

Vertical zonality of fractionated granite plutons reflected in zircon chemistry: the Cínovec A-type versus the Beauvoir S-type suite

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Abstract: We studied vertical changes in the chemical composition of zircon from two contrasting Variscan granite systems. The Beauvoir system (Massif Central, France) composed of three successive intrusions (B1, B2, B3) represents typical peraluminous S-type granite extremely enriched in P, F, Li, Rb, Cs, Be, Sn, Nb, Ta, and poor in Zr, Th, REE and Y. The Cínovec system (Krušné hory Mts/Erzgebirge, Czech Republic/Germany) composed of two successive intrusions (protolithionite granite, zinnwaldite granite) is only slightly peraluminous, P-poor, F, Li, Rb, Cs, U, Th, REE, Y, Sc, Sn, W, Nb, Ta-rich granite, which may be classified as A-type. In both localities, the most fractionated intrusions are located on the top of the system. Samples from borehole GPF-1 (Beauvoir) represent an 800 m long vertical section through the entire granite stock, while CS-1 borehole (Cínovec) reached a depth of 1600 m. Chemical compositions of zircons from both granite systems show distinct vertical zonality, but their shape and elemental speciation is highly contrasting. At Beauvoir, zircon shows a remarkable increase in Hf-content from 2–4 wt. % HfO₂ (~0.03 apfu Hf) in the deepest B3-unit to 15–19 wt. % HfO₂ (up to 0.18 apfu Hf) in the uppermost B1-unit. The highest contents of F, P, and U were detected in the intermediate unit B2 at a depth of 400–600 m. At Cínovec, Hf shows only moderate enrichment from ca. 2 wt. % HfO₂ in the deeper protolithionite granite to 5–10 wt. % HfO₂ in the uppermost part of the zinnwaldite granite. High contents of Th (3–8 wt. % ThO₂) are entirely bound in the uppermost section of the granite copula to a depth of 200 m, but below this level the contents only sporadically exceed 1 wt. % ThO₂. Concentrations of U, Y, HREE, Sc and Bi also reach their highest values in the uppermost parts of the zinnwaldite granite, but their decrease downward is much gentler. Extreme enrichment of outer zones of zircon crystals from some granites with Hf or high contents of Th, U, REE, Y, Nb and of some other elements in zircons from other localities is not considered to be a specific phenomenon characterizing melts of A- or S-type granite, but reflects a high degree of fractionation of systems rich in Na and F.

Key words: zircon, Cínovec, Beauvoir, trace elements analyses, S-type granite, A-type granite, fractionation.

Introduction

Zircon is almost a ubiquitous and relatively stable accessory mineral in the majority of types of granitoids. Its grains that show no obvious metamictization provide information about the chemical composition of the melt, which the granite crystallized from. In common I- and S-type granite, zircon belongs among the first crystallizing minerals, although some slightly Hf-enriched grains may precipitate during the final stage of rock crystallization. Zircon is frequently embedded in biotite and its crystallization results in the decrease of contents of not only Zr (and Hf), but also of Th, Y and HREE in the melt. On the contrary, in strongly fractionated peraluminous S-granites, generally low in Zr, zircon is one of the late-crystallizing minerals. It is interstitial and strongly to extremely enriched with U, P, F and with a number of “ore” elements (Nb, Ta, W, Bi). In the A-type granites, zircon crystallizes during the whole process of the melt differentiation, so that in relatively less differentiated intrusions the zircon crystallized as an early mineral, while in later highly differentiated intrusions it may also be filling interstices.

The contents of trace elements in zircon have been extensively investigated since the early 1960s (summary in Görz

1974). However, only the routine use of electron probe micro-analysis and LA-ICP MS methods during the last 20 years has produced reliable data concerning the contents of many elements (Uher et al. 1998; Wang et al. 2000; Huang et al. 2002; Rubatto 2002; Hoskin & Schaltegger 2003; Finch & Hancher 2003; Pettke et al. 2005; Johan & Johan 2005; Breiter et al. 2006; Pérez-Soba et al. 2007; Grimes et al. 2007; Van Lichtervelde et al. 2009). So far, the most comprehensive study of the chemical composition of zircons from various types of magmatic rocks obtained using the ICP-MS method was published by Belousova et al. (2002). The following average contents (medians) were established in zircons from granites: ca. 0.1 wt. % P₂O₅, 0.25 wt. % Y, tens ppm of LREE, hundreds ppm of HREE, 4 ppm Nb, 2 ppm Ta, 9 ppm Pb, 368 ppm Th and 764 ppm U. Zircon from fractionated granites was found to be relatively rich in REE (total 1.5–2 wt. %). Metamict zircon can be LREE enriched. A positive Ce-anomaly is common. Belousova et al. (2002) also report contents of 100–1000 ppm Nb and 10–100 ppm Ta in zircon. The average Nb/Ta ratio in zircon is 3, whereas the chondrite value is 17. The Th/U ratio in zircon usually corresponds to 0.1–1.0, while the ratio of these elements in the Earth’s crust is equal to ca. 4. Contents of Th and U show a

positive correlation with Y and increase with increasing fractionation of magmas from ultramafic rocks up to granites. Belousova et al. (2002) consider high contents of P to be primary because phosphorus is compensated by the sum of REE+Y as a consequence of xenotime substitution.

The majority of published analyses of zircons have been obtained using the electron microprobe (see below). However, only a few of the most abundant elements occurring in zircon were analysed using this technique (in addition to Zr, Hf and Si also U, Th, Y, some REE, Al and Ca). Complete analyses for the 20 or more trace elements that contribute to the chemical composition of individual zircon grains are still scarce (Förster 2006; Breiter et al. 2006, 2009; Uher et al. 2009; Förster et al. 2011).

The Zr/Hf ratio in chondrites is 37 (Hoskin & Schaltegger 2003), but this ratio in zircons varies considerably. There is a general rule that the Zr/Hf ratio in crystallizing zircon decreases with progressive fractionation of the melt. The content of Hf in zircon from rocks ranging from kimberlites to common granites remains almost the same (0.8–1.7 wt. %) and increases significantly only in strongly fractionated granites (Belousova et al. 2002). The highest concentrations of Hf in zircon were found in pegmatites. Černý & Siivola (1980) found 13.3–17.9 wt. % HfO₂ (0.136–0.166 apfu Hf) in zircon from the Tanco pegmatite in Manitoba (Canada). Recently, Van Lichtervelde et al. (2009) reported from this locality late zircon with up to 38.9 wt. % HfO₂. Raimbault (1998) reported 5.5–12.8 wt. % HfO₂ (0.055–0.116 apfu Hf) and up to 11.67 wt. % P₂O₅ (0.33 apfu P) in a zircon from the Li-F pegmatite at Chedeville (France), while contents of UO₂ do not exceed 3 wt. % and those of ThO₂ are 0–11.9 wt. %. Contents of Y and Sc are a few tenths of a percent. Contents of REE are not given. Uher & Černý (1998) found in beryl-columbite pegmatites from Slovakia up to 22 wt. % HfO₂. Hafnion, the Hf-dominant member of the zircon group was found in rare-metal pegmatite at Zambezia, Mozambique (Correia Neves et al. 1974).

Wang et al. (2000) analysed zircons from granites of I- and A-type in Laoshan, P.R.China. Zircons from the I-type granites are generally poor in trace elements (HfO₂<2 wt. %, UO₂, ThO₂, Y₂O₃<1 wt. %), while zircons from the more fractionated facies of A-type granites contain as much as 12.4 wt. % HfO₂ and 4.3 wt. % ThO₂, but only small amounts of UO₂ (<0.4 wt. %), Y₂O₃ (<1.4 wt. %) and P₂O₅ (<0.75 wt. %). Contents of REE were not analyzed here either. Wang et al. (1996) found an extremely high content of Hf (up to 34.8 wt. % HfO₂, 0.353 apfu Hf) in zircon from an A-type granite at Suzhou, P.R.China. This zircon is U- and Th-free, and Y-, P-poor (<0.5 wt. % Y₂O₃, <1 wt. % P₂O₅). Other elements were not reported. Huang et al. (2002) found up to 22.0 wt. % HfO₂ in zircon from Yichun topaz-lepidolite granite, P.R. China.

Uher et al. (1998) described a zircon rich in Hf and P, but very poor in U, Th, Y and REE from the strongly peraluminous Homolka muscovite granite of the South Bohemian Pluton. Hoskin et al. (2000) analysed zircon from the zoned I-type Boggy Plain pluton, Australia, and found 0.30–3.98 wt. % HfO₂. Pérez-Soba et al. (2007) were able to distinguish two types of zircon in Spanish peraluminous

granites: older prismatic crystals with low contents of trace elements and high Zr/Hf ratio embedded mostly in biotite, and younger, mostly interstitial zircon enriched with U, Th, Y and REE and having a low Zr/Hf ratio.

Kempe et al. (2004) pointed out that extreme Hf-enrichment is typical of zircons with patchy structure from P-poor granites. This observation contradicts the results of analysis of zircons from European Variscan rare-metal granites obtained by us. The highest contents of Hf we found in zircons from the peraluminous P-rich granites at Beauvoir (this study) and at Argemela in Portugal (Breiter & Škoda 2010).

Zircons from peralkaline rocks contain in general less trace elements. De Liz et al. (2009) described zircons from shoshonite association of the Lavras do Sul intrusive complex in Brazil to contain on average 1.0–1.4 wt. % HfO₂, 3–75 ppm Nb, 195–414 ppm Th, 400–800 ppm U and 700–2000 ppm Y. Nardi et al. (2012) found zircons from several intrusions of peralkaline granites of A-type near the tin-bearing deposit of Pitinga in Brazil to contain on average 1.8–5.0 wt. % HfO₂, 8–825 ppm Nb, 200–6649 ppm Th, 456–2975 ppm U and 2003–9211 ppm Y.

The chemistry of zircon from the Beauvoir granite was investigated by Wang et al. (1992). The published compositions are as follows: 2.4–8.1 wt. % (one grain with 18 wt. %) HfO₂, UO₂ up to 7.6 wt. %, ThO₂ max. 0.35 wt. % and PbO up to 0.55 wt. %. Elements such as P, Y and REE were not analysed.

Johan & Johan (2005) analysed the following 16 elements in zircon from Cínovec: P, Si, Zr, Hf, Th, U, Pr, Sm, Dy, Er, Yb, Y, Sc, Fe, Ca, and F and found significant differences in the compositions of zircons from the zinnwaldite and protolithionite granites. Their interpretation is based on the idea that the zinnwaldite granite is of metasomatic origin. This view, however, is different from that of the majority of other investigators (Breiter et al. 1999; Förster et al. 1999; Thomas et al. 2005).

This paper on an example of two geologically well-documented small ore-bearing granites — the Beauvoir and the Cínovec is intended to demonstrate the different behavior of zircon during the crystallization of fractionated magma of S- and A-type granites and to show differences in zircon chemistry with depth and its relationship to an overall chemistry of the granite pluton.

Geology and samples

The late Variscan Cínovec granite lies on both sides of the Czech-German border in the eastern sector of the Krušné hory/Erzgebirge Mts. Here, the late Variscan tin-bearing granites form ca. 20 km long NW-SE- oriented belt intruded into the Upper Proterozoic paragneisses and Upper Carboniferous rhyolites. Only a few small exposures less than 1 km² in size, in the form of small copulas (Cínovec, Altenberg) or vertical stocks (Krupka, Sadisdorf), are exposed on the surface. The pluton consists of two main types of granite: (i) the older medium- to fine-grained mostly distinctly porphyritic biotite to protolithionite granites compose the majority of the known volume of the pluton; (ii) the younger medium- to fine-grained not porphyritic albite-topaz-zinnwaldite granites ac-

accompanied by Sn-W (Nb, Ta, Mo, Sc) mineralization of greisen type form small separate intrusions. The spatial relationship between the two types of granite is different: the younger ore-bearing granites can form stocks or stock-works with steep contacts which intrude in older granites proved by numerous boreholes and underground workings made at Krupka (Eisenreich & Breiter 1993), or intruded in the form of tongue-like bodies along the upper contact of older granites having formed rather flat copulas in their roof (Cínovec and its surroundings). Contacts of both types of granite are evidently intrusive.

The Cínovec granite copula exposure 1.4×0.3 km large was studied to a depth of 1596 m by borehole CS-1 (Štemprok & Šulcek 1969). An albite-topaz-zinnwaldite granite (hereinafter "zinnwaldite granite", ZiG) was proved to exist in several textural varieties to a depth of 735 m, while an albite-protolithionite granite (hereinafter "protolithionite granite", PrG) continues to greater depths (Fig. 1). A fractionation *in situ* can be observed in the zinnwaldite granite showing increasing concentrations of volatile and lithophile elements upward. The apical part of the copula has been eroded, but a facies with mica corresponding to lepidolite is preserved to a depth of ca. 80 m below the present surface (Rub et al. 1998). From the viewpoint of geochemistry, the Cínovec pluton represents

strongly fractionated A-type granites: it is only slightly peraluminous, enriched with F, Li, Rb, Zr, Th, HREE, Sc, Sn, W, Nb and Ta, and depleted of P, Ti, Mg and Ca (Table 1). Common accessory minerals comprise fluorite, topaz, cassiterite, columbite, microlite, pyrochlore, Nb-rutile, zircon, thorite, xenotime, fluorides, oxo-fluorides and carbonates of REE (Cocherie et al. 1991; Rub et al. 1998; Breiter et al. 1999; Förster et al. 1999; Johan & Johan 2005; Breiter 2011).

The Beauvoir granite forms a small body (<0.2 km²) at the southern edge of the late Variscan Echassieres granite pluton in the northern part of the Massif Central, France. Geochemically it is a highly specialized, strongly peraluminous (S-type), rare metal-bearing granite enriched with P, F, Li, Rb, Nb, Ta, Sn, and W, and depleted of Si, Fe, Ti, Mg, Sr, Y, REE etc. (Cuney et al. 1992; Raimbault et al. 1995). The Beauvoir granite is the latest intrusion in a peraluminous granitic complex composed of three successively emplaced units: the hidden more or less hypothetical La Bosse granite, the Colettes two-mica granite, and the Beauvoir topaz-lepidolite-albite granite (Cuney & Autran 1987; Cuney et al. 1992). All gran-

Table 1: Whole-rock chemical composition of granites from Cínovec (major elements in wt. %, trace elements ppm).

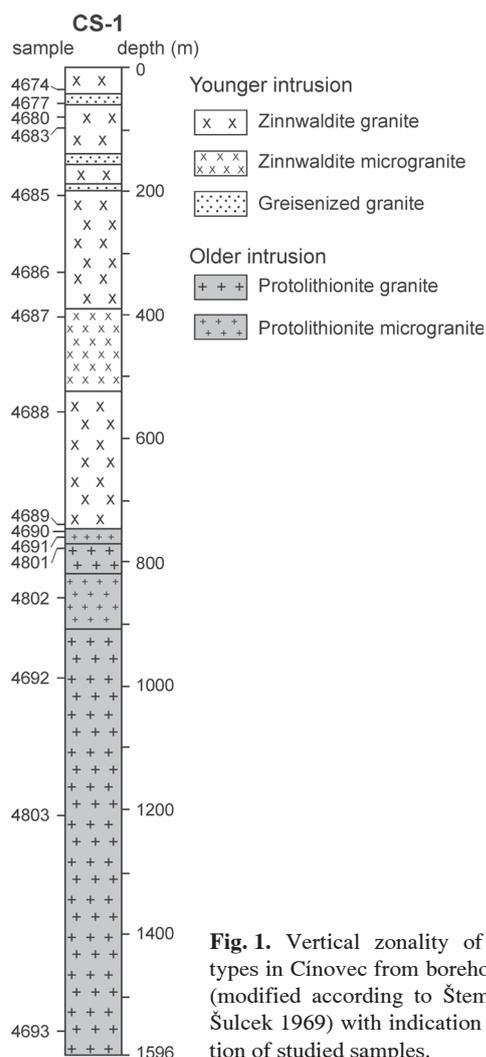


Fig. 1. Vertical zonation of granite types in Cínovec from borehole CS-1 (modified according to Štemprok & Šulcek 1969) with indication of position of studied samples.

Unit	ZiG	ZiG	PrG	PrG
Depth (m)	60	559	749	1579
SiO ₂	72.22	74.69	75.56	75.53
TiO ₂	0.01	0.03	0.05	0.07
Al ₂ O ₃	15.92	13.21	12.76	12.54
Fe ₂ O ₃	0.20	0.32	0.32	0.60
FeO	0.45	0.58	0.79	0.78
MnO	0.09	0.06	0.05	0.05
MgO	0.09	0.03	0.06	0.07
CaO	0.38	0.35	0.45	0.64
Li ₂ O	0.216	0.167	0.061	0.055
Na ₂ O	4.83	4.02	3.66	3.49
K ₂ O	2.39	4.53	4.78	4.73
P ₂ O ₅	0.015	0.012	0.009	0.011
F	0.79	0.75	0.46	0.51
LOI	1.95	0.78	0.72	0.87
Total	99.55	99.54	99.73	99.98
Rb	1440	1900	1133	802
Sr	72	6	12	13
Ga	54	40	31	25
Zr	44	58	125	124
Hf	9.1	6.8	8.1	6.9
Th	15	32	52	58
U	4	8.6	39	32
Nb	109	74	56	52
Ta	52	31	8	7
W	13	41	14	12
Y	7.5	49	114	103
La	3.9	22.5	42	34
Ce	13.5	62	105	83
Pr	1.84	7.2	12.4	10.3
Nd	4.9	22	44	40
Sm	1.54	6.4	12.6	10.4
Eu	<0.02	<0.02	0.08	0.12
Gd	1.03	5.4	12.4	40.5
Tb	0.33	1.4	2.8	2.3
Dy	2.4	10.1	19	15.5
Ho	0.51	2.1	3.9	3.4
Er	1.9	7.2	12.6	11.1
Tm	0.46	1.6	2.3	1.9
Yb	4.2	12.4	16.3	13.1
Lu	0.65	1.9	2.4	1.9

ite types intruded into lower-Paleozoic micaschists. The 900 m deep borehole GPF-1 allowed study of the vertical evolution of the Beauvoir granite over a section more than 700 m long (Fig. 2). Three granitic units marked B1 to B3 were distinguished by Rossi et al. (1987) and Raimbault & Azencot (1987). Later, a detailed geochemical study divided the Beauvoir granite into two major units: B and B' (Raimbault et al. 1995). The B-unit forms the upper part of the stock representing geochemically more evolved, more fluid-enriched part of the Beauvoir initial magma. The B'-unit, smaller in volume, represents a relatively less evolved and later emplaced portion of the Beauvoir magma. Separation of the B- and B'-melts occurred at the early stage of evolution of the granite system. Later, both melts in fact fractionated independently. Thus, the upper B-unit can be divided into three sub-units, from the uppermost ultimately fractionated B1-unit (at a depth of 98–423 m), through the B2-unit (at a depth of ca. 423–571 m), to the B3-unit (in a depth of 765–790 m). Within the lower B'-unit, the relatively more fractionated B' 2-unit (at a depth of ca. 571–746 m), and less fractionated B' 3-unit (at a depth of ca. 850–870 m) can be distinguished. All granite units are built of quartz, K-feldspar, albite and Li-mica. Chemical composition of the latter mineral ranges from lepidolite (B1) to Li-enriched biotite (B' 3). Amblygonite and alkali-feldspars (Breiter et al. 2002) are the main hosts of phosphorus. Common accessory minerals include apatite, topaz, cassiterite, minerals of the columbite group and zircon. A number of other minerals were also identified (Raimbault

et al. 1995). Comprehensive whole-rock chemical data from Beauvoir were published by Cuney & Raimbault (1991) and Raimbault et al. (1995).

Altogether 15 samples from borehole CS-1 drilled at Cínovec, representing mineralogical and chemical development of the pluton to a depth of 1596 m, were collected and analysed. A total of 10 samples from borehole GPF-1 drilled at Beauvoir, representing all intrusive units defined by Raimbault et al. (1995), except for the B3-unit, were collected and analysed.

Analytical methods employed

In order to study zircon grains in relation to rock-forming minerals polished thin sections were made from all collected samples. Back-scattered electron (BSE) images were taken prior to analysis to study the internal zoning of individual mineral grains and their relative position to rock-forming minerals. Zircon and associated minerals such as monazite, xenotime, thorite, and other similar mineral phases were analysed using the identical set-up and included all of the chemical elements identified in at least one of the above-mentioned minerals. Elemental abundances of W, P, As, Nb, Ta, Si, Ti, Zr, Hf, Th, U, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Al, Sc, Bi, Mn, Fe, Ca, Pb, S, and F in oxide minerals were determined using a CAMECA SX100 electron microprobe (Masaryk University and Czech Geological Survey, Brno) equipped with five WD spectrometers. Minerals were analysed at an accelerating voltage and beam current of 15 keV and 40 nA, respectively, and with a beam diameter ranging from 1 to 5 μm . The following standards were used: U — metallic U, Pb — PbSe, Th — ThO₂, P — fluorapatite, Y — YAG, La — LaB₆, Ce — CeAl₂, Pr — PrF₃, Nd — NdF₃, Sm — SmF₃, Gd — GdF₃, Dy — DyP₅O₁₄, Er — YErAG, Yb — YbP₅O₁₄, Al — almandine, Si, Ca, Fe — andradite, Mn — rhodonite, W — scheelite, S — barite, F — topaz, As — InAs, Nb — columbite, Ta — CrTa₂O₆, Ti — titanite, Zr — zircon, and Sc — ScVO₄. Empirical formulae of zircon were calculated on the basis of 4 atoms of oxygen in a formula unit (4 O apfu).

Contents of major elements in whole rock samples from Cínovec were established using the standard methods of wet chemistry at the Laboratory of the Czech Geological Survey, Praha, while the trace elements were analysed in the ACME Laboratory, Vancouver, Canada using the ICP-MS method.

Results

Position of zircon crystals in granite and its internal structure

In Cínovec, zircon in the zinnwaldite granite forms tiny isometric crystals 10–50 μm in size (Fig. 3). They are enclosed in quartz and feldspars, but some of the grains that crystallized later occupy the interstices between the other minerals. Some crystals contain μm -sized inclusions of quartz and feldspars and numerous tiny cavities. Most of the crystals are not zoned in the BSE image. The internal composition is patchy with domains enriched in Hf, Y and Th. In the few zoned grains, the

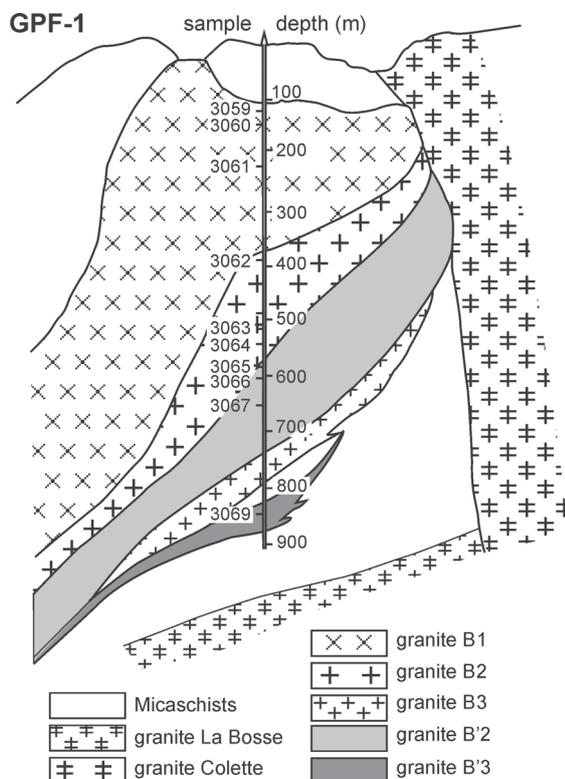


Fig. 2. Geological cross-section of the Beauvoir granite stock along the borehole GPF-1 Eschassieres (modified according to Raimbault et al. 1995) with indication of position of studied samples.

cores are patchy and heterogeneous, porous and enriched with uranium, whereas the rims are compact, homogeneous and enriched with Hf. Individual analyses of crystal cores give totals significantly lower than 100 wt. %, usually 90–95 wt. % that indicate a high degree of hydration due to metamict state. On the other hand, analyses of the compact rims give totals close to 100 wt. %. The majority of zircon crystals in the pro-

tolithionite granite are enclosed in mica. They are of similar size (10–50 μm), but crystals showing a distinct zonal structure and contrasting blebs of exsolved mineral phases close to xenotime and thorite in composition are relatively more abundant. However, even in this case, the crystal cores are porous.

In spite of low concentrations of Zr in the rock, all studied facies of the Beauvoir granite contain abundant hypidiomorphic

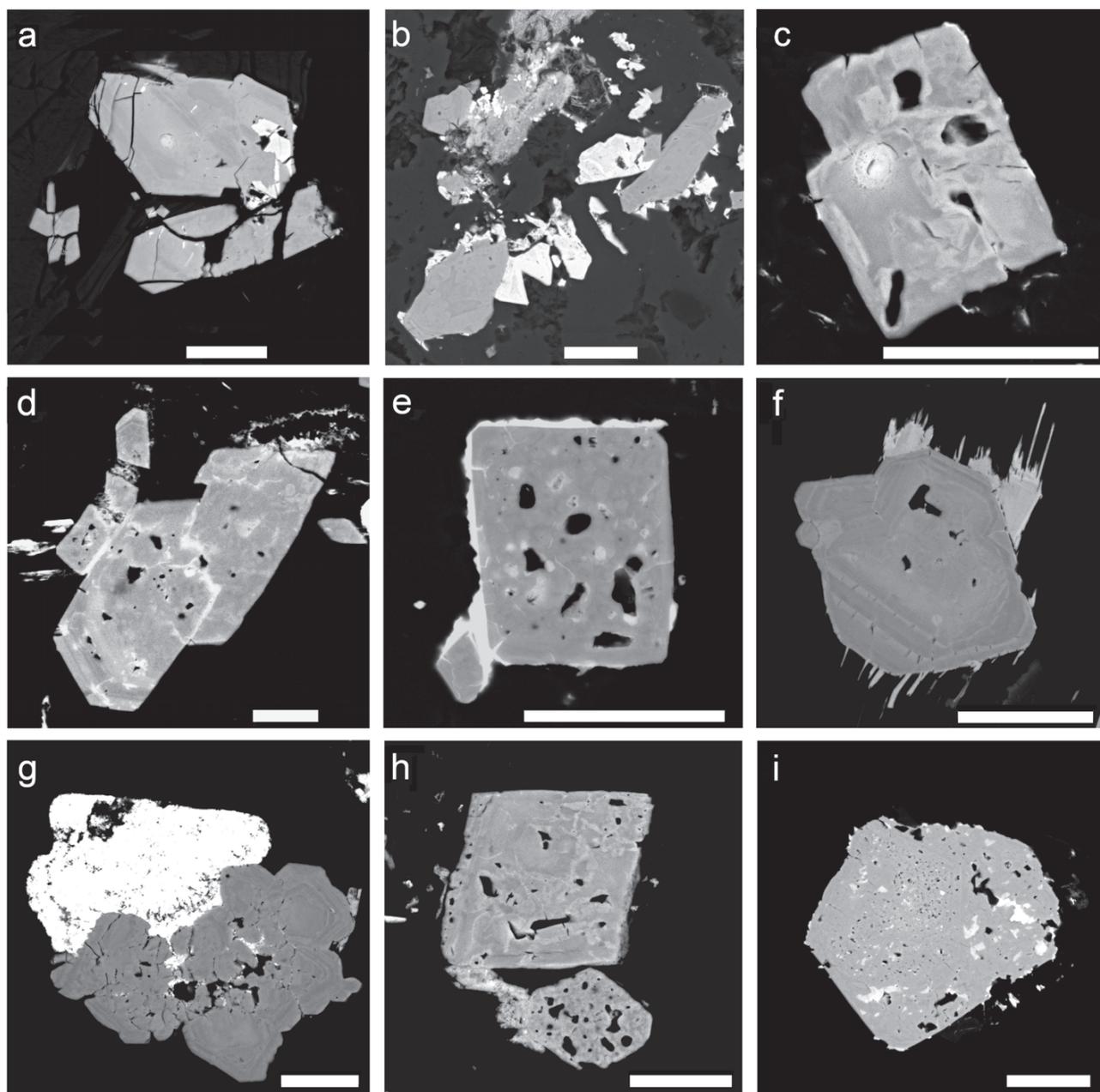


Fig. 3. Typical crystals of zircon from the Cínovec granite (BSE-images), scale bars in all cases 20 μm : **a** — zinnwaldite granite depth 97 m, two zircon grains with bright inclusion of Yb-rich xenotime-(Y); **b** — zinnwaldite granite depth 336 m, partly altered patchy zoned zircons (grey) with younger grains of Yb-rich xenotime-(Y) (bright); **c** — zinnwaldite granite depth 413 m, zircon with Hf-enriched rim; **d** — zinnwaldite granite depth 735 m, group of zircon crystal; **e** — vacuolized zircon with xenotime-(Y) rim, zinnwaldite granite, depth of 735 m; **f** — zoned zircon crystal embedded in protolithionite (black) with younger Yb-rich xenotime-(Y) (bright), xenotime-(Y) penetrates the protolithionite along cleavage, protolithionite microgranite, depth of 741 m; **g** — zoned zircon crystal with younger grain of thorite (bright), protolithionite microgranite, depth of 741 m; **h** — protolithionite microgranite depth 749 m, two patchy zoned and vacuolized zircons; **i** — protolithionite granite depth 1579 m, zircon (grey) with patchy domains enriched in Y (light grey) and inclusions of thorite (bright).

to idiomorphic zircon grains 10–50 μm large, rarely as much as 80 μm in size (Fig. 4). Zircon grains showing irregular spotty texture without any observable zoning or with only indistinct zoning in outer part of crystals prevail in more frac-

tionated facies. The number of grains with distinct zoning increases with growing depth in relatively less fractionated granite facies. Only a few relatively broad zones always exist, but a thick oscillatory zoning, which is common in zircon

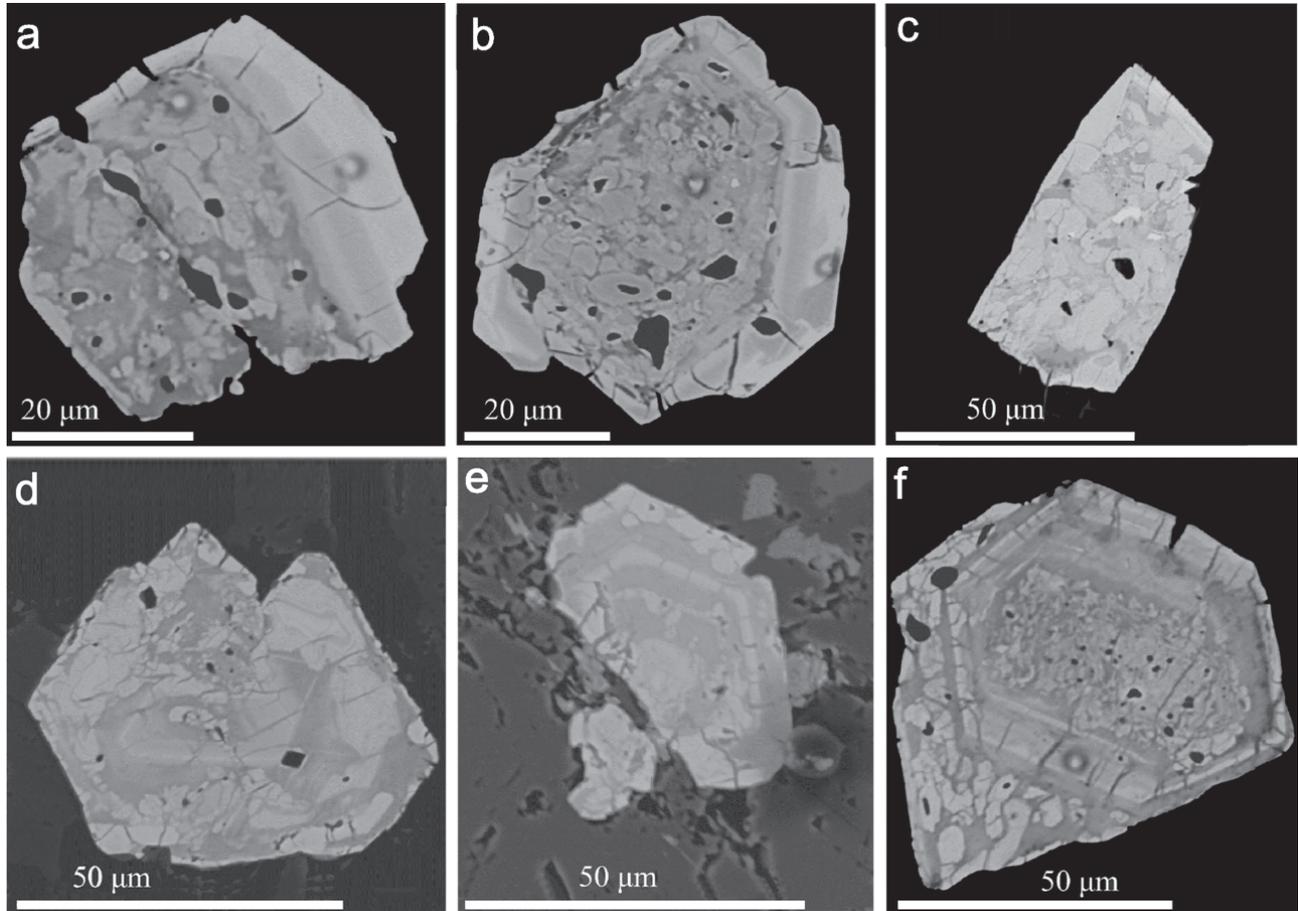


Fig. 4. Typical crystals of zircon from the Beauvoir granite (BSE-images): **a** — distinctly zoned zircon crystal with metamictized core and homogeneous Hf-rich rim, granite B1, depth 130 m; **b** — distinctly zoned zircon crystal with patchy U-rich core and Hf-rich rim, granite B1, depth 130 m; **c** — zircon crystal with irregular patchy texture, granite B1, depth 228 m; **d** — shady zoned zircon crystal with patchy texture, granite B'2, depth 573 m; **e** — well zoned zircon crystal with 4 Hf-rich and 3 U-rich metamictized zones, granite B'2, depth 637 m; **f** — complex zircon crystal with patchy core, well zoned transition zone and patchy rim, granite B3, depth 858 m.

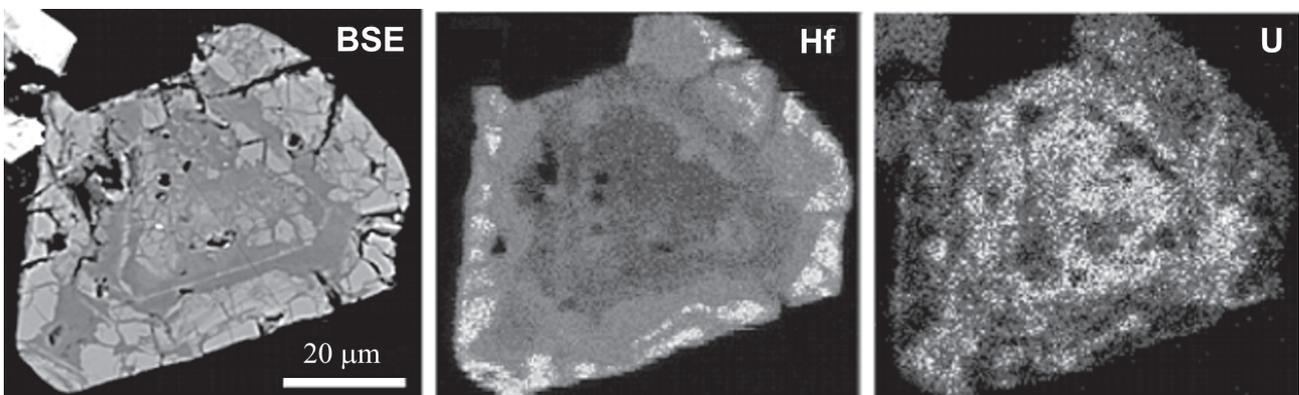


Fig. 5. Typical zircon crystal from the deeper part of the Beauvoir granite (depth of 583 m, unit B'2): BSE-image (scale bar 20 μm) and distribution of Hf in the outer part of the crystal, and U mainly in the core.

from other types of granite, has never been found. Zoning of several crystals was studied by X-ray mapping which showed that the bright colour of rims, commonly observable in BSE, is caused particularly by an increased content of Hf (Fig. 5).

Chemical composition of zircon

Approximately 120 microprobe analyses of zircon from Cínovec and 90 from Beauvoir were performed (Table 2; Figs. 6–8). Chemical compositions of zircons from both granite systems show distinct vertical zoning, but their shape and elemental speciation is highly contrasting.

Hafnium tends to accumulate in both systems in their uppermost highly fractionated parts. The increase in Hf concentration can be seen not only between individual subsequent intrusions but also *in situ* within one single intrusion. Greater ability of Hf, compared with Zr, to remain in the melt results in distinctly zonal structure of late zircon crystals with Hf-rich rims. At Cínovec the zircon crystals from the most fractionated facies of granite attain max. 8–10 wt. %. The area of high Hf contents extends to a depth of ca. 100 m below the surface. Zircon crystals from Beauvoir are even more Hf-enriched. Concentrations of HfO₂ in zircon from the uppermost part of the Beauvoir stock increase from 8 wt. % in crystal core up to 19.3 wt. % (0.184 apfu Hf, Fig. 6) in its marginal zones. The contents of HfO₂ in deeper parts of both plutons only rarely exceed 5 wt. %.

Uranium: contents of U range mostly between 0–2 wt. % UO₂, but concentrations of up to 4 % weight are relatively frequent at both localities, at Cínovec may occasionally reach as much as approximately 6 wt. % UO₂. The vertical distribution of U in zircon was found to be random (Fig. 6). At Cínovec the higher contents of uranium were detected in the upper parts of both types of granite, at depth levels of 0–200 m and

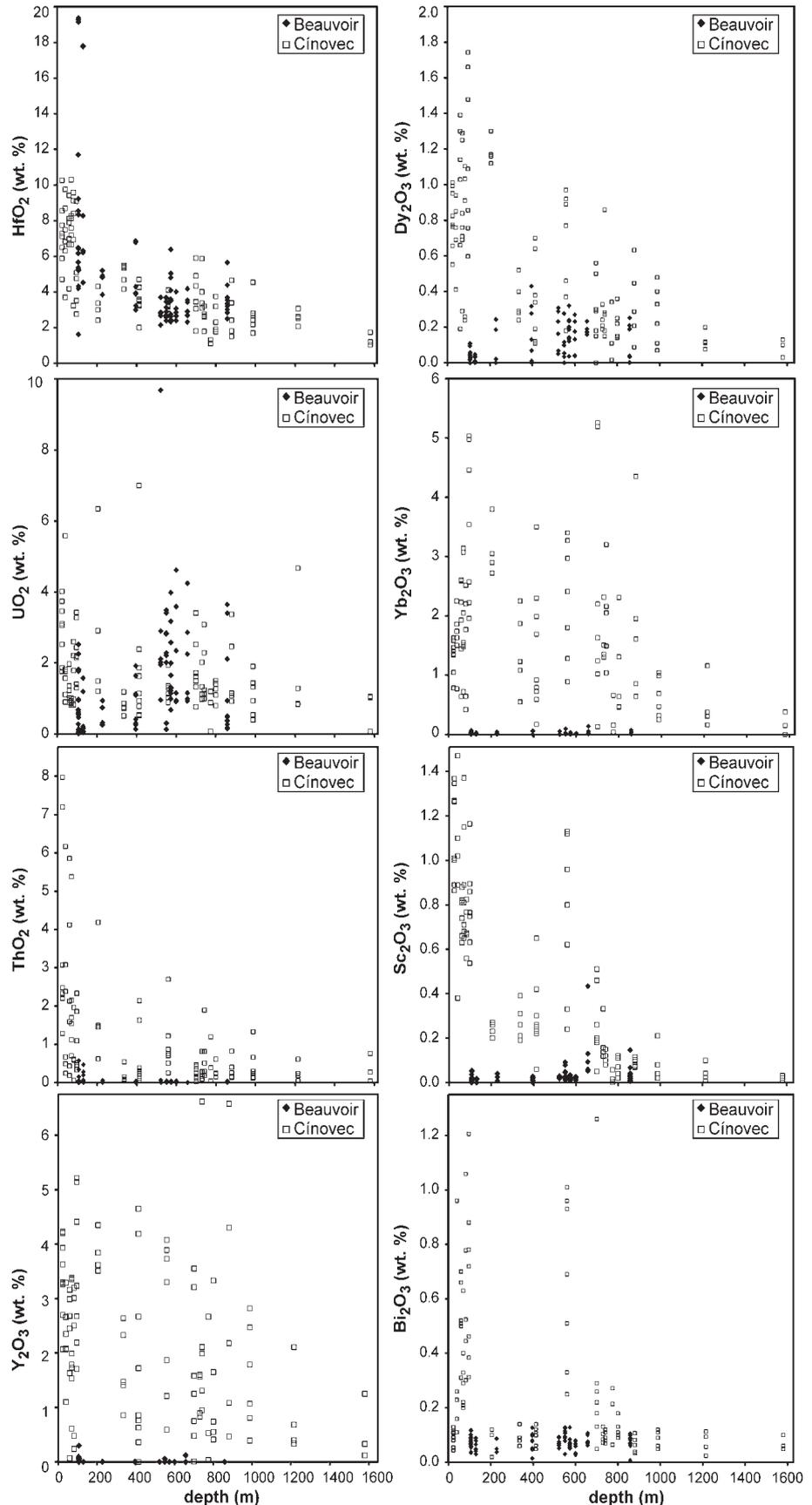


Fig. 6. Vertical distribution of selected chemical elements in zircon: Hf, U, Th, Y, Dy, Yb, Sc, Bi.

Table 2: Representative electron-microprobe analyses (wt. %) and structural formula (apfu) of zircon from Cinovec (ZiG, PrG) and Beauvoir (B1, B2, B'2, B3).

Unit	ZiG	ZiG	ZiG	ZiG	PrG	PrG	PrG	B1	B1	B2	B2	B'2	B'2	B3	B3
Depth (m)	24	97	413	559	860	988	1580	107	228	396	522	600	657	858	858
Sample	4672	4683	4687	4688	4802	4692	4693	3059B	3061	3062	3063	3066	3067	3069	3069
SO ₃	0.00	0.01	0.01	0.03	0.02	0.01	0.01	0.04	0.03	0.02	0.33	0.04	0.04	0.01	0.02
P ₂ O ₅	2.48	2.72	0.44	1.10	0.61	0.38	0.22	0.29	5.97	0.30	7.35	0.21	4.50	0.02	1.95
As ₂ O ₅	0.76	0.33	1.09	1.30	0.17	0.20	0.07	0.56	0.22	0.20	0.06	0.09	0.07	0.11	0.29
SiO ₂	23.26	24.04	25.46	24.76	29.95	29.76	30.65	30.60	23.31	31.15	19.11	29.92	20.93	32.02	26.49
Al ₂ O ₃	0.60	0.57	0.83	0.75	0.22	0.16	0.13	0.02	1.41	0.04	1.23	0.10	2.64	0.02	0.67
WO ₃	0.03	0.47	0.64	0.67	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Nb ₂ O ₅	0.84	0.89	0.45	0.39	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Ta ₂ O ₅	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.02	0.02	0.03	0.03	0.02	0.01	0.00	0.02	0.05	0.00	0.00	0.00	0.05	0.00	0.02
ZrO ₂	39.54	40.98	44.24	45.12	54.30	59.84	61.25	48.16	53.37	60.29	46.75	57.93	51.74	62.94	55.32
HfO ₂	10.27	3.53	2.01	3.18	2.42	2.80	1.74	19.15	4.82	6.78	2.15	2.66	2.69	4.39	2.84
ThO ₂	2.19	1.86	1.63	0.51	0.14	0.23	0.27	0.34	0.06	0.03	0.07	0.00	0.01	0.03	0.03
UO ₂	3.46	2.19	7.00	1.35	3.37	0.54	1.03	0.12	0.74	0.14	9.69	4.62	4.25	0.17	2.11
Sc ₂ O ₃	1.27	0.86	0.30	0.80	0.08	0.04	0.01	0.00	0.04	0.00	0.02	0.02	0.06	0.01	0.03
Y ₂ O ₃	3.27	4.41	2.67	3.89	1.08	1.07	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La ₂ O ₃	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Ce ₂ O ₃	0.20	0.37	0.34	0.52	0.05	0.02	0.02	0.00	0.03	0.00	0.00	0.00	0.00	0.02	0.00
Pr ₂ O ₃	0.00	0.06	0.02	0.00	0.02	0.10	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00
Nd ₂ O ₃	0.00	0.05	0.03	0.07	0.04	0.01	0.00	0.05	0.00	0.03	0.03	0.00	0.00	0.00	0.06
Sm ₂ O ₃	0.11	0.13	0.00	0.01	0.02	0.02	0.00	0.00	0.03	0.00	0.00	0.00	0.02	0.00	0.00
Gd ₂ O ₃	0.22	0.25	0.02	0.11	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00
Dy ₂ O ₃	0.76	1.48	0.34	0.89	0.21	0.22	0.13	0.02	0.19	0.00	0.16	0.04	0.17	0.03	0.21
Er ₂ O ₃	0.72	1.41	0.64	0.92	0.26	0.20	0.05	0.18	0.03	0.03	0.02	0.02	0.00	0.05	0.01
Yb ₂ O ₃	1.47	4.46	1.99	2.97	0.86	0.32	0.15	0.00	0.00	0.06	0.00	0.00	0.02	0.04	0.00
Bi ₂ O ₃	0.09	0.46	0.06	0.93	0.11	0.05	0.10	0.07	0.05	0.01	0.09	0.06	0.10	0.10	0.01
MnO	0.08	0.09	0.14	0.80	0.25	0.16	0.33	0.01	0.74	0.07	0.57	0.06	0.45	0.02	0.98
FeO	1.19	0.19	0.50	1.13	0.38	1.12	0.23	0.04	0.45	0.00	0.30	0.06	0.28	0.05	1.52
CaO	1.18	0.87	1.73	1.93	0.61	0.44	0.48	0.05	2.36	0.12	2.83	0.10	2.27	0.02	0.59
MgO	0.00	0.01	0.01	0.00	0.03	0.01	0.01	0.00	0.14	0.02	0.17	0.01	0.30	0.00	0.03
PbO	0.00	0.00	0.04	0.02	0.01	0.03	0.10	0.00	0.01	0.02	0.00	0.21	0.02	0.03	0.04
F	2.39	2.09	0.50	0.66	0.33	0.16	0.09	0.00	0.97	0.00	1.09	0.31	1.97	0.00	0.85
Total	96.37	95.09	93.17	94.87	95.60	97.91	97.41	99.75	95.04	99.35	92.02	96.43	92.60	100.07	94.12
S	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.009	0.001	0.001	0.000	0.000
P	0.076	0.084	0.014	0.033	0.017	0.010	0.006	0.008	0.167	0.008	0.222	0.006	0.134	0.001	0.056
As	0.014	0.006	0.021	0.024	0.003	0.003	0.001	0.010	0.004	0.003	0.001	0.002	0.001	0.002	0.005
Si	0.845	0.873	0.925	0.877	0.993	0.959	0.981	1.011	0.769	0.986	0.681	0.988	0.735	0.997	0.896
Al	0.026	0.024	0.036	0.031	0.009	0.006	0.005	0.001	0.055	0.001	0.052	0.004	0.109	0.001	0.027
B-site	0.961	0.987	0.996	0.966	1.022	0.978	0.993	1.031	0.996	0.998	0.965	1.001	0.980	1.001	0.984
W	0.000	0.004	0.006	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nb	0.014	0.015	0.007	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ta	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.001
Zr	0.701	0.726	0.784	0.780	0.878	0.940	0.956	0.776	0.858	0.931	0.813	0.933	0.886	0.956	0.913
Hf	0.107	0.037	0.021	0.032	0.023	0.026	0.016	0.181	0.045	0.061	0.022	0.025	0.027	0.039	0.027
Th	0.018	0.015	0.013	0.004	0.001	0.002	0.002	0.003	0.000	0.000	0.001	0.000	0.000	0.000	0.000
U	0.028	0.018	0.057	0.011	0.025	0.004	0.007	0.001	0.005	0.001	0.077	0.034	0.033	0.001	0.016
Sc	0.040	0.027	0.010	0.025	0.002	0.001	0.000	0.000	0.001	0.000	0.001	0.001	0.002	0.000	0.001
Y	0.063	0.085	0.052	0.073	0.019	0.018	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
La	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ce	0.003	0.005	0.005	0.007	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pr	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Nd	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Sm	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Gd	0.003	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dy	0.009	0.017	0.004	0.010	0.002	0.002	0.001	0.000	0.002	0.000	0.002	0.000	0.002	0.000	0.002
Er	0.008	0.016	0.007	0.010	0.003	0.002	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Yb	0.016	0.049	0.022	0.032	0.009	0.003	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Bi	0.001	0.004	0.001	0.008	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.001	0.001	0.000
Mn	0.002	0.003	0.004	0.024	0.007	0.004	0.009	0.000	0.021	0.002	0.017	0.002	0.013	0.001	0.028
Fe	0.036	0.006	0.015	0.034	0.011	0.030	0.006	0.001	0.012	0.000	0.009	0.002	0.008	0.001	0.043
Ca	0.046	0.034	0.067	0.073	0.021	0.015	0.016	0.002	0.083	0.004	0.108	0.003	0.085	0.001	0.021
Mg	0.000	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.007	0.001	0.009	0.000	0.016	0.000	0.001
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000
A-site	1.096	1.071	1.077	1.138	1.004	1.048	1.023	0.968	1.035	1.001	1.061	1.003	1.074	1.000	1.054
F	0.274	0.240	0.058	0.074	0.034	0.016	0.009	0.000	0.101	0.000	0.123	0.032	0.219	0.000	0.091
Zr/Hf at.	6.6	19.8	37.6	24.2	38.4	36.5									

740–800 m, while at the Beauvoir locality the highest values were detected in B2 and B' 2 units at a depth of 550–650 m.

Thorium: it is one of the elements for which the contents differ most in the two plutons studied (Fig. 6). In the upper part of zinnwaldite granite in Cínovec, to a depth of 200 m, Th-content in zircon commonly reach 1–5 wt. % (max. 8 wt. %) but in deeper parts of the pluton fluctuate only around 0.5 wt. % ThO₂. Contents of Th in the Beauvoir pluton are almost always lower than 0.05 wt. % ThO₂, and only in B1 unit sporadically exceed 0.1 wt. % ThO₂.

Yttrium: it is another element behaving differently at both localities (Fig. 6). At Cínovec the contents of Y₂O₃ in zircons are generally high, fluctuating in zinnwaldite granite mostly between 0.3–5 wt. %, in the upper part of protolithionite granite, they range mostly between 0.2–3 wt. %, whereas in its deeper section only 0.1–1 wt. % Y₂O₃ (but here the zircon is associated with xenotime). Conversely, contents of Y in zircon from Beauvoir are negligible (only sporadically exceed 0.05 wt. % Y₂O₃).

HREE: due to the dimensions of its crystal lattice, zircon is able to absorb the heavy REE in particular (Figs. 6, 8). The most abundant elements are Yb and Dy, the former element correlates well with Y and its distribution at both localities is similar as that of Y as far as attains its absolute contents (up to 5 wt. % Yb₂O₃ at Cínovec) and also regarding differences in its vertical distribution. Dy at Cínovec behaves like Yb, but its contents are ca. 3 times lower than those of Yb (max. 1.7 wt. % Dy₂O₃). Dy at Beauvoir compared to Y is markedly enriched reaching 0.3 wt. % Dy₂O₃ at a depth interval of 400–650 m (units B2 and B' 2). Anomalous enrichment of Dy in relation to other REE is well demonstrated in the Dy/Yb ratio the values of which range between 0.1 and 0.9 at Cínovec, but between 4 and 9 at the above mentioned depth interval in borehole GPF1. It is to be pointed out, that chondritic Dy/Yb ratio is 1.15.

LREE: contents of light REE in zircon are commonly low (Fig. 8), usually near the detection limits of the microprobe. When comparing both localities studied, the LREE-contents are slightly higher in Cínovec (0.2–0.7 wt. % Ce₂O₃ and 0.1–0.20 wt. % Nd₂O₃).

Scandium: it is another element exhibiting significantly higher concentrations in zircon from Cínovec (Fig. 6). The contents of Sc₂O₃ reach 0.6–1.5 wt. % in the upper 100 m thick section of lepidolite and zinnwaldite granite, but its contents decrease randomly with depth. Contents of Sc in protolithionite granite at Cínovec and in all types of granite at Beauvoir are markedly lower, mostly not exceeding 0.1 wt. % Sc₂O₃.

Bismuth: it is a characteristic trace element occurring in a number of European Variscan tin-bearing granites. While some zircons from the upper section of zinnwaldite granite (from a depth of 50–100 m) at Cínovec contain as much as 1.0–1.2 wt. % Bi₂O₃, zircons from Beauvoir usually contain only around 0.05–0.10 wt. % Bi₂O₃, (Fig. 6).

Phosphorus: it is a common minor element incorporated in zircon (Fig. 7). At Cínovec, contents up to 4 wt. % P₂O₅ were detected in the upper 200 m of the granite copula. However, with increasing depth the concentration of P only rarely exceeds 1 wt. % P₂O₅. Although the Beauvoir granite system is

strongly P-enriched, zircons from the uppermost B1 unit in Beauvoir contain only 0.5–1 wt. % P₂O₅; higher contents up to 8 wt. % P₂O₅ were found only scarcely. In the deeper units B2 and B' 2 at a depth interval of 500–700 m the contents of 5–8 wt. % P₂O₅ were often found more frequently.

Arsenic: it is only rarely analysed in zircon, although it is likely to be a relatively common minor or trace element bound in this mineral. Arsenic at Cínovec appears to be more abundant when its contents of 0.2–1.0 (max. 1.6) wt. % As₂O₃ were detected to a depth of 1000 m, but at greater depths its concentration again decreases to 0.1 wt. % As₂O₃ (Fig. 7). Zircons from the Beauvoir locality contain mostly 0.1–0.2 wt. % As₂O₃ and close to the upper granite contact as much as 0.8 wt. % As₂O₃.

Fluorine: it is a substantial component of fractionated granite magmas and at the end of crystallization it enters crystal lattice of numerous silicates where it replaces oxygen or OH radical. High contents of fluorine in zircons from Cínovec were established to a depth of ca. 200 m (1.0–2.5 wt. % F, Fig. 7), and then gradually decrease to 0.0–0.2 wt. % F at a depth of 1600 m. At the Beauvoir locality the highest concentrations of F in zircon, similar to phosphorus, were detected in lower sections of borehole GPF-1 with a maximum of 1.5 wt. % F at a depth interval of 500–700 m. Zircons in the uppermost section of the borehole contain surprisingly only 0.0–0.8 wt. % F.

Niobium, tantalum and tungsten: these elements form in granites individual minerals such as columbite/tantalite and wolframite but they also enter the crystal lattice of zircon. Tungsten and niobium were commonly detected in zircons from Cínovec to a depth of ca. 800 m (up to 1 wt. % WO₃ and 1.3 wt. % Nb₂O₅). Tantalum was found only rarely in contents of 0.1–0.4 wt. % Ta₂O₅. Contents of all three elements at depths below 800 m are below their detection limits. Their concentrations at the Beauvoir locality are markedly lower: Ta and W always below their detection limits, Nb was detected only in one sample from a depth of 573 m (top of the B' 2 unit) showing a content of 0.1–0.8 wt. % Nb₂O₅.

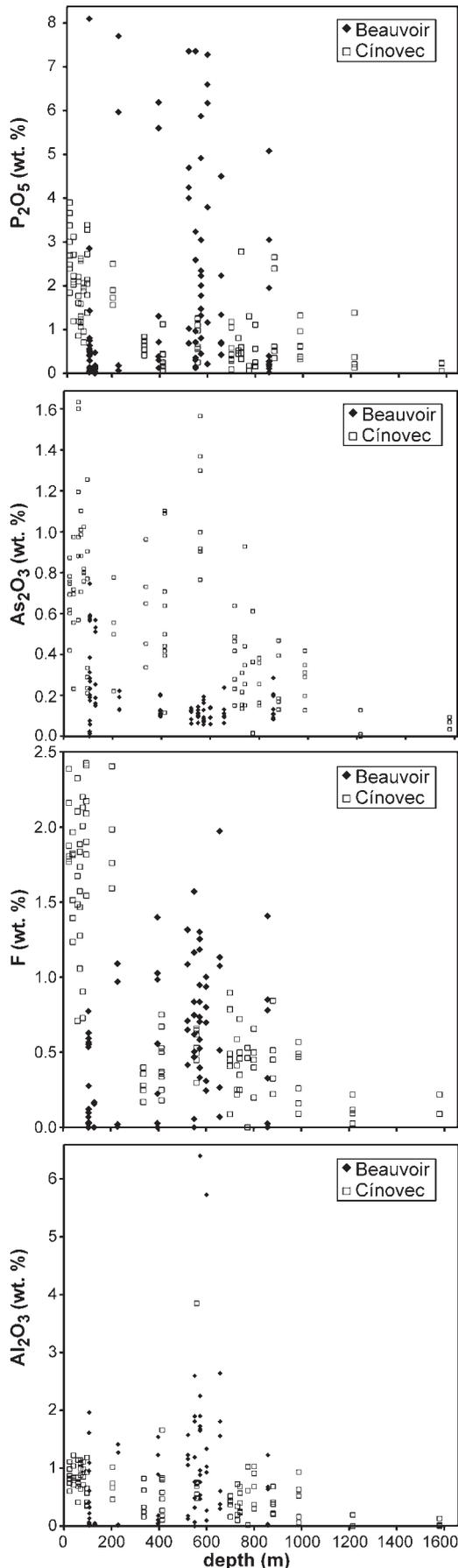
Titanium: its contents at both localities are low and its distribution similar: 0.0–0.06 (up to 0.1) wt. % TiO₂ and tends to decrease with depth.

Lead: contents of this element at both localities are low, mostly below the detection limit, only rarely exceeding 0.1 wt. % PbO with no signs of any vertical zoning. No correlation exists between U and Pb or between (Th+U) and Pb either. If all lead in zircon is considered to be of radiogenic origin then a substantial part of it in the studied zircons must have been leached out.

Sulphur: was detected in measurable amount only in zircons from the uppermost section of the Cínovec granite copula to a maximum depth of 80 m (0.5–4 wt. % SO₃).

Aluminum: contents of Al at Cínovec range between 0.0 and 1.2 wt. % Al₂O₃ and tend to decrease gently with depth. At Beauvoir the highest concentrations (1–3 wt. % Al₂O₃) were found at a depth interval of 500–700 m. Its contents both upward and downward are slightly lower (Fig. 7).

Iron, manganese, calcium and magnesium: iron in zircons from both localities shows contents of 0–1.5 wt. % FeO regardless of the depth which the samples were collected from.



Manganese was found to be more abundant at the Beauvoir locality (up to 1.5 wt. % MnO) relative to the Cínovec locality (max. 0.8 wt. % MnO). The highest contents of this element were detected in zircons from medium depths of 400–800 m. Calcium is also more abundant at Beauvoir (up to 3 wt. % CaO) than in zircons from Cínovec (max. 2 wt. % CaO). The highest concentrations of Ca, similar to Mn, were detected in zircons from medium depths. On the contrary, the contents of Mg differ significantly: while at Cínovec they do not exceed 0.07 wt. % MgO, at Beauvoir they attain 0.5 wt. % MgO in the middle section of borehole GPF-1. Divalent elements Ca, Mg, Fe and Mn, due to their ionic radii, are unsuitable to enter the crystal lattice of zircon. Elevated Ca-, Fe-, Mn- and Mg- contents were found mainly in metamict areas of analysed zircon grains, we suppose that these elements were incorporated in zircon after its metamictization.

Associated U, Th, Y, REE-minerals

Xenotime-(Y) was found to be the major host for Y and HREE in the granites from Cínovec. In the zinnwaldite granite, this mineral is abundant. It forms homogeneous subhedral crystals with a maximum size of 10 μm . Whenever this mineral is in direct contact with zircon, xenotime-(Y) is always younger. Thin coatings of xenotime-(Y) enveloping whole zircon grains were observed in deeper parts of the zinnwaldite granite. A substantial proportion of Y and HREE is located in the primary magmatic fluorite. Thorite is rather sporadic in the zinnwaldite granite, but secondary minerals of the bastnäsite group containing Th, U and REE are abundant and mostly occur in contact with fluorite.

Thorite and xenotime-(Y) are relatively abundant accessories in the Cínovec protolithionite granite, occurring together with zircon as inclusions in mica, but monazite-(Ce) is rare. Zircon was not found in direct contact with these minerals so it is difficult or impossible to establish their relative age of crystallization in relation to zircon. Neither uraninite nor coffinite was identified at the Cínovec locality. Uranium at Cínovec, apart from zircon, is bound in minerals of the bastnäsite group, which crystallized at the later stages of granite evolution.

Separate REE, Y and Th minerals were not found in either of the types of granite at Beauvoir because contents of these elements are generally low (Cuney et al. 1992; Raimbault et al. 1995). Rossi et al. (1987) described only scarce uraninite in some samples from a depth exceeding 475 m (deeper part of unit B2, and units B3, B' 2, B' 3).

Discussion

Aluminum and divalent elements in zircon, metamictization and hydration, low totals of analyses

The position of Al, Ca, Fe, Mn and Mg in the zircon structure can be explained in two ways: (i) by primary incorporation of these elements in the lattice sites to compensate the substitution of Nb, Ta, and W for Zr and/or substitution of P and As for Si, (ii) through secondary entry of these elements into metamictized parts of zircon crystal lattice in the fluids responsible for alteration.

Geisler et al. (2002, 2003) and Schmidt et al. (2006) demonstrated that there is significant removal of Si, Zr, U, Th, Pb and uptake of Al, Mg and Ca due to the interaction of chloride-bearing fluids with metamict zircon. This means that the present chemical composition of porous metamictized

Fig. 7. Vertical distribution of selected chemical elements in zircon: P, As, F, Al.

cores in zircons may be quite different from those produced by crystallization from the initial magma. Moreover, the reaction of zircon with fluids accelerates the restoration (annealing) of the lattice structure in amorphized domains (Geisler et al. 2003). Nevertheless, rational evaluation of the primary and secondary contents of Al, Ca, Fe, Mn and Mg remains problematic. For instance, Geisler & Schneider (2000) consider contents of CaO exceeding 2 wt. % to be strongly indicative for post-metamictization chemical changes in zircon. Ca-enriched zircons from Cínovec usually show to high occupancy of the A-site (Table 2), which is a strong argument for late, post-metamict input of Ca. Nyman et al. (1984) and Crichton et al. (2005) found similarities in structures of CaSO_4 , CePO_4 and ZrSiO_4 and proposed so-called clinoanhydrite substitution ($\text{Ca}^{2+} + \text{S}^{6+} \leftrightarrow \text{REE}^{3+} + \text{P}^{5+}$) as a possible way to incorporate Ca into monazite lattice. In Cínovec, occasionally 1–4 wt. % SO_3 was found, but there is no correlation between Ca and S. So, in the case of the studied zircons, existence of the ($\text{Ca}^{2+} + \text{S}^{6+} \leftrightarrow \text{Zr}^{4+} + \text{Si}^{4+}$)-substitution is unlikely. On the other hand, the Al bound in tetrahedral position according to berlinite substitution ($\text{Al}^{3+} + \text{P}^{5+} \leftrightarrow \text{Si}^{4+} + \text{Si}^{4+}$) is believed to be primary magmatic (Breiter et al. 2006).

Analytical totals for zircon obtained using EMPA are often significantly lower than 100 wt. %. The deficit in the analyses is commonly interpreted as being due to the OH ion in the mineral structure or to molecular H_2O in the amorphous domains of the metamict zircon structure. This is only partly true because a substantial part of the missing matter may be accounted for other elements that were not analysed. For instance, As, Bi, Nb and Ta, that are analysed only sporadically, may constitute as much as a several wt. % of zircon. The direct determination of the water content in zircon is rare but analyses do exist. For instance, Nasdala et al. (2009) found up to 8.8 wt. % H_2O in Archaean zircon from Jack Hills, Australia. Caruba & Baumer (1985) synthesised zircon with as much as 0.8 apfu $(\text{OH},\text{F})_4$ replacing the (SiO_4) group in the structure of the mineral. These authors predict that hydration takes place only in tetrahedral sites (SiO_4) without affecting the occupancy of the Zr position.

Remarkable contents of As (Breiter et al. 2009; Förster et al. 2011) and Bi (Breiter et al. 2006, 2009) reported recently from granitic zircons from Krušné Hory/Erzgebirge are supposed to be a product of high-temperature hydrothermal overprinting taking place shortly after granite crystallization, and so prior to metamictization.

High contents of fluorine in many zircon grains from Beauvoir and Cínovec correlate with enhanced content of U, thus with grade of metamictization. Contents >0.5 wt. % F in Beauvoir and >1.5 wt. % F in Cínovec were found mainly in zircons with >2 wt. % UO_2 . On the other hand, there is no correlation between F and Hf: the Hf-enriched rims of zircon crystals crystallizing from residual F-rich melt are actually poor in F. In that case, strong enrichment of F in some zircons should be interpreted as results of reaction of late F-enriched fluids with U-rich parts (dominantly cores) of some zircon grains. Enrichments of W, Nb, Ta and Sc in zircons from Cínovec correlated well with enrichment of F. Thus, entry of all these elements in the zircon structure may also be better explained via reaction of zircon with high-temperature F- and

metal-rich fluids after granite solidification. All fractionated granites in the Erzgebirge intruded at a very shallow subvolcanic level and were fast cooled after intrusion (Jarchovský & Pavlů 1991; Seltmann & Schilka 1991; Breiter et al. 1999, 2005). Thus, the question of whether the short-lived high-temperature hydrothermal fluids reacted with still fully-ordered or already metamictized zircons, remains unresolved.

Taken together, high contents of Hf, U, Th, Y and REE in studied zircons are probably primary magmatic and mirror high grade of fractionation of evolved granitic melt, while unusually high contents of F, As, W, Nb, Ta, Ca, Fe and Mg resulted from later hydrothermal overprint. In the case of phosphorus and alumina, P in xenotime substitution and P+Al in berlinite substitution are primary magmatic in origin. The additional P in pretulite and ximengite substitution (Breiter et al. 2006) and the additional Al are very probably of secondary hydrothermal origin.

Comparison between the studied zircons and whole-rock chemical composition

The differences in the geochemical character of the granites from Beauvoir and Cínovec enables conclusions to be drawn about which features of the chemistry of the zircons investigated are governed by the type of granite magma involved (S- or A-type) and which resulted because of the high degree of fractionation of residual melt regardless of the magma type.

Strongly fractionated rare metal-bearing granites and pegmatites are in general enriched with F, Li, Rb, Sn, W, Nb and Ta, but differ markedly in contents of Zr, Th, REE and Y. The A-type granites are Zr, Th, REE, Y-rich, while granites of S-type are poor in these elements. Similarly, pegmatites are classified as LCT-type (strongly peraluminous, enriched with Li, Cs, Ta, Rb, P, Ga, etc.) and NYF-type (enriched with Nb, Y, F, REE, Sc, Zr, U, Th, etc., Černý & Ercit 2005). Zircon from fractionated and F-rich granites was often found to contain high concentrations of minor and trace elements. A high content of complex-forming fluorine in particular, and also high concentrations of sodium in the magma are reported to enable the entry of “exotic” elements into the crystal lattice of zircon (Kempe et al. 2004). Although many authors (cf. Raimbault et al. (1995) and references therein) pointed out the high activity of F-rich fluids in Beauvoir, the zircons from Beauvoir are nearly pure stoichiometric $(\text{Zr},\text{Hf})\text{SiO}_4$. In contrast, at Cínovec, zircon absorbed not only “common” minor and trace elements such as Y, HREE, U and Th, from the melt, but also contains significant amounts of “exotic” elements like W, Nb, Ta, Sc, Bi, As. For example, the content of W in granites from Beauvoir is about 40 ppm, while in Cínovec the content is about 20 ppm. Zircons from Cínovec generally contain 0.5–1.0 wt. % WO_3 , while zircons from Beauvoir are W-free. The content of Nb in granites from both localities is similar, ca. 100–150 ppm, but zircon from Cínovec contains about 0.5 (up to 2) wt. % Nb_2O_5 , whereas zircon from Beauvoir is Nb-free. Entry of elements like Sc, Bi, Nb, Ta, and W into the structure of zircon from Cínovec are thought not to be due to the specific type of melt (A-type vs. S-type), while zircons from some fractionated S-type granites from the Erzgebirge are also Nb,

Ta, W, Bi, Sc-enriched (cf. Breiter et al. 2006). Concentrations of Ta in zircon crystallizing from Li-rich pegmatite melt may be occasionally as high as 4.7 wt. % Ta₂O₅ (Van Lichtervelde et al. 2009); contents of Nb are usually much lower (Van Lichtervelde et al. 2011).

High contents of Th, Y and HREE in zircon from Cínovec and very low contents of all these elements in zircon from Beauvoir correlate well with concentrations of these elements in all granite varieties from both localities (10–60 ppm Th, 7–114 ppm Y and 4–16 ppm Yb in Cínovec, <1 ppm Th, <10 ppm Y, <0.05 ppm Yb in Beauvoir).

At Beauvoir, high contents of U, P and F in zircons from the interval 500 to 700 m deep do not correlate with the chemical composition of the whole-rock. Contents of F in granite at a depth of about 520 m decrease from 2.0 to 1.6 wt. %, while contents of P₂O₅ below the depth of 550 m decrease from 1.3 to 0.8 wt. %. Contents of U are stable at around 15 ppm. Enrichment of zircon with U, P and F is believed to have resulted from intensive mineral-fluid reactions taking place in the B2 and B'2 granite units in the interval from 500 to 700 m deep (compare also Raimbault et al. 1995). It is also worth mentioning that high contents of U are found in the cores of zircon crystals from both Beauvoir and Cínovec, while their outer zones and rims are poor in uranium. Consequently, uranium is thought to have entered the zircon structure particularly at higher temperature at the beginning of its crystallization. During the final stages of crystallization uranium preferentially entered the minerals of the bastnäsite group crystallizing from water-saturated melt or aqueous fluids.

The content of any trace element in crystallizing mineral is theoretically determined by its concentration in the melt and by partition coefficient $Kd^{mineral/melt}$ for the given trace element. Partition coefficients $Kd^{mineral/melt}$ for zircon were established experimentally (Thomas et al. 2002; Luo & Ayres 2009) or by comparison of their contents in zircon and in bulk rock (de Liz et al. 2009; Nardi et al. 2012), zircon and surrounding glass (Sano et al. 2002) or zircon and surrounding leucosome (Bea et al. 1994). However, results obtained and referred by the above-mentioned authors differ significantly (Table 3). The reason for such large differences in the determination of Kd lie only partly in analytical inaccuracies when establishing low contents of the given trace elements. Different composition of the parent rock melt is considered to play a fundamental role in distribution of trace elements in zircon, specifically its peraluminosity or otherwise its peralkalinity, the content of water, fluorine and other fluxing agents.

Temperature and pressure are also believed to affect the partition coefficient. Moreover, the relative older zircons (or their cores) crystallized from parental melt, while their rims and the late, interstitial zircons in the whole crystallized from residual melt; nevertheless the chemical composition (trace-element content) of parental and residual melt differ substantially. In such complex cases, the determination of real $Kd^{zircon/melt}$ is impossible. Therefore, we at least determined empirical enrichment factors (hereafter Ef) of zircon/whole rock for elements of which concentrations in zircon from Cínovec and Beauvoir could be established with sufficient accuracy (Table 3). Contents of Y, HREE and Th in whole-rock samples of granites from Cínovec correlate well with the content of Zr which indicates that the Th/Zr, Y/Zr and HREE/Zr ratios in the melt were stable during the major part of fractionation. In spite of this, the enrichment factor for all the above-mentioned elements and also for Ce and Nb was found to be higher in more differentiated zinnwaldite granite than in protolithionite granite. The Ef values determined by us are also higher than the Kd established by the above-mentioned authors in less differentiated granites.

As emerges from the comparison of Kd and Ef shown in Table 3, both coefficients for all the studied elements in slightly to strongly peraluminous rocks are higher than those in alkaline rocks. In this context the occurrence of solid solutions zircon-xenotime and zircon-thorite found at some localities in the Krušné hory/Erzgebirge area (Förster 2006; Breiter et al. 2009; Förster et al. 2011) indicates that zircon under specific conditions of fractionated melts rich in water and F is able to absorb by order of magnitude higher contents of Th, U, Y, HREE, than would correspond to Kd coefficients established in granitoids of “common” composition. In the case of enrichment of some zircons in Nb, Ta, Sc and Bi, the ratio between the primary magmatic and secondary fluid-induced portion of particular element remain unresolved.

Based on the above-mentioned analyses and considerations the zircons from strongly differentiated granites and pegmatites can be divided into two basic types:

1. zircons strongly enriched with Hf (>10 wt. % HfO₂, (particularly in rims), and poor in all other HFS-elements. This type was reported from some European Variscan strongly peraluminous granites (Beauvoir and Argemela/Portugal (Breiter & Škoda 2010)), LCT pegmatites (Tanco/Canada (Van Lichtervelde et al. 2009), Chedeville/France (Raimbault 1998)), but also from some A-type granites (Suzhou, China (Wang et al. 1996));

Table 3: Partition coefficient $Kd^{zircon/melt}$ from laboratory experiments (Sano et al. 2002; Thomas et al. 2002; Luo & Ayres 2009) and natural granitoids (Bea et al. 1994; de Liz et al. 2009; Nardi et al. 2012) and empirical enrichment factors $Ef^{zircon/whole\ rock}$ calculated in this work.

Source	Remark	Ce	Dy	Yb	Y	Nb	U	Th
Bea et al. 1994	peraluminous leucosome	2.04	38.8	278	71.4		354	22.1
Sano et al. 2002	melt of dacite glass	0.36	45.9	277				
Thomas et al. 2002	melt inclusions in zircon from tonalite	0.43–2.06	12.4–73	14–97	2.4–191	204–312		
Luo & Ayres 2009	melt of peralkaline rhyolite	0.14–3.3		11–83	6.8–66		2.1–32	2–18
de Liz et al. 2009	shoshonitic rocks	1.6–3.0	29–64	150–544	54–114	0.2–3.6	71–168	14–19
Nardi et al. 2012	peralkaline A-type granites	1.5	73	307	106	2.1	168	23
this work	Cínovec protolithionite granite	1–10	49–147	118–914	43–158	<10	192–742	32–106
this work	Cínovec zinnwaldite granite	9–144	140–3451	595–6212	106–2694	13–66	307–2807	63–1412
this work	Beauvoir						270–1760	210–650

2. zircons moderately enriched with Hf (< 10 wt. % HfO₂), as well as moderately to strongly enriched with Th, Y, HREE, (Nb, Sc, Ta, Bi). This type is typical of the Krušné hory/Erzgebirge area: A-type granites at Čínovec (Förster 2006) and Hora Svaté Kateřiny (Breiter et al. 2009), S-type granites at Podlesí (Breiter et al. 2007). A similar type of zircon, but with lower absolute contents of Th, Y and REE, was also described from peralkaline A-type granites in Eastern China (Wang et al. 2000; Xie et al. 2005), peraluminous granites from Spain (Pérez-Soba et al. 2007), granites and pegmatites from Japan (Hoshino et al. 2010) and leucogranites from Slovakia (Uher & Ondrejka 2009).

Consequently, it is evident that high contents of minor elements in zircon are not determined only by their concentrations in the melt or by the type of melt as such or even by the degree of its peraluminosity and or alkalinity, and the degree of melt fractionation, but other phenomena or parameters of the crystallizing system seem to play a decisive role in this case. For instance, the concentration of Li (up to 1 wt. % Li₂O in rocks with HFSE-poor zircon and only 0.1–0.2 wt. % in granites with HFSE-rich zircon) may play some role or the pressure can also affect the process of crystallization. All granites in the Krušné hory/Erzgebirge area containing HFSE-rich zircons are of subvolcanic nature and underwent explosive degasation and resurgent boiling followed by intensive F-rich fluid percolation (Breiter et al. 2005).

Some authors (e.g. Kempe et al. 2000; Pettke et al. 2005; Uher et al. 2009) argued for post-magmatic origin of the HFSE- and REE-enriched late zircons or rims of zoned zircon crystals. But in case of zircon from the Čínovec borehole (this study) and similar A-type granites from the Krušné hory/Erzgebirge Mts (Breiter et al. 2009; Förster et al. 2011), during the fluid-related processes zircons are enriched in As, P, and F, while released REEs form secondary minerals like chernovite and bastnäsite.

Fractionation of HREE

Zircon preferentially concentrates HREE. Experiments carried out by Hanchar et al. (2001) showed that zircon crystals doped with REE+P displayed an increase of approximately 1000-fold in contents of REE from La through Lu as a result of shrinking ionic radii. Of the LREE, zircon tends to selectively accumulate Ce⁴⁺, which often results in a distinct positive Ce anomaly. Negative Eu anomalies are typical of zircon from slightly to strongly peraluminous granites (cf. summary in Hoskin & Schaltegger 2003), but absent in zircon from sub-alkaline and shoshonitic rock (de Liz et al. 2009); relative concentration of Eu in zircon mimic those in the whole rock.

The distribution of HREE at Čínovec is homogeneous. HREE are more abundant than LREE and there is a distinct positive Ce-anomaly (Fig. 8). Granites from Čínovec are characteristic of a distinct “tetrad effect” in chondrite-normalized distribution of REE (Cocherie et al. 1991). Imprint or transfer of tetrad effect from a melt into zircon has been interpreted as a proof of late crystallization of this mineral after separation of fluid phase from F-rich melt (Nardi et al. 2012). However, because of the applied analytical method only contents of even-numbered elements (more abundant in

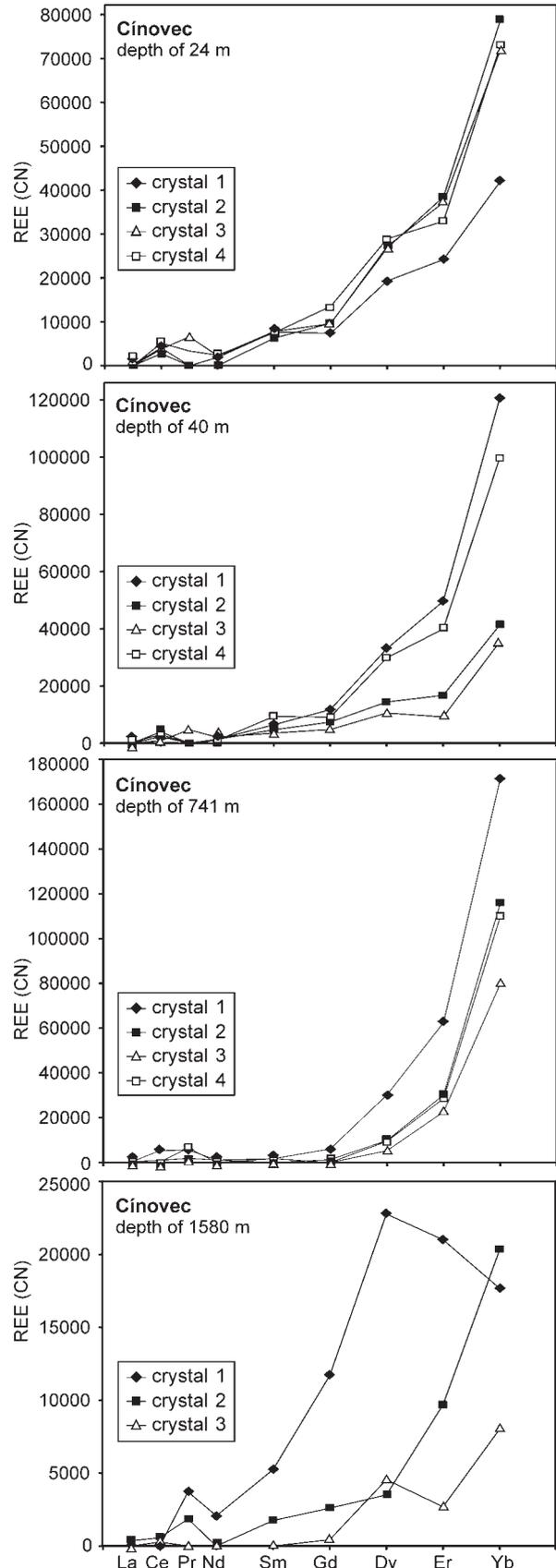


Fig. 8. Chondrite-normalized distribution of REE in zircons from Čínovec (normalized according to McDonough & Sun 1995).

nature) were established in zircon, it would be inappropriate to comment the above-mentioned phenomenon.

Contents of REE in zircon from Beauvoir are very low, usually near or below the detection limit of the microprobe.

Phosphorus in the zircon crystal lattice

Kimura & Hironaka (1936) first described zircon enriched with P and Y, and Hata (1938) explained this as the result of zircon-xenotime miscibility. Hanchar et al. (2001) experimentally confirmed the tendency for zircon to accommodate Y and REE in its lattice dominantly by the xenotime substitution ($YPO_4 \leftrightarrow ZrSiO_4$). This may explain the P-enrichment in zircons from the generally P-poor, but Y, REE-enriched A-type granites. In peraluminous P-rich and Y, HREE-poor granites, the high P-contents can be explained by the berlinite substitution $Al + P \leftrightarrow Si + Si$ (Breiter et al. 2006). In special cases of Sc-enriched zircons, pretulite-type substitution ($Sc + P \leftrightarrow Zr + Si$) also plays a role (Breiter et al. 2006).

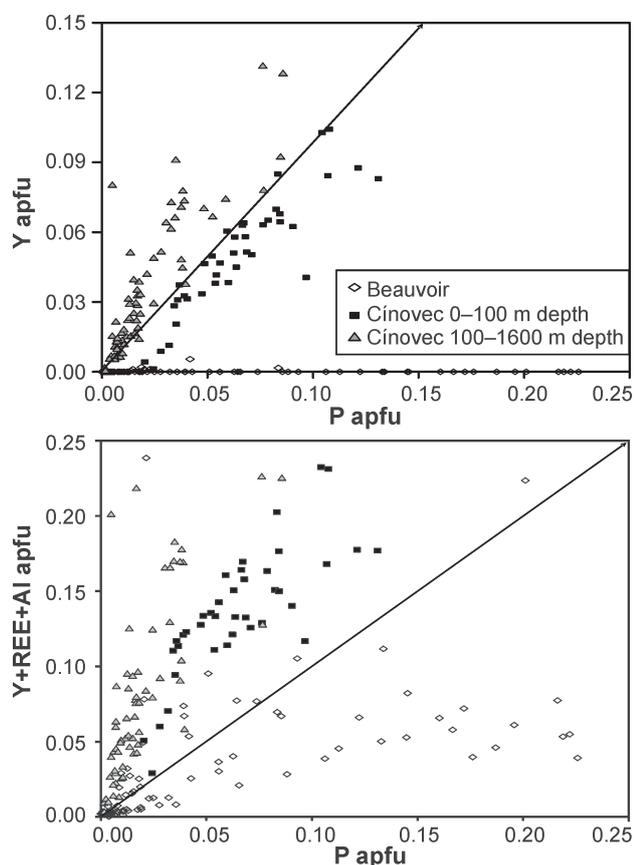


Fig. 9. Crystallochemical relations in zircon: a) correlation between P and Y: zircon from the uppermost 100 m interval in Cinovec follows xenotime-(Y) substitution ($Y + P \leftrightarrow Zr + Si$) with only small deficiency of Y, while in zircon from the Cinovec deeper part yttrium markedly prevails and is probably compensated by Nb and Ta ($Y + Nb \leftrightarrow Zr + Zr$) or by Li ($Y + Li \leftrightarrow Zr$). Zircon from Beauvoir is Y-free and phosphorus enters the lattice mainly acc. to berlinite substitution ($Al + P \leftrightarrow Si + Si$); b) taking into account all trivalent elements, there is clear deficiency of P in all samples from Cinovec, and still overabundance of P in Beauvoir.

Among the zircons studied, the Beauvoir zircons are Y-free and follow the berlinite substitution with P predominant over Al, particularly in the B2 and B'2 units. Zircons from Cinovec generally follow the xenotime substitution with significant predominance of Y+REE over P (Fig. 9). Surprisingly, the excess of Y+REE is greater in the deeper part of the pluton relative to the upper section that was rich in fluorine and fluids. The occurrence of trivalent elements in zircon from the uppermost part of the cupola must be explained by another type of substitution. One possibility is the substitution $(Y, REE) + (Nb, Ta) \leftrightarrow Zr + Zr$ (Van Lichtervelde et al. 2011) or perhaps even the incorporation of lithium or other small ions in interstitial positions apart from the main lattice sites. Lithium is abundant in fractionated granites and its ion, due to its small size, can enter a number of minerals not only in the principal lattice sites but also in their interstices. Lithium cannot be analysed using the electron probe so that data on its content and distribution in mineral structures is sporadic. Ushikubo et al. (2008) found as much as 259 ppm Li in zircons from granitoids, and suggested that the coupled substitution $(Y, REE) + Li_{interstitial} \leftrightarrow Zr$ was responsible for accommodation of trivalent ions in zircon crystal lattice.

Conclusions

The main results of the present study can be summarized as follows:

- The chemistry of zircons from the highly fractionated S-type and A-type granites at Beauvoir and Cinovec differ significantly from one another. Zircons from the A-type granite at Cinovec are markedly enriched with Th, Y, REE and Sc, while zircons from the S-type granite at Beauvoir are more enriched with P and Hf;
- A distinct vertical zoning of zircon compositions was found in both granites with a tendency for the content of Hf to increase at higher levels of the crystallizing system more enriched with fluids;
- High contents of uranium at both localities were always detected in the cores of zircon crystals, while their rims are enriched with Hf;
- Enrichments of F and U in zircons at Cinovec correlate with the concentration of these elements in the parent rock and increase systematically upwards in the granite body. At Beauvoir, these elements are mostly concentrated in the middle part of the profile and show no correlation with their contents in the parent rock. The chemistry of zircons at Beauvoir correlates more with the initial vertical division of the system into B1, B2 and B3 units (Cuney et al. 1992) rather than the classification into B and B' units later proposed by Rimbault et al. (1995);
- Zircons from highly differentiated granites can generally be divided into two chemical types: (i) zircons strongly enriched with Hf (>10 wt. % HfO_2 , particularly in rims), and poor in all other HFS-elements. These zircons are typical of peraluminous strongly Li-enriched granites and LCT pegmatites, but also of some A-type granites; (ii) zircon moderately enriched with Hf (<10 wt. % HfO_2), as well as moderately to strongly enriched with Th, Y, HREE, (Nb, Sc, Ta, Bi). These zircons are characteristic of moderately Li-enriched

and strongly F-enriched subvolcanic granites of both S- and A-types of the Krušné hory/Erzgebirge area, but occasionally were found in evolved S- and A-type granites and granitic pegmatites worldwide.

- High contents of minor elements in zircon are not directly determined by their concentrations in the melt, but by combination of enrichment of the melt with water, Al, F, Na and Li, and the pressure. High degree of peraluminosity and high content of Li seem to be favourable phenomena facilitating crystallization of zircon rich in Hf, whereas subvolcanic conditions of the intrusion linked with explosive degasation and secondary boiling support the crystallization of zircon high in Th, U, Y, REE, Nb and W. Influence of late- to post-magmatic fluid-driven zircon alteration also play a role.

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