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Chemistry of P-, U-, Nb-, Bi-, Sc-, and F-rich zircon from peraluminous granites: the Podlesí granite system, Czech Republic

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Introduction

In the frame of a systematic study of the highly evolved, F- and P-rich peraluminous granite suite at Podlesí, in the western Erzgebirge/Krušné Hory of the Czech Republic (Breiter et al. 1999, 2005), a detailed investigation of the composition and alteration of zircon has been undertaken. The studied rocks comprise (a) albite–topaz–biotite granites of the main intrusive phase of the Nejdek–Eibenstock pluton (0.5–1.0 wt% F, 0.2–0.4 wt% P_2O_5), (b) more highly fractionated albite–topaz–protolithionite granites (0.5–1.2 wt% F, ~0.5 wt% P_2O_5), (c) flat dykes of late, extremely fractionated albite–topaz–zinnwaldite granites (1.0–3.0 wt% F, ~1 wt% P_2O_5).

Results

About 350 quantitative electron-microprobe analyses of zircon in 25 representative granite and greisen samples were conducted using CAMECA SX100 (Masaryk University Brno) and CAMECA SX50 (GeoForschungsZentrum Potsdam) electron microprobes. Representative results of electron-microprobe analyses of zircon grains from the various types of rocks are listed in the Table 1. In all types of granites, zircon is chemically strongly variable even at the scales of a thin section or individual grain. However, a systematic shift in zircon composition between the early biotite granites and the late zinnwaldite granites is obvious. With increasing degree of melt fractionation, zircon composition changes from U-, Hf-, P-poor, well-zoned, unaltered crystals stoichiometrically close to endmember $ZrSiO_4$ to U-, P-, Al-, Ca-, Fe-, F-rich, hydrated, patchy-zoned and strongly altered, metamict grains depleted in Zr (down to 0.57 *apfu*, formula calculated on the base of four oxygen atoms) and Si (down to 0.30 *apfu*).

The most intriguing feature of the zircon from Podlesí consists in the enrichment of P. The P contents increases from 1–3 wt% P_2O_5 in the biotite granite up to about 20 wt% P_2O_5 (0.60 *apfu* P) in the late zircon from the highest fractionated zinnwaldite granite. In zoned crystals, the P-content in the core is higher than that in the rim. A high concentration of P is typically accompanied by an elevated to strong enrichment of U, Al, Ca, and Fe.

The distribution of U in individual grains is irregular and lacks a systematic core-to-rim evolution. Zircon grains containing more than 1 wt% UO_2 are metamict and hydrated. The intensity of U enrichment shows no correlation with the rock type and reached a maximum of 14.75 wt% UO_2 in a zircon from the protolithionite granite. The contents of Nb and Bi in zircon are heterogeneous and display no correlation with the rock type as well. Niobium range in concentration from below the microprobe detection limit up to 2 wt%, occasionally up to 6.7 wt% Nb_2O_3 (0.12 *apfu* Nb). The majority of zircon grains contain Bi in concentrations below the detection limit, but some grains from the protolithionite granite contain up to 7.7 wt% Bi_2O_3 (0.079 *apfu* Bi). The concentration of Sc in zircon is less variable and normally range from below the detection limit to 1.5 wt% Sc_2O_3, exceptionally up 3.42 wt% (0.11 *apfu* Sc). Fluorine is usually present in the metamict grains, maximally up to 3.5 wt% in zircon from the zinnwaldite granite. The LREE abundances are mostly below their detection limits. The contents of Y and the HREE are variable, from below their detection limits to maximal 7.93 wt% Y_2O_3 (0.145 *apfu* Y). The highest Hf concentration (9.1 wt% HfO_2; equivalent to 8.5 mole% $HfSiO_4)$was determined in a zircon grain from the upper part of the protolithionite granite. Among the other elements, aluminium reaches concentrations up to 5.5 wt% Al_2O_3, iron up to 3.6 wt% FeO, and calcium up to 4 wt% CaO.

Conclusions

Some zircon grains from the P–F-rich peraluminous granite system at Podlesí are extraordinarily enriched in several of those elements, which constitute trace components in ordinary zircon. Some of the elements enriched approach concentrations, which are novel or correspond to the highest reported to date. The most important substitution reactions triggering the enrichment of some of these elements include the molecules of berlinite (P^{5+} + Al^{3+} ⇔ $2Si^{4+})$, xenotime [(REE + Y)$^{3+}$ + P^{5+} ⇔ Zr^{4+} + Si^{4+}], brabantite [Ca^{2+} + (U + Th)$^{4+}$ + $2P^{5+}$ ⇔ $2Zr^{4+}$ + $2Si^{4+}$], ximengite (Bi^{3+} + P^{5+} ⇔ Zr^{4+} + Si^{+}), and pretulite (Sc^{3+} + P^{5+} ⇔ Zr^{4+} + $Si^{4+})$. The formation of the abnormal zircon compositions can be attributed to a combination of two processes.

One population of zircon crystallized late-magmatically, from a P-, F- and water-rich melt strongly enriched in Nb, Ta, Bi, and U, which has undergone a prolonged history of fractionation. Part of the zircons grains experienced subsequent alteration, and associated further compositional modification, in response to the interaction with P- and F-rich postmagmatic fluids. The compositional signatures of zircon from strongly greisenized granites imply that zircon may completely dissolve and regrown during the interaction with greisenizing fluids of the sort that originated from the most fractionated residual melts at Podlesí.

References

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Table 1. Representative electron-microprobe analyses (in wt%) of zircon from Podlesí

Rock type	Biotite granite		Protolithionite granite				Zinnwaldite granite			
P_2O_5	0.17	7.96	7.57	5.35	0.00	6.02	2.66	12.03	**20.22**	**19.12**
Nb_2O_5	na	na	na	**6.29**	0.00	1.76	0.00	2.35	na	na
SiO_2	32.25	19.71	22.61	18.25	30.20	20.80	22.25	14.48	*8.16*	*12.95*
ZrO_2	65.10	49.40	39.13	*34.19*	53.97	*36.06*	49.67	39.07	40.64	42.37
HfO_2	1.06	1.70	1.94	1.38	**9.09**	1.65	2.66	1.68	2.87	3.15
ThO_2	0.00	0.20	0.76	3.51	0.01	0.59	0.12	0.65	0.03	0.15
UO_2	0.11	1.82	2.13	2.86	1.21	**14.75**	3.95	3.41	1.29	1.25
TiO_2	0.00	0.15	na	0.19	0.02	0.16	0.00	0.21	0.16	0.18
Al_2O_3	0.01	1.25	2.14	0.74	0.19	1.05	2.20	**5.49**	3.30	3.47
Sc_2O_3	0.02	0.24	0.45	0.44	0.24	0.52	**3.42**	1.93	0.57	0.80
Y_2O_3	0.12	2.34	**7.93**	0.49	0.00	0.79	0.00	1.13	0.28	0.22
Bi_2O_3	0.00	0.16	na	**7.68**	0.00	0.00	0.00	**5.61**	2.45	na
Ce_2O_3	na	na	0.09	0.00	0.00	0.07	0.05	0.00	na	0.02
Nd_2O_3	na	na	0.13	0.00	0.00	0.05	0.02	0.00	na	0.05
Sm_2O_3	na	na	0.18	0.00	0.00	0.06	0.00	0.00	na	0.00
Gd_2O_3	na	na	1.04	0.18	0.00	0.08	0.06	0.14	na	na
Dy_2O_3	0.00	0.21	1.41	0.03	0.00	0.06	0.00	0.08	0.00	0.18
Yb_2O_3	0.05	0.28	0.52	0.07	0.00	0.14	0.03	0.12	0.14	0.06
CaO	0.00	2.47	0.86	0.77	0.38	2.79	1.67	1.57	3.71	3.12
FeO	0.70	**3.59**	1.27	2.76	0.80	0.44	1.36	0.24	1.00	2.06
MnO	0.03	0.35	na	0.05	0.18	0.65	0.30	0.21	0.69	0.00
PbO	0.00	0.01	0.00	0.17	0.13	0.00	0.10	0.06	0.04	0.05
F	0.00	1.77	0.80	0.47	0.79	0.54	0.59	0.60	1.57	0.00
$F=O_2$	0.00	0.75	0.34	0.20	0.33	0.23	0.25	0.25	0.66	0.00
Total	99.60	93.59	90.62	88.77	96.87	88.79	90.84	90.78	87.09	89.27

na = not analyzed. 0.00 = below detection limit. Extremely high values are marked in bold, extremely low values in italics.