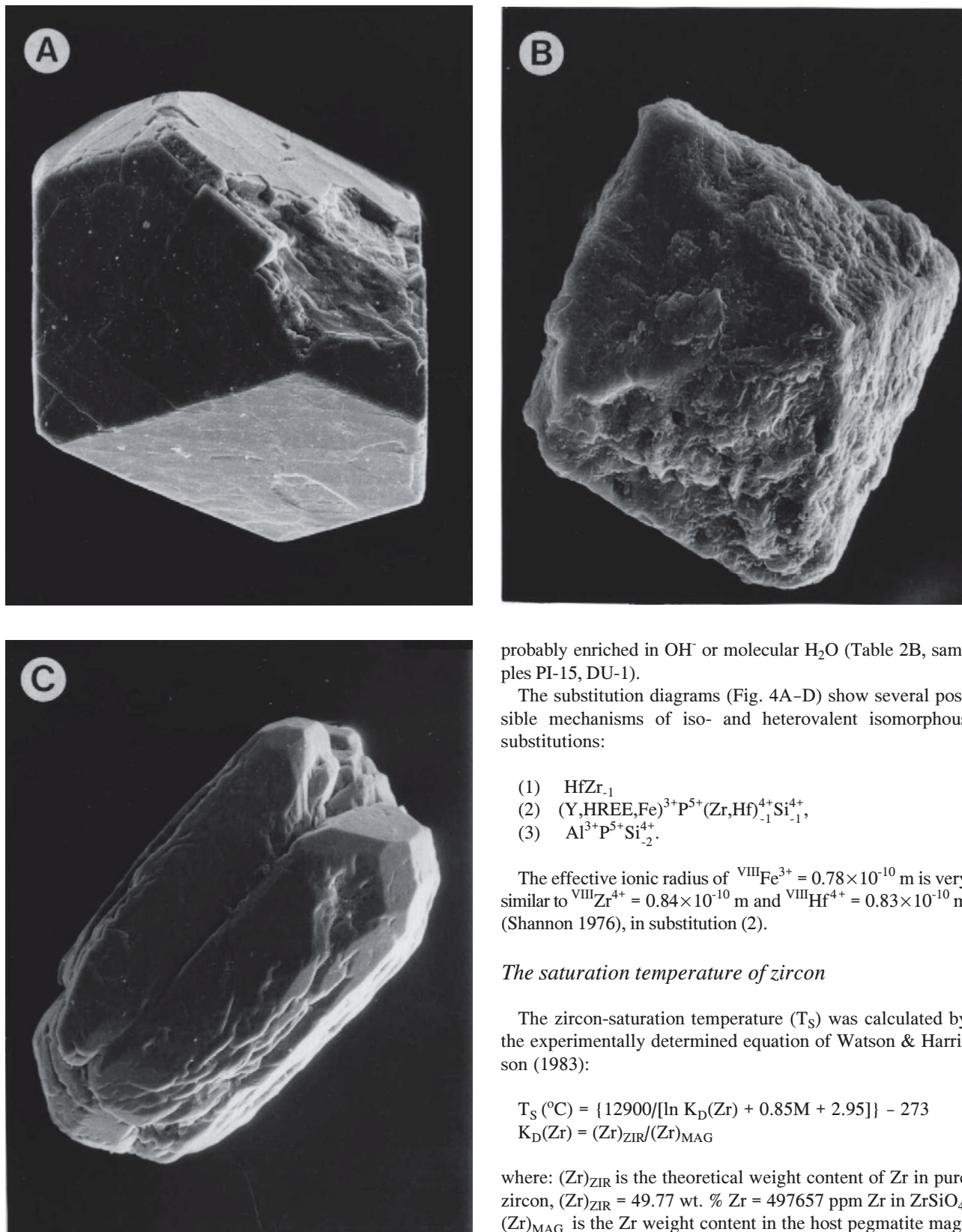


Fig. 2. Morphology of zircon crystals. **A** — G₂-type, Kamzík pegmatite (BM-8). **B** — A-type, Moravany nad Váhom pegmatite (PI-15Ab), **C** — S₄-type, Sopotnica pegmatite (S2B). SEM, size of crystals 0.1–0.3 mm.

probably enriched in OH⁻ or molecular H₂O (Table 2B, samples PI-15, DU-1).

The substitution diagrams (Fig. 4A–D) show several possible mechanisms of iso- and heterovalent isomorphous substitutions:

- (1) HfZr_{-1}
- (2) $(\text{Y, HREE, Fe})^{3+}\text{P}^{5+}(\text{Zr, Hf})_{-1}^{4+}\text{Si}_{-1}^{4+}$,
- (3) $\text{Al}^{3+}\text{P}^{5+}\text{Si}_{-2}^{4+}$.

The effective ionic radius of $^{\text{VIII}}\text{Fe}^{3+} = 0.78 \times 10^{-10}$ m is very similar to $^{\text{VIII}}\text{Zr}^{4+} = 0.84 \times 10^{-10}$ m and $^{\text{VIII}}\text{Hf}^{4+} = 0.83 \times 10^{-10}$ m (Shannon 1976), in substitution (2).

The saturation temperature of zircon

The zircon-saturation temperature (T_s) was calculated by the experimentally determined equation of Watson & Harrison (1983):

$$T_s (\text{°C}) = \{ 12900 / [\ln K_D(\text{Zr}) + 0.85M + 2.95] \} - 273$$

$$K_D(\text{Zr}) = (\text{Zr})_{\text{ZIR}} / (\text{Zr})_{\text{MAG}}$$

where: $(\text{Zr})_{\text{ZIR}}$ is the theoretical weight content of Zr in pure zircon, $(\text{Zr})_{\text{ZIR}} = 49.77$ wt. % Zr = 497657 ppm Zr in ZrSiO_4 , $(\text{Zr})_{\text{MAG}}$ is the Zr weight content in the host pegmatite magma in ppm. If the system was closed and no old inherited solid zircon is present (as indicated by BSE images), the $(\text{Zr})_{\text{MAG}} = \text{Zr}$ content in the present rock (in ppm), assuming that zircon is the only carrier mineral of Zr.

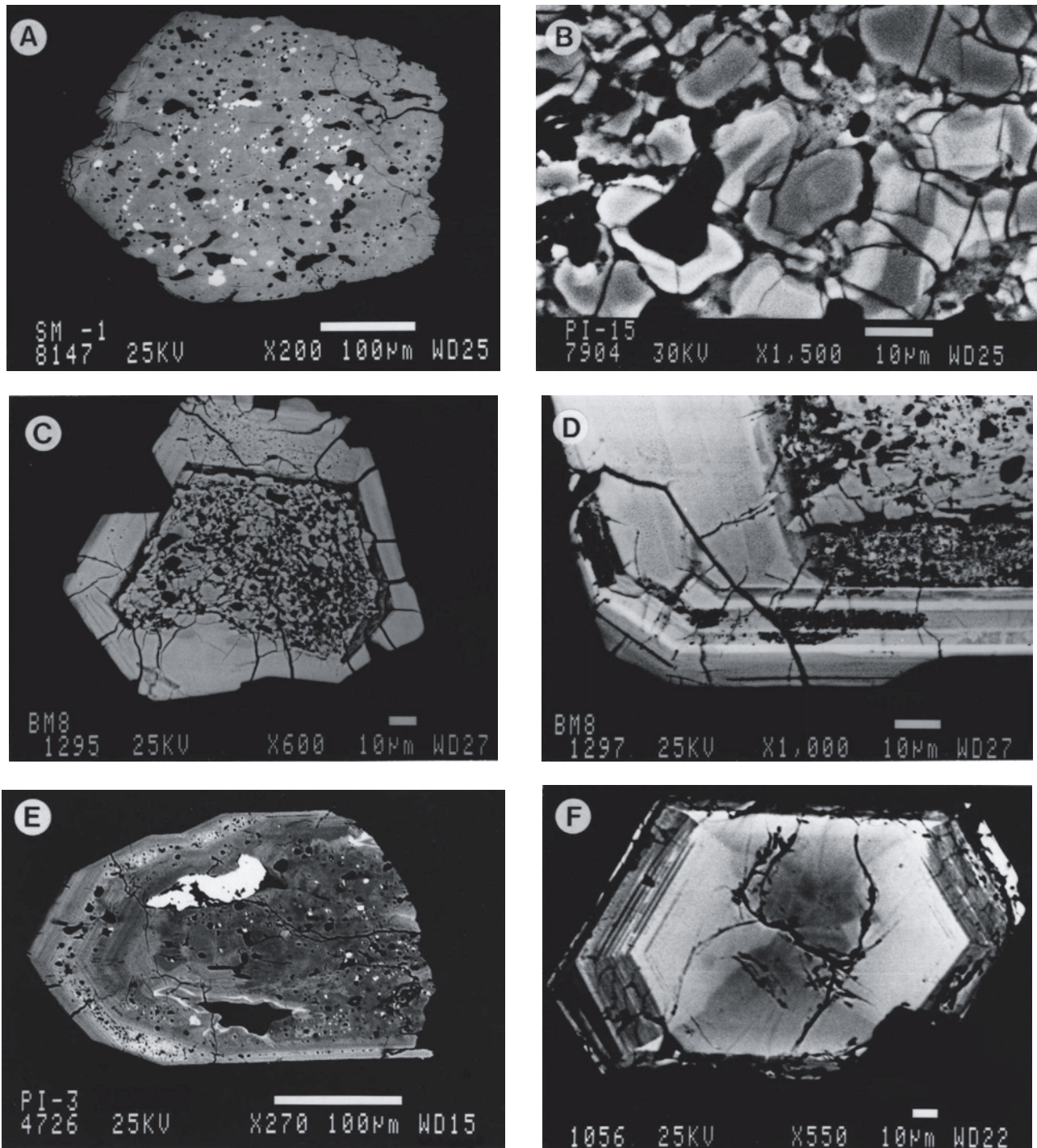


Fig. 3. BSE images of zircon. **A** — Metamict grain with numerous uraninite inclusions, Valaská Belá pegmatite (SM-1). **B** — Detail of irregularly zoned grain, Moravany nad Váhom pegmatite (PI-15). **C** — Crystal with a metamict center and oscillatory zoned rim, Kamzík pegmatite (BM-8). **D** — Detail of C with thin oscillatory Hf-rich zone (up to 22 wt. % HfO₂). **E** — Crystal with metamict irregularly zoned center and oscillatory zoned rim; large white inclusion is xenotime-(Y) and numerous small inclusions are uraninite, Soľnísko pegmatite (PI-3). **F** — Transparent crystal with sector zoning in the center and oscillatory zoning in the rim, Kunerad pegmatite (MF-1).

$$M = \text{molar } [(2\text{Ca} + \text{Na} + \text{K})/(\text{Si} + \text{Al})]_{\text{ROCK}},$$

where $\text{Si} + \text{Al} + \text{Fe} + \text{Mg} + \text{Ca} + \text{Na} + \text{K} + \text{P} = 1$.

If the theoretical K_D Zr of pure zircon/magma = $497657/Z_{\text{T-MAG}}$ (49.77 wt. % Zr in ZrSiO₄), then a correction for Hf can be introduced, because the real concentration of Zr in

natural zircon is usually lower than the theoretical 497657 value, and this difference must be compensated mainly by the real Hf concentration in zircon. The real Zr and Hf can be obtained from microprobe data as their average contents from the central parts of zircon crystals. Although the Hf-correction is more realistic for natural zircon, especially for Hf-rich pegma-

Table 2A: Representative compositions of zircon from studied West-Carpathian barren granitic pegmatites (in wt.%). Sample abbreviations and locations: see the Appendix. Zr/Hf_w — weight ratio, Hf# % = 100Hf/(Hf+Zr) atom.

	BM-3		PI-3		SM-1		Z-3		MF-1	
	center	rim	center	rim	center	rim	center	rim	center	rim
P ₂ O ₅	0.30	0.50	n.a.	n.a.	0.10	0.31	0.50	0.16	0.15	0.14
SiO ₂	32.24	29.20	31.08	29.64	32.18	30.99	32.39	33.37	32.10	32.56
ZrO ₂	61.52	58.57	60.64	56.19	62.82	57.54	62.27	65.26	64.68	64.19
HfO ₂	2.65	2.51	5.94	8.42	3.94	4.51	2.72	1.80	1.57	1.59
ThO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.01	0.00	0.02
UO ₂	0.16	0.61	n.a.	n.a.	0.19	0.67	0.96	0.07	0.31	0.68
Al ₂ O ₃	0.05	0.13	0.00	0.00	0.06	0.08	0.06	0.00	0.00	0.00
Fe ₂ O ₃	0.08	0.22	0.00	0.00	0.03	0.26	0.08	0.00	0.00	0.00
Sc ₂ O ₃	0.00	0.00	n.a.	n.a.	0.01	0.00	0.04	0.04	0.05	0.06
Y ₂ O ₃	0.08	0.46	0.07	0.53	0.00	0.28	0.45	0.00	0.12	0.10
Ce ₂ O ₃	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.01
Sm ₂ O ₃	0.01	0.00	n.a.	n.a.	0.08	0.00	0.04	0.00	0.07	0.01
Tb ₂ O ₃	0.00	0.00	n.a.	n.a.	0.00	0.02	0.00	0.00	0.00	0.01
Dy ₂ O ₃	0.00	0.00	n.a.	n.a.	0.02	0.00	0.10	0.08	0.00	0.06
Er ₂ O ₃	0.03	0.05	n.a.	n.a.	0.00	0.11	0.12	0.00	0.07	0.04
Yb ₂ O ₃	0.05	0.08	n.a.	n.a.	0.00	0.04	0.14	0.03	0.05	0.05
CaO	0.08	0.27	0.01	0.06	0.00	0.15	0.02	0.00	0.00	0.03
F	0.05	0.05	n.a.	n.a.	0.07	0.06	0.05	0.00	0.00	0.07
Cl	0.02	0.01	n.a.	n.a.	0.02	0.06	0.01	0.00	0.01	0.00
Total	97.29	92.66	97.74	94.84	99.49	95.04	100.04	100.83	99.20	99.59
FORMULAE BASED ON 16 OXYGEN ATOMS										
P ⁵⁺	0.032	0.057	-	-	0.011	0.034	0.052	0.016	0.016	0.015
Si ⁴⁺	4.057	3.907	3.986	3.973	4.007	4.042	4.002	4.048	3.984	4.019
Zr ⁴⁺	3.775	3.822	3.792	3.672	3.814	3.660	3.751	3.860	3.915	3.864
Hf ⁴⁺	0.095	0.096	0.217	0.322	0.140	0.168	0.096	0.062	0.056	0.056
Th ⁴⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.001
U ⁴⁺	0.004	0.018	-	-	0.005	0.019	0.026	0.002	0.009	0.019
Al ³⁺	0.007	0.021	0.000	0.000	0.009	0.012	0.009	0.000	0.000	0.000
Fe ³⁺	0.008	0.022	0.000	0.000	0.003	0.026	0.007	0.000	0.000	0.000
Sc ³⁺	0.000	0.000	-	-	0.001	0.000	0.004	0.004	0.005	0.006
Y ³⁺	0.005	0.033	0.005	0.038	0.000	0.019	0.030	0.000	0.008	0.007
Ce ³⁺	0.000	0.001	-	-	0.000	0.000	0.001	0.000	0.001	0.000
Sm ³⁺	0.000	0.000	-	-	0.003	0.000	0.002	0.000	0.003	0.000
Tb ³⁺	0.000	0.000	-	-	0.000	0.001	0.000	0.000	0.000	0.000
Dy ³⁺	0.000	0.000	-	-	0.001	0.000	0.004	0.003	0.000	0.002
Er ³⁺	0.001	0.002	-	-	0.000	0.005	0.005	0.000	0.003	0.002
Yb ³⁺	0.002	0.003	-	-	0.000	0.002	0.005	0.001	0.002	0.002
Ca ²⁺	0.011	0.039	0.001	0.009	0.000	0.021	0.003	0.000	0.000	0.004
F ⁻	0.020	0.021	-	-	0.028	0.025	0.020	0.000	0.000	0.027
Cl ⁻	0.004	0.002	-	-	0.004	0.013	0.002	0.000	0.002	0.000
O ²⁻	15.976	15.977	16.000	16.000	15.968	15.962	15.978	16.000	15.998	15.973
∑ cat.	7.997	8.020	8.002	8.014	7.994	8.008	7.999	7.998	8.001	7.997
Zr/Hf _w	20.3	20.4	8.91	5.82	13.9	11.1	20.0	31.6	36.0	35.2
Hf# %	2.45	2.45	5.41	8.06	3.54	4.39	2.50	1.58	1.41	1.43

titic zircons, the difference of T_S after Hf-correction is negligible, only 3 to 9 °C higher for the studied pegmatites.

The temperature interval is ca. 700–580 °C and there are no differences in T_S between the barren and beryl-columbite pegmatites (Table 3).

Discussion

Our results of zircon morphology and typology corroborate the older data (e.g. Lyakhovich 1968; Pupin 1980): the crystals are short prismatic to dipyrnidal (mainly G₁₋₂, rarely L₁₋₅ and A types) which indicate a relatively low crystallization temperature. The pure dipyrnidal {111} A-type zircon indicates the lowest temperature (cf. Pupin, l.c.), it occurs only at Moravany nad Váhom, in the most fractionated beryl-columbite pegmatite in the Western Carpathians (Uher 1991; Uher &

Broska 1995). In contrast, the correlation between zircon typology versus parent-rock composition does not work: the peraluminous quartz+alkali-feldspar+muscovite+(biotite) pegmatites contain mainly “alkaline”(G₁₋₂, A, L₅) types of zircon, but and the clearly metaluminous blocky K-feldspar pegmatite in Kunerad with bulk-rock A/CNK = 0.96 shows only “aluminous” (L₂₋₄) types of zircon, according to the classification of Pupin (1980).

The chemical composition of zircon shows increasing of Hf from the barren to the beryl-columbite pegmatites; the average 100Hf/(Hf+Zr) is 2.77 and 6.67 respectively. Our data are in good accordance with electron microprobe zircon compositions from the barren pegmatites of the Malé Karpaty Mts. (Gbelský 1979). The Hf abundance in zircon tends to be proportional to the overall fractionation level of granitoid magmas: correlation with alkali fractionation seems to be poor (Černý et al. 1985). Nevertheless, the lowest Zr/Hf val-

Table 2B: Representative compositions of zircon from studied West-Carpathian beryl-columbite granitic pegmatites (in wt.%). Sample abbreviations and locations: see the Appendix. Zr/Hf_w — weight ratio, Hf# % = 100Hf/(Hf+Zr) atom.

	BM-8				PI-15		Z-5		DU-1	
	center	rim1	rim2	rim3	center	rim	center	rim	center	rim
P ₂ O ₅	0.94	0.34	0.17	0.05	3.86	0.20	0.16	0.12	0.14	0.61
SiO ₂	31.12	31.69	32.01	31.00	23.23	29.14	31.26	30.57	31.65	29.31
ZrO ₂	59.07	53.69	50.05	46.10	49.16	52.79	58.64	54.00	56.10	49.00
HfO ₂	5.45	13.23	17.53	22.31	3.90	10.91	6.35	11.27	9.55	14.17
ThO ₂	0.04	0.11	0.10	0.00	0.11	0.09	0.03	0.00	0.00	0.00
UO ₂	0.36	0.36	0.34	0.29	1.84	1.55	0.68	0.40	0.51	1.39
Al ₂ O ₃	0.18	0.10	0.05	0.08	1.09	0.01	0.03	0.01	0.00	0.03
Fe ₂ O ₃	0.20	0.04	0.08	0.03	1.96	0.03	0.11	0.12	0.63	1.11
Sc ₂ O ₃	0.00	0.00	0.01	0.00	0.04	0.00	0.01	0.00	0.03	0.08
Y ₂ O ₃	0.17	0.00	0.00	0.00	1.68	0.00	0.07	0.00	0.00	0.55
Ce ₂ O ₃	0.02	0.02	0.01	0.01	0.14	0.15	0.04	0.01	0.00	0.00
Sm ₂ O ₃	0.00	0.00	0.01	0.01	0.11	0.09	0.00	0.00	0.11	0.00
Tb ₂ O ₃	0.01	0.03	0.00	0.00	0.04	0.05	0.00	0.00	0.00	0.01
Dy ₂ O ₃	0.00	0.05	0.00	0.00	0.32	0.08	0.07	0.00	0.00	0.05
Er ₂ O ₃	0.08	0.09	0.05	0.07	0.22	0.09	0.12	0.10	0.17	0.25
Yb ₂ O ₃	0.02	0.00	0.00	0.03	0.17	0.15	0.03	0.01	0.01	0.07
CaO	0.07	0.01	0.04	0.01	1.05	0.03	0.01	0.02	0.08	0.20
F	0.00	0.09	0.09	0.00	0.22	0.04	0.03	0.00	0.06	0.14
Cl	0.00	0.00	0.03	0.00	0.08	0.04	0.01	0.01	0.15	0.05
Total	97.73	99.81	100.53	99.99	89.11	95.41	97.64	96.64	99.13	96.95
FORMULAE BASED ON 16 OXYGEN ATOMS										
P ⁵⁺	0.101	0.037	0.019	0.006	0.462	0.023	0.017	0.013	0.015	0.069
Si ⁴⁺	3.953	4.066	4.136	4.127	3.282	3.964	4.020	4.045	4.045	3.944
Zr ⁴⁺	3.659	3.359	3.153	2.993	3.387	3.501	3.677	3.484	3.496	3.215
Hf ⁴⁺	0.198	0.485	0.647	0.848	0.157	0.424	0.233	0.426	0.348	0.544
Th ⁴⁺	0.001	0.003	0.003	0.000	0.004	0.003	0.001	0.000	0.000	0.000
U ⁴⁺	0.010	0.010	0.010	0.009	0.058	0.047	0.019	0.012	0.015	0.042
Al ³⁺	0.027	0.015	0.008	0.013	0.182	0.002	0.005	0.002	0.000	0.005
Fe ³⁺	0.019	0.004	0.008	0.003	0.208	0.003	0.011	0.012	0.061	0.112
Sc ³⁺	0.000	0.000	0.001	0.000	0.005	0.000	0.001	0.000	0.003	0.009
Y ³⁺	0.011	0.000	0.000	0.000	0.126	0.000	0.005	0.000	0.000	0.039
Ce ³⁺	0.001	0.001	0.000	0.000	0.007	0.007	0.002	0.000	0.000	0.000
Sm ³⁺	0.000	0.000	0.000	0.000	0.005	0.004	0.000	0.000	0.005	0.000
Tb ³⁺	0.000	0.001	0.000	0.000	0.002	0.002	0.000	0.000	0.000	0.000
Dy ³⁺	0.000	0.002	0.000	0.000	0.015	0.004	0.003	0.000	0.000	0.002
Er ³⁺	0.003	0.004	0.002	0.003	0.010	0.004	0.005	0.004	0.007	0.011
Yb ³⁺	0.001	0.000	0.000	0.001	0.007	0.006	0.001	0.000	0.000	0.003
Ca ²⁺	0.010	0.001	0.006	0.001	0.159	0.004	0.001	0.003	0.011	0.029
F ⁻	0.000	0.037	0.037	0.000	0.098	0.017	0.012	0.000	0.024	0.060
Cl ⁻	0.000	0.000	0.007	0.000	0.019	0.009	0.002	0.002	0.032	0.011
O ²⁻	16.000	15.963	15.957	16.000	15.883	15.974	15.986	15.998	15.943	15.929
Σ cat.	7.995	7.989	7.992	8.004	8.076	7.998	8.001	8.002	8.007	8.025
Zr/Hf _w	9.46	3.54	2.49	1.80	11.0	4.22	8.06	4.18	5.13	3.02
Hf# %	5.13	12.6	17.0	22.1	4.43	10.8	5.96	10.9	9.05	14.5

ues are found in zircon from the complex Li,Cs,Ta-rich rare-element pegmatites, e.g. Zambézia area, Mozambique (up to hafnon, Correa Neves et al. 1974; Törnroos 1982, 1985), Tanco, Canada (Černý & Siivola 1980), Mixeriqueira, Brasil (Cassedanne et al. 1985) or from highly evolved Li, Sn, Nb, Ta, F-rich granites, e.g. Beauvoir, France (Wang et al. 1992), Central Eastern Desert, Egypt (Renno 1995) and Suzhou, China (Wang et al. 1996). However, the maximum Hf-values in zircon from relatively primitive beryl-columbite the Kamzik pegmatite (20–22 wt. % HfO₂) exceed the Hf-content in zircon from the Tanco as well as some Zambézia district complex pegmatites with up to 18 and 21 wt. % HfO₂, respectively (cf. Černý & Siivola l.c., Törnroos l.c.). This could be explained by a local extreme fractionation of hafnium, accumulated in very thin (< 50 μm) outer zones; the Tanco zircon is largely homogeneous in this respect (Černý & Siivola 1980). However, the Col Dret pegma-

tite from France is another example of Hf-rich zircon (up to 26 wt. % HfO₂) in a relatively less evolved beryl-columbite pegmatite (Fontan et al. 1980).

The substitution diagrams (Fig. 4A–D) show possible mechanisms of iso- and heterovalent isomorphous substitutions from the routine HfZr₁ to the xenotime- (Y,HREE, Fe)³⁺P⁵⁺(Zr,Hf)₋₁Si₋₁⁴⁺ and berlinite-type Al³⁺P⁵⁺Si₂⁴⁺ substitution. All these substitutions are close to the 1:1 substitution vector with high correlation coefficients R = 0.78–0.94.

The calculation of zircon saturation temperature (T_S) was previously applied mainly to granites (Watson & Harrison 1983), not to pegmatites. Experimental data were obtained only for temperatures above 700 °C; however, Watson and Harrison expected a linear extrapolation of the saturation line for t < 700 °C. Thus, it is also possible to calculate meaningful T_S for granitic pegmatites. Our T_S = 700 to 590 °C are in good accordance with experimental data on pegmatite solidifica-

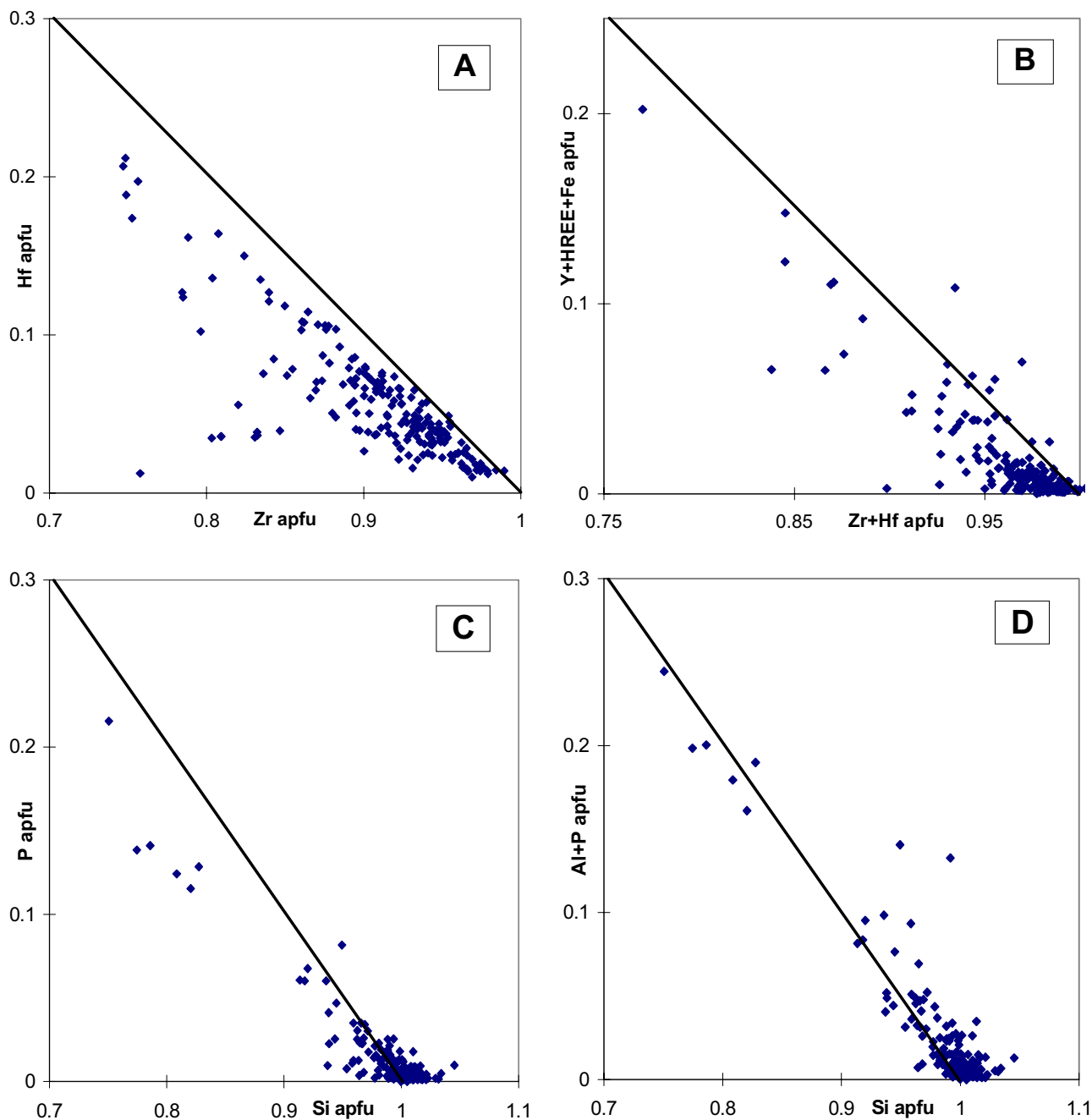


Fig. 4. Substitution diagrams of zircon, atoms per formula unit (apfu). **A** — HfZr_{-1} ; **B** and **C** — $(\text{Y,HREE,Fe})^{3+}\text{P}^{5+}(\text{Zr,Hf})_1^4\text{Si}_1^4$; **D** — $\text{Al}^{3+}\text{P}^{5+}\text{Si}_2^4$. The diagonal lines indicate 1:1 substitution vector.

tion (cf. London 1992). In addition, our results for zircon solidification correspond to the crystallization interval of homogeneous K-feldspar in coexistence with albite-oligoclase ($T = 625$ to 565 °C) for the feldspars-quartz-mica zone of the Považský Inovec pegmatites, Western Carpathians (Dávidová 1994).

Conclusions

(1) Zircon shows variable internal structures; crystals are unzoned, and irregularly or oscillatory zoned. Locally, a two-

stage evolution is observed with metamict Hf-poor central zone and oscillatory zoned, transparent, Hf-rich outer zone.

(2) The Hf contents of zircon from the more primitive, barren pegmatites are lower than those in zircon from more evolved, beryl-columbite bodies. A local extreme fractionation at the end of zircon crystallization led to the crystallization of thin oscillatory zones (10–50 μm) very enriched in Hf (8–22 wt. % HfO_2).

(3) A good positive correlation between P and Y+HREE indicates limited incorporation of the isostructural component of xenotime-(Y); possible substitution mechanisms are: HfZr_{-1} , $(\text{Y,HREE,Fe})^{3+}\text{P}^{5+}(\text{Zr,Hf})_1^4\text{Si}_1^4$ and $\text{Al}^{3+}\text{P}^{5+}\text{Si}_2^4$.

Table 3. Zircon saturation temperatures (T_s) of the studied West-Carpathian pegmatites.

Sample	T_s (°C)
Bratislava, Rössler Quarry (BM-3)	611
Bratislava, Kamzík Hill A (BM-7)	645
Bratislava, Kamzík Hill B (BM-8)	603
Bratislava, Dúbravka (BM-21)	646
Moravany, Striebornica (PI-15)	585
Podhradie, Železnica Valley (PI-25)	694
Valaská Belá, Velké Bystřé (SM-1)	624
Sklené, Háj Quarry (Z-3)	596
Ráztočno, Uhlisko (Z-5)	644
Kunerad, Kunerad Valley (MF-1)	585
Brusno, Velká Chochuľa Hill (NT-1)	606
Dúbrava, Sb-deposit, dumps (DU-1)	673

(4) The application of saturation temperature (T_s) to zircon from granitic pegmatites, gave realistic results of ca. 700 to 580 °C, which are in accordance with other experimental data as well as previous two-feldspar geothermometry results.

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Appendix: Sample locations, (Be)-beryl-, (CT)-columbite-tantalite-bearing pegmatites:

BM-1: quartz-feldspars-muscovite-(CT) pegmatite. Bratislava, Kramer quarry, Malé Karpaty Mts.
BM-3: quartz-feldspars-muscovite-biotite pegmatite. Bratislava, Rössler quarry, Malé Karpaty Mts.
BM-7: saccharoidal albite-quartz-muscovite pegmatite. Bratislava, Kamzík Hill A, Malé Karpaty Mts.
BM-8: quartz-feldspars-muscovite-(Be, CT) pegmatite. Bratislava, Kamzík Hill B, Malé Karpaty Mts.
BM-21: quartz-feldspars-muscovite-(Be) pegmatite. Bratislava, Dúbravka, E of Švábsky Hill, Malé Karpaty Mts.
PI-3: quartz-feldspars-muscovite pegmatite. Prašice, Duchonka, Soľnísko Hill, Považský Inovec Mts.
PI-15: quartz-feldspars-muscovite-(Be, CT) pegmatite. Moravany nad Váhom, Striebornica Ridge, Považský Inovec Mts.
PI-15Ab: saccharoidal albite-quartz-muscovite-(CT) pegmatite. Moravany nad Váhom, Striebornica Ridge, Považský Inovec Mts.
PI-22: quartz-feldspars-muscovite pegmatite. Bojná, Hradná Valley, southern quarry, Považský Inovec Mts.
PI-25: quartz-feldspars-muscovite pegmatite. Podhradie, Železnica Valley, W of Hrabový Hill, Považský Inovec Mts.
SM-1: quartz-feldspars-muscovite pegmatite. Valaská Belá, Velké Bystřé forest, Suchý-Malá Magura Mts.

Z-3: quartz-feldspars-muscovite-(Be) pegmatite. Sklené, quarry at S slope of Háj Hill, Žiar Mts.

Z-5: saccharoidal albite-quartz-muscovite-(CT) pegmatite. Ráztočno, forest over Uhlisko gamekeeper's lodge, Žiar Mts.

MF-1: K-feldspar blocky pegmatite. Kunerad, Kunerad Valley, Malá Fatra Mts.

S2A: Quartz-feldspars-muscovite-(CT) pegmatite. Brusno, Sopotnica Valley, Nízke Tatry Mts.

S2B: Quartz-feldspars-(CT) pegmatite. Brusno, Sopotnica Valley, Nízke Tatry Mts.

NT-1: Quartz-feldspars-muscovite-(Be, CT) pegmatite. Brusno, E of Veľká Chochuľa Hill, Nízke Tatry Mts.

NT-4: Quartz-feldspars-muscovite-(CT) pegmatite. Dúbrava, PA-9Z adit, antimony deposit, Nízke Tatry Mts.

DU-1: Quartz-feldspars-biotite-(Be, CT) pegmatite. Dúbrava, dumps of the antimony deposit, Nízke Tatry Mts.

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