Residence of elements in minerals of a single granite sample (Říčany granite, Variscan Central Bohemian Plutonic Complex)

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A single large (~30 kg) sample of coarse grained, weakly porphyritic biotite (–muscovite) Říčany granite (Central Bohemian Plutonic Complex) was studied in terms of petrography and mineral chemistry, combining electron-microprobe, *in situ* LA ICP-MS and ICP-MS analyses of dissolved mineral separates. This information was used to assess the distribution of individual elements among the main-rock forming minerals and accessories, with general consequences for petrogenesis of the granite and availability of selected geochemical species during the hypergene processes.

The commonly used approaches to modal analysis (point counting, image analysis of a stained polished rock slab, XRD, Granite Mesonorm and least-squares method) were first tested on the major elements, Rb, Sr and Ba, all hosted by the main rock-forming minerals. The best estimate yielded the constrained least-squares method, as implemented in the *GCDkit* (www.gdckit.org). Following the subtraction of the elements' inventory stored by the main rock-forming minerals, the modal percentages of accessories were obtained by least-squares fit using selected trace elements.

The final balance and relative contributions of individual phases was visualized by the "balloon plot" (see examples in Fig. 1). Among major elements, Si is shared almost equally by Qtz, Kfs, and Pl, most Al is bound in feldspars (Pl > Kfs), Pl is the main sink for Ca and Na, and Kfs for K. Bulk of the mafic cations Ti, Fe and Mg resides in Bt. Rutile takes 20 wt.% of TiO_2 and Ap 86 % of the P_2O_5.

	wt. % minerals	Or, 29.178	Pl, 36.379	Qtz, 24.527	Bt, 9.285	Ms, 0.199	Ap, 0.289	Mnz, 0.04	Zrn, 0.023	Rt, 0.081	Σ
(wt. %)	SiO_2	18.72	22.91	24.49	3.48	0.1			0.01		69.71
	TiO_2				0.31					0.08	0.39
	Al_2O_3	5.39	7.3		1.37	0.06					14.12
	FeOt	0.01			1.6	0.01					1.62
	MgO				1.24						1.24
	CaO		1.44				0.16				1.60
	Na_2O	0.28	3.35		0.01						3.64
	K_2O	4.55	0.16		0.88	0.02					5.61
	P_2O_5		0.01				0.12	0.01			0.14
(ppm)	Rb	156.56	57.2	0.02	68.64	1.23			0.01		283.7
	Sr	133.84	181.91	0.03	0.16	0.36	0.43	0.04	0.01	0.02	316.8
	Ba	832.34	49.31	0.08	116.33	2.21	0.01	0.01	0.06	0.13	1000.5
	Th	1.88	1.14	0.14	0.04	0.96	0.02	1.52	0.22	1.75	7.7
	U	0.87	0.6	0.01	0.01	0.12	0.07	0.16	0.11	0.5	2.5
	Zr	19.01	3.71	0.05	0.12	1.37		4	104.36	36.21	168.8
	Nb	0.4	2.02		9.65	0.09		0.01	0.76	3.8	16.7
	La	1.74	8.63		0.05	2.14	1.23	10.54	0.11	1.51	25.95
	Eu	0.35	0.26		0.01		0.05	0.02		0.01	0.70
	Yb	0.07			0.01	0.01	0.21	0.02	0.02	0.06	0.40

Fig. 1. The "balloon plot" (of R-language package *gplots*) giving the balance of selected elements in the studied Říčany granite sample (concentration in the mineral × its modal abundance). The relative contributions of individual phases are expressed by the size of circles; top row gives the "best" modal analysis obtained by the least-squares technique.

Over a half of the Rb is hosted by Kfs and a quarter by Bt; Sr is distributed mostly between the feldspars but the Kfs represents a key host for Ba. Most Be is concentrated in Pl and Pb is hosted by feldspars (Kfs > Pl). The four accessories, Ap, Mnz, Zrn and Rt incorporate more than half of the LREE and over three-quarters of HREE, Y, Zr and Hf. They also represent important reservoirs for Th, U, Ti, Ni, Co, Nb and Ta. Some 60 % of the Nb and Ta budget are stored in Bt, probably as submicroscopic inclusions. The feldspars seem to incorporate most of U. For Th, almost equally significant are Kfs, Mnz and Rt and, less so, Pl and Ms. Minerals such as Zrn and Ap play only marginal role in hosting the radioactive elements. On the other hand, important seems the newly recognized, REE-, Th and U-rich zircon-like ABO_4 phase, the complete chemistry and modal abundances of which could not have been determined, though.

In Říčany, 83 % of the whole-rock Zr and Hf and *c.* 10–30 % of HREE, U, Th, Nb, Ta, Ti, Cd, Co and Ni are contained in resistant accessory phases Zrn and Rt. Thus the pressure bomb or sample fusion – and not merely a combined acid attack – are vital were these elements to be determined quantitatively.

A great deal of essential structural components (P, Zr, LREE) used in Ap, Zrn and Mnz saturation thermometry is incorporated into other minerals and this leads to overestimation of the liquidus temperatures. In the present case, the saturation temperatures for Zrn are *c.* 40 °C (5.1 %) and for Mnz *c.* 70 °C (9.6 %) higher. This effect is negligible for Ap, and there the more important become analytical errors as the isotherms of the saturation model rapidly converge for felsic compositions.

The study demonstrates that for modal analyses of coarse-grained or porphyritic granites, the most appropriate are chemistry-based approaches, especially those taking into account the true mineral chemistries (e.g., linear programming and constrained least squares). They represent a large volume of the sample and thus (i) smooth out any local variations caused e.g. by the small-scale crystal accumulation, (ii) account for the presence of phenocrysts, and (iii) eliminate the effects of fabric.

The current research confirms the notion that the accessory phases play a key role in controlling the behaviour of many trace elements during the differentiation of felsic granitic systems by processes such as partial melting or fractional crystallization. Especially the REE seem of little value in petrogenetic modelling of felsic igneous suites, unless the role of accessories is properly assessed and saturation models for apatite, zircon, monazite and rutile are carefully considered.

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