

Trace element composition of quartz from different types of pegmatites: A case study from the Moldanubian Zone of the Bohemian Massif (Czech Republic)

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ABSTRACT

The evolution of the trace-element patterns of quartz during crystallization of pegmatite melt was investigated using laser ablation inductively coupled plasma mass spectrometry. The contents of Al, B, Ba, Be, Cr, Fe, Ge, Li, Mn, P, Rb, Sn, Sr and Ti were analysed in quartz from the border, intermediate and core zones of four granitic pegmatites differing in degree of fractionation and origin. The material investigated originates from the pegmatite district of the Strážek Unit, Moldanubian Zone, Bohemian Massif, Czech Republic and includes: lepidolite LCT (Li-Cs-Ta) pegmatite from Rožná; beryl-columbite LCT pegmatite from Věžná; anatectic pegmatite from Znětín; and intragranitic NYF (Nb-Y-F) pegmatite Vladislav from the Třebíč Pluton. The abundances of the elements analysed varied over wide intervals: <1 to 32 ppm Li, 0.5 to 6 ppm B, <1 to 10 ppm Ge, 1 to 10 ppm P, 10 to 450 ppm Al, 1 to 45 ppm Ti and <1 to 40 ppm Fe (average sample contents). Concentrations of Be, Rb, Sr, Sn, Ba, Cr and Mn are usually <1 ppm. Quartz from LCT pegmatites exhibits a distinct evolutionary trend with a decrease in Ti and an increase in Al, Li and Ge from the pegmatite border to the core. In comparison with the most fractionated rare-metal granites, pegmatitic quartz is relatively depleted in Al and Li, but strongly enriched in Ge. Quartz from simple anatectic and NYF pegmatites is poor in all trace elements with their evolution marked by a decrease in Ti and a small increase in Ge. There is little Al or Li and neither shows any systematic change with pegmatite evolution. Using the Ti-in-quartz thermometer, the outer zones of the Znětín and Vladislav pegmatites crystallized at ~670°C, whereas the border zone in the Rožná pegmatite yields a temperature near 610°C.

KEYWORDS: quartz, pegmatite evolution, mineralogy, trace elements, Moldanubian Zone, Bohemian Massif.

Introduction

THE composition of rock-forming minerals and, in particular, their trace-element abundances, is widely used for studies of the fractionation trends of granites and pegmatites (Černý *et al.*, 1984; London, 1992; Charoy *et al.*, 1995; Larsen, 2002; Breiter *et al.*, 2005a; Müller *et al.*, 2008b; Čopjaková *et al.*, 2013). Minerals such as

feldspars, hornblende and micas are commonly affected by post-magmatic hydrothermal and meteoric processes. In contrast, quartz is more resistant during fluid-related processes and its primary trace-element signature is commonly preserved (Monecke *et al.*, 2002; Götte *et al.*, 2004; Müller *et al.*, 2010).

After several pioneering studies from the 1960s to the 1980s (Dennen, 1967; Lyakhovich, 1972; Suttner and Leininger, 1972; Schrön *et al.*, 1988), further investigations addressing the composition of igneous quartz were published during the last

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decade as a result of the improvement in micro-analytical methods. Apart from numerous studies of quartz from granites (Jacamon and Larsen, 2009; Müller and Koch-Müller, 2009; Breiter and Müller, 2009; Deans, 2010; Breiter *et al.*, 2012b, 2013), several authors focused their interest on quartz from granitic pegmatites (Larsen *et al.*, 2000, 2004; Götze *et al.*, 2004, 2005; Müller *et al.*, 2008a; Beurlen *et al.*, 2011; Müller and Ihlen, 2012). Unfortunately, the majority of these studies characterized each pegmatite body by investigating only one representative sample without any data regarding the internal structure of the pegmatite. Only Beurlen *et al.* (2011) and Müller *et al.* (2008a, 2013) studied quartz with respect to the internal zoning of several pegmatites. While quartz from the Frohland pegmatites, Norway (Müller *et al.*, 2008a) is homogeneous, quartz from the Borborena, Brazil (Beurlen *et al.*, 2011) and Evje pegmatites, Norway (Müller *et al.*, 2013) show distinct evolution from the border to the core.

The abundances of trace elements in quartz are controlled principally by their abundance in melt, fractionation into coexisting minerals and by temperature and pressure, although the exact behaviour is still matter of debate (Larsen *et al.*, 2004; Jacamon and Larsen, 2009; Huang and Audétat, 2012). Nevertheless, a decrease in the Al/Ti (Müller *et al.*, 2002; Breiter and Müller, 2009; Jacamon and Larsen, 2009; Breiter *et al.*, 2012b) and Ge/Ti (Jacamon and Larsen, 2009) ratios is generally accepted as a reliable indicator of the degree of silicate-melt fractionation.

In the present study, the evolution of the trace-element patterns in quartz during the crystallization of pegmatitic melt is examined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Samples are from four well characterized granitic pegmatites differing in terms of the degree of fractionation and origin from the classical pegmatite province in western Moravia, Strážek Unit, Moldanubian Zone and adjacent Třebíč Pluton (Fig. 1, Novák *et al.*,

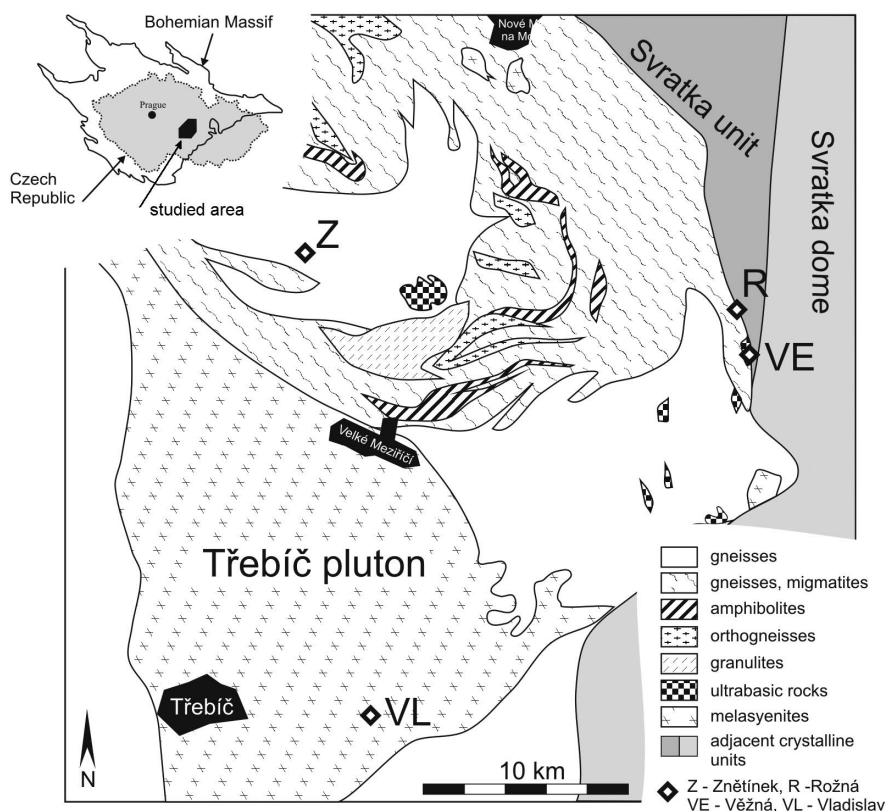


FIG. 1. Simplified geological map of the area investigated.

2013). The objectives of this study are: (1) to describe the evolution of the trace-element patterns in quartz during crystallization of particular pegmatite bodies; (2) to define the evolution of quartz in pegmatites of different types and families (Černý *et al.*, 2012); and (3) to compare the composition of quartz from the rare-element pegmatites and fractionated granites.

Brief review of granitic pegmatites in the Moldanubian Zone

Granitic pegmatites are widespread throughout the Moldanubian Zone of the Bohemian Massif (Cháb *et al.*, 2010). The following groups were distinguished (Novák *et al.*, 2013):

Anatectic pegmatites including several distinct pegmatite groups: (1) dumortierite-bearing dykes enclosed in high-grade metamorphic rocks (Cempírek and Novák, 2006; Cempírek *et al.*, 2006); (2) borosilicate-bearing (werdingite, boralsilite) pegmatite veinlets cutting leucogranulite of the Bory Granulite Massif (Cempírek *et al.*, 2010); (3) coarse-grained, cordierite-rich leucosomes with pegmatitic textures in migmatized gneisses and granulites of the Bory Granulite Massif (Povondra *et al.*, 1992); (4) abundant anatectic pegmatites showing simple zoning that are widespread, mainly in the Strážek Unit (studied locality Znětín), commonly containing large crystals of smoky quartz, feldspars, muscovite and tourmaline (schorl, dravite, foitite, magnesio-foitite) developed typically in pockets (Gadas *et al.*, 2012).

Pegmatites of the rare-element class are the most abundant and exhibit much variability in shape, size, textures, degree of fractionation and mineralogy. Pegmatites of the LCT family are typically enriched in B with tourmaline as an omnipresent accessory to minor minerals. Less evolved common pegmatites are characterized by the presence of tourmaline (schorl, oxy-schorl, dravite; Novák *et al.*, 2004), sometimes with andalusite, cordierite and garnet. More fractionated beryl-type pegmatites (locality Věžná I) contain the accessory minerals: tourmaline (schorl, dravite), beryl, fluorapatite, niobian rutile, ilmenite, monazite-(Ce), xenotime, zircon, cordierite, garnet, columbite–tantalite and Y,REE-oxide minerals. The most evolved complex Li-bearing pegmatites (Li-micas $\approx$ Li-tourmalines $>$ amblygonite/montebrazite $>$ petalite), some with a variety of accessory minerals (see Novák and Cempírek, 2010 and references

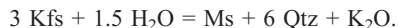
therein), include the lepidolite-subtype (locality = Rožná-Hradisko), elbaite-subtype and petalite-subtype pegmatites.

Intracranitic pegmatites of the NYF family (Škoda and Novák, 2007; Novák *et al.*, 2011, 2012) occur exclusively in the Třebíč Pluton, western Moravia and in the Čertovo Břemeno (Milevsko) Pluton, southern Bohemia. Both plutons belong to the shoshonitic association of ultrapotassic plutonic rocks ($\text{MgO} > 3$ wt.%, $\text{K}_2\text{O}/\text{Na}_2\text{O} > 2$ wt.%) (Holub, 1997). Euxenite-subtype pegmatites occur with more primitive allanite-type pegmatites (Škoda and Novák, 2007) as dykes and lenses up to 2 m thick, with sharp-to-transitional contacts to the host granite-syenite (locality Vladislav). Abundant phlogopite is accompanied by typical accessory minerals including: allanite-(Ce), tourmaline (dravite, schorl), titanite, ilmenite, aeschynite- and euxenite-group minerals, actinolite and rare beryl.

Description of the pegmatites investigated

Anatectic pegmatite Znětín

This pegmatite forms a concordant subhorizontal dyke (~1 m thick) with gradational to locally sharp contacts to the host migmatized biotite-sillimanite gneiss of the Strážek Unit. The pegmatite consists of: (1) an outermost, medium- to coarse-grained granitic unit ($\text{Pl} + \text{Qtz} + \text{Kfs} \pm \text{Bt} \pm \text{Ms}$); (2) a graphic unit ($\text{Qtz} + \text{Kfs} \pm \text{Bt/Ms}$); (3) a rare blocky K-feldspar unit; and (4) a pocket unit lined with crystals of K-feldspar, albite, muscovite-I, tourmaline (schorl, dravite, foitite) and with crystals of smoky quartz in two generations. Smoky quartz I forms large, perfectly developed crystals, up to 20 cm long. Sub-parallel intergrowths of small crystals of smoky quartz II are closely associated with muscovite-II on strongly-corroded crystals of K-feldspar and are the product of the reaction:



The mineral assemblages of granitic and graphic units and in blocky K-feldspar include: (together with major and minor minerals) rare muscovitized andalusite, fluorapatite and ilmenite.

Beryl-columbite pegmatite Věžná I (LCT)

The NNW-trending dyke of the Věžná I pegmatite, up to 4 m thick and 130 m long, intrudes a serpentinite body ~1 km south of the

village of Věžná. A tectonic slab of serpentinite enclosed in migmatitic gneiss is situated along the border of the Strážek Unit and the Svratka Unit. The Věžná I pegmatite dyke exhibits almost symmetrical zoning: (1) a narrow, medium- to coarse-grained granitic unit (Kfs + Plg + Qtz + Phl with $X_{Mg} = 0.72\text{--}0.75$); (2) a dominant graphic unit of K-feldspar (>oligoclase) + quartz, with local graphic aggregates of albite + quartz, grading into; (3) a core-margin of a blocky K-feldspar unit + subordinate albite-cleavelandite, which surrounds; (4) isolated central pods of a quartz core. Beryllian cordierite ($X_{Mg} = 0.71\text{--}0.79$), beryl, schorl to dravite ($X_{Mg} = 0.45\text{--}0.66$), muscovite, niobian rutile, monazite-(Ce), xenotime and zircon occur in the units (2), (3) and (4). The most evolved fraction of the pegmatite was found close to the quartz core (4) and occurs as a small single pod (5) of brownish K-feldspar + pollucite + albite with: lepidolite (in part Cs-dominant), elbaite, triplite, beryl, cheralite and several accessory minerals.

Rožná-Hradisko (LCT)

This lepidolite pegmatite dyke is located along the contact of the Strážek Unit and the Svratka Unit and is hosted dominantly by leucocratic migmatized biotite paragneiss. The pegmatite dyke, ~1 km long and ~35 m wide, is orientated parallel to the NNW-trending foliation of the host metapelites and dips ~60° WSW (Novák and Cempírek, 2010). The almost symmetrically zoned internal structure consists of the following textural-paragenetic units: (1) a very rare, coarse-grained border unit (Qtz + Kfs + Plg ± Bt); (2) an abundant, coarse-grained unit (Qtz + Kfs + Plg + Tur + Ms), locally; with blocks of (3) a graphic unit (Kfs + Qtz + Ab + Ms + Tur); and masses (or veins?) of (4) a fine-to-medium grained granitic unit (Qtz + Kfs + Ab + Tur + Ms); (5) a relatively rare blocky core-margin unit (Kfs + Qtz); (6) an albite-lepidolite unit. The latter is very heterogeneous in texture and mineralogy and contains locally abundant elbaite and rare amblygonite-montebrazite and surrounds and partly penetrates a (7) quartz core. The outer albite subunit (6a), contains common muscovite to Li-muscovite, black-to-green (blue) tourmaline, cassiterite, fluorapatite and rare amblygonite-montebrazite. The inner lepidolite subunit (6b) adjacent to the quartz core is dominated by lepidolite (trilithionite >> polyolithionite) and locally contains: abundant albite, quartz, relatively common

elbaite to rossmanite, fluorapatite, topaz, beryl, amblygonite-montebrazite, manganocolumbite and cassiterite (Novák and Cempírek, 2010).

Euxenite-subtype pegmatite Vladislav (NYF)

The NNW-trending dyke of the Vladislav pegmatite, ~1 m thick, shows gradational contacts with the host syenite of the Třebíč Pluton. This symmetrically zoned pegmatite includes from the contact inwards: (1) a border of medium- to coarse-grained granitic unit (Kfs + Qtz + Plg + Phl); (2) a graphic unit (Kfs + Qtz, scarce Ab + Qtz); (3) minor unit of blocky K-feldspar; and (4) a quartz core. The mineral assemblage is characterized by the dominance of K-feldspar over albite, common phlogopite in the outer zone and the absence of primary muscovite. Tourmaline (schorl, dravite) is a typical minor to accessory mineral concentrated in, or adjacent to, the quartz core. Other accessory minerals include: allanite-(Ce), titanite, ilmenite, zircon and rare aeschynite/euxenite group minerals.

The above review of the granitic pegmatites investigated provides only basic information about the localities, their internal structure and mineralogy. Further information on these pegmatites can be found as follows: anatectic Znětín pegmatite (Gadas *et al.*, 2012); beryl-columbite Věžná I pegmatite (Černý *et al.*, 1984, 2003; Teertstra *et al.*, 1995; Dosbaba and Novák, 2012); lepidolite Rožná-Hradisko pegmatite (Černý *et al.*, 1995; Selway *et al.*, 1999; Novák and Cempírek, 2010); euxenite-type Vladislav pegmatite (Škoda and Novák, 2007; Novák *et al.*, 2011). The pegmatites of rare-element class (LCT) crystallized over a short period at ~332±3 Ma (Rožná; Melleton *et al.*, 2012) and ~335±3 Ma (Věžná; Novák *et al.*, 1998). The intrusion of the Třebíč Pluton with the NYF Vladislav pegmatite was determined as ~343–335 Ma (Holub *et al.*, 1997; Kusiak *et al.*, 2010; Kotková *et al.*, 2010). The anatectic pegmatite with pockets from Znětín should be younger than MP-HT metamorphism so less than ~340 Ma old. Consequently, all pegmatites crystallized over a limited time span at ~335 Ma.

Sampling and analytical methods

Samples of quartz were collected systematically from all the zones of pegmatites investigated. Polished sections 150–200 µm thick were prepared from representative quartz grains (Table 1).

TRACE-ELEMENT COMPOSITION OF QUARTZ

TABLE 1. List of samples.

Locality	Sample	Description
Znětínek	4911	Graphic unit with biotite (MM A3656)
	4912	Blocky unit (MM A5372)
	4913	Crystal of smoky quartz I from pocket (MM A4974)
	4914	Crystal of smoky quartz II from pocket (MM A5179)
Věžná	Věž1	Granitic unit with biotite
	Věž2	Granitic to coarse-grained unit with biotite
	Věž3	Graphic unit
	Věž5	Blocky unit
Rožná	Ro1	Coarse-grained border unit with biotite
	Ro2	Graphic unit with muscovite
	Ro3	Granitic unit with schorl
	Ro4	Coarse-grained albite subunit with schorl to Fe-rich elbaite
	Ro5	Albite subunit with lepidolite and Fe-rich elbaite
	Ro6	Quartz core
Vladislav	4916	Coarse-grained border granitic unit with biotite
	4917	Graphic unit with biotite
	4918	Coarse-grained graphic to blocky unit close to quartz core
	4919	Quartz core with dravite-schorl

Cathodoluminescence (CL)

The quartz grains were studied optically before the LA-ICP-MS measurements using a hot cathodoluminescence microscope to locate analytical points for laser analysis of particular internal zones of quartz.

The CL images were obtained using two methods. One was hot-cathode luminescence using a HC2-LM microscope (Lumic at the Department of Geological Sciences, Masaryk University, Brno, Czech Republic). The accelerating voltage was 14 kV, current density 10–40 $\mu\text{A}/\text{mm}^2$. The images were captured with an Olympus C-5060 digital camera (setting: ISO 400, exposure time 1–10 s). Additional colour scanning electron microscopy (SEM) CL images were obtained using a TESCAN VEGA3 scanning microscope at the Institute of Geology, Academy of Sciences of the Czech Republic, in Prague. The microscope is equipped with a TESCAN CL detector allowing collection of live colour luminescence in a spectral range of ~400–800 nm.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

The trace-element abundances of quartz in polished sections (>100 μm thick) were deter-

mined at the Institute of Geology, Academy of Sciences of the Czech Republic, in Prague, using a Thermo-Finnigan Element 2 sector field ICP-MS coupled with a 213 nm NdYAG laser (New Wave Research UP-213) and the analytical protocol described in detail by Breiter *et al.* (2012b). The laser was fired at a repetition rate of 20 Hz, the laser energy was 8–10 J/cm^2 , beam sizes 55–100 μm were used and laser patterns were 100 μm long. Data for the gas blank were acquired at 35 s followed by 100 s for the laser ablation signal. The washout time between the measurements of the individual laser spot lines was 120 s. The sample introduction system was modified to enable the simultaneous nebulization of a tracer solution through an Aridus IITM desolvating nebulizer (CETAC Technologies) using procedures outlined in Horn *et al.* (2000). During the course of the investigation, the formation of oxides (MO^+/M^+) was monitored using the $^{254}\text{UO}/^{238}\text{U}$ ratio, which was typically <0.005. The following isotopes were measured at the low mass resolution mode ($m/\Delta m = 300$): ^7Li , ^9Be , ^{11}B , ^{74}Ge , ^{85}Rb , ^{88}Sr , ^{137}Ba and ^{118}Sn . The isotopes: ^{27}Al , ^{31}P , ^{47}Ti , ^{52}Cr , ^{55}Mn and ^{56}Fe required a medium resolution ($m/\Delta m = 4\,000$) to avoid potential argide, oxide and nitride interferences on the selected masses (Flem *et al.*,

2002). The ^{29}Si and ^{30}Si isotopes were used as the internal standards for low and medium/high resolutions, respectively, based on the presumption that the analysed quartz contains 99.95 wt.% SiO_2 . All data were calibrated against an external synthetic silicate glass standard (NIST SRM 612). Except for P, the values from Jochum *et al.* (2011) were used to calculate the absolute trace element abundances in the quartz samples. The P concentration (45.9 ppm) for NIST SRM 612 was adopted from Müller *et al.* (2008c) because it defines the LA-ICP-MS calibration curve more accurately than older recommended values for NIST standards (Gao *et al.*, 2002). The time-resolved signal data were processed using *Glitter* software (van Achterbergh *et al.*, 2001). A special precaution was taken to constrain the signal of the chemically homogeneous parts of the crystals and to avoid any inclusions and inhomogeneities present in the analysed quartz. The instrument detection limits ($\text{IDL} = 2.3 \cdot \sqrt{(2B)}$, where B is the total count in the background interval) for individual samples are listed in the Supplementary Table 1 (which has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html). The precision of the laser ablation analyses (as relative 1 sigma error – RSD) ranges between 5 and 15% for most of the detected elements. The accuracy was monitored by analysing soda-lime float glass NIST 1830 (0.1 wt.% Al_2O_3) as the quartz reference material is not available. The calculation of accuracy was compared with the published values of Flem and Bédard (2002) and ranges between 5 and 15% for all elements except Sn, which yields greater accuracy (~45%).

Results

The applicability of the proposed analytical methodology for the geological interpretation of pegmatite zoning was tested on samples from the Věžná LCT pegmatite. Discussion of preliminary data (Breiter *et al.*, 2012a) from this pegmatite confirmed the feasibility of this approach. The same methodology was therefore applied to other pegmatite localities.

Detailed optical, SEM-CL and hot CL observations guided the choice of analytical points for LA-ICP-MS to avoid fluid or solid micro-inclusions and recrystallized quartz. Generally, pegmatitic quartz displays no (or only a very low) CL signal without any

primary magmatic zoning. The complete data set of 153 LA-ICP-MS analyses from the Rožná, Znětín and Vladislav pegmatites is given in Supplementary Table 1. Analytical data from the Věžná pegmatite are available in Breiter *et al.* (2012a). For a better illustration of the trace-element variations, the averages and standard deviations for the individual samples are given in Table 2. Among the trace elements analysed, Al and Ti have the greatest abundance and are the most important for insights into the evolution of melt during pegmatite crystallization (Fig. 2a). Large amounts of Al were encountered in the graphic, granitic, blocky and quartz-core zones of the Rožná LCT pegmatite (averages between 147 and 320 ppm Al), in the graphic and blocky zones of the Věžná pegmatite (averages of 140 and 211 ppm Al) and the graphic and blocky zone in Znětín (averages of 196 and 186 ppm Al). Slightly smaller Al contents were found in the granitic and albite units of Rožná (109 and 121 ppm Al) and the granitic zone of Věžná (114 ppm). The smallest Al contents were found in the Vladislav NYF-pegmatite (average of all zones between 24 and 65 ppm Al), in the border zone of Věžná (72 ppm Al) and in crystals of smoky quartz from pockets in Znětín, which are probably of hydrothermal origin (average of 34 and 99 ppm Al).

The largest amounts of Ti (means of 43–45 ppm) were found in the border zone from Vladislav, the graphic zone from Znětín and the blocky zone from Věžná. Slightly smaller Ti contents were found in other samples from the graphic and blocky zones of these three pegmatites and in the border and graphic zones of Rožná (averages in the interval of 11–39 ppm Ti). The smallest Ti contents were found in crystals of smoky quartz II from a pocket in Znětín of hydrothermal origin and in the albite unit and quartz core units of Rožná (1–3 ppm Ti).

The Al/Ti ratio in quartz is a good indicator of the degree of fractionation of granitic/pegmatitic melt (e.g. Jacamon and Larsen, 2009; Breiter *et al.*, 2012b). This ratio is therefore used as a basis for visualizing the behaviour of other analysed elements during the evolution of individual pegmatites. In the samples investigated, this ratio ranges from ~0.2 to >200 in individual analyses and between 1 and 168 for average composition (Fig. 2b–h). Binary plots of Al vs. Ti from the individual pegmatites (Fig. 2a) show several distinct trends. In Rožná, a weak to negligible negative correlation is seen with an

TRACE-ELEMENT COMPOSITION OF QUARTZ

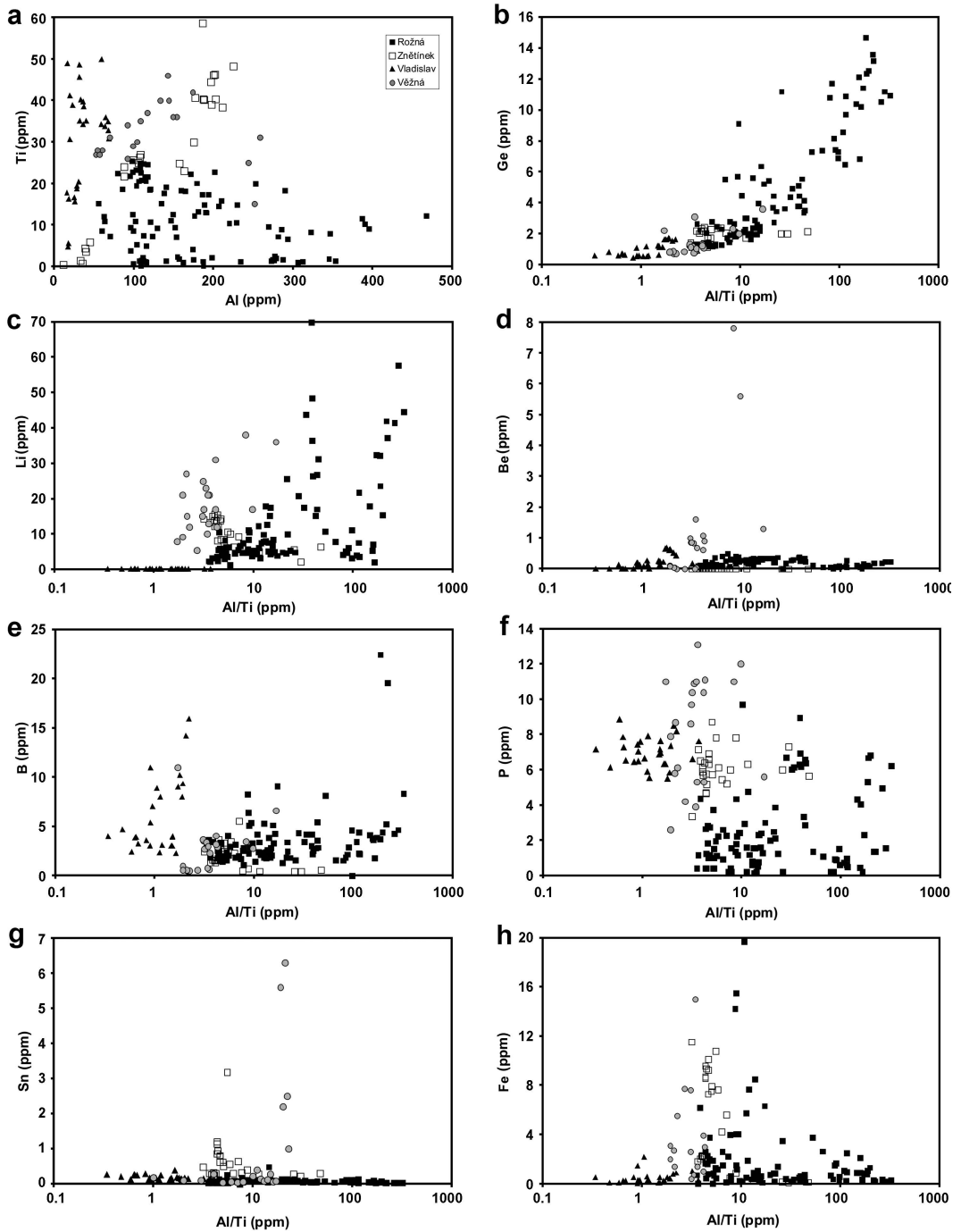


FIG. 2. Trace-element contents in pegmatite quartz (for sample details see Table 1): (a) Al vs. Ti; (b) Al/Ti vs. Ge; (c) Al/Ti vs. Li; (d) Al/Ti vs. Be; (e) Al/Ti vs. B; (f) Al/Ti vs. P; (g) Al/Ti vs. Sn; (h) Al/Ti vs. Fe.

TABLE 2. Trace element concentrations (means and standard deviations in ppm) in quartz determined by LA-ICP-MS.

Locality	Sample no.	Li	Be	B	Ge	Rb	Sr	Sn	Ba	Al	P	Ti	Cr	Mn	Fe
Rožná	RO1	Mean	4.9	2.3	1.3	0.10	0.046	0.063	0.030	109	1.4	22	0.085	0.25	1.8
		Std dev	2.1	0.72	0.2	0.22	0.029	0.062	0.033	19	1.1	2.1	0.022	0.17	1.5
	RO2	Mean	6.6	4.3	2.6	0.065	0.077	0.17	0.12	153	1.6	16	0.037	1.1	10
		Std dev	2.2	0.08	2.2	0.062	0.080	0.35	0.16	39	1.2	4.7	0.019	2.1	17
	RO3	Mean	7.5	2.4	3.4	0.050	0.028	0.11	0.13	147	2.1	11	—	0.12	0.90
		Std dev	4.5	0.74	1.0	0.072	0.0	0.1	0.1	64	1.9	3.6	—	0.2	1.6
	RO4	Mean	32	0.29	3.5	4.2	0.049	0.066	0.015	320	5.9	8.9	—	0.078	0.39
		Std dev	16	0.058	0.91	0.67	0.036	0.10	0.039	82	1.7	2.3	—	0.1	0.2
	RO5	Mean	4.2	0.050	2.0	9.6	0.2	0.10	0.085	121	0.52	1.5	0.019	2.6	1.4
		Std dev	1.2	0.013	0.9	1.8	0.049	0.016	0.031	27	0.26	0.87	0.014	1.5	1.1
	RO6	Mean	23	0.13	5.8	10	0.12	0.22	0.048	235	2.8	1.4	0.041	0.51	1.4
		Std dev	16	0.074	5.7	3.7	0.11	0.19	0.013	77	2.2	0.65	0.042	0.70	2.0
Znětinek	4911	Mean	14	—	2.9	1.3	0.32	—	1.2	196	5.7	45	0.030	2.0	9.7
		Std dev	1.5	—	0.47	0.090	0.22	—	0.91	9.7	1.5	7.0	0.013	0.29	1.5
	4912	Mean	8.3	—	3.3	2.1	0.07	0.04	—	186	6.0	35	0.028	0.56	7.2
		Std dev	1.3	—	1.0	0.33	0.057	0.019	—	24	1.3	9.3	0.006	0.35	1.7
	4913	Mean	14	—	1.5	2.2	—	—	0.28	99	6.3	25	—	0.14	2.2
		Std dev	1.4	—	0.15	0.10	—	—	0.039	9.8	0.53	1.8	—	0.021	0.21
	4914	Mean	5.1	—	0.53	1.9	—	—	0.31	34	6.50	2.69	—	0.02	0.31
		Std dev	1.54	—	0.10	0.17	—	—	0.056	12	0.86	2.21	—	0.01	0.31
	4916	Mean	—	—	3.8	0.61	0.020	0.092	—	30	6.7	44	—	0.020	0.26
		Std dev	—	—	0.52	0.11	0.010	0.046	—	14	0.79	6.9	—	0.010	0.17
	4917	Mean	—	0.13	5.7	0.64	0.052	0.23	0.14	0.050	7.3	28	0.024	0.068	0.70
		Std dev	—	0.036	3.1	0.21	0.032	0.15	0.022	8.6	0.79	14	0.015	0.043	0.70
Vladislav	4918	Mean	—	0.58	11	1.6	0.15	0.087	0.16	65	7.0	34	—	0.11	0.50
		Std dev	—	0.090	3.2	0.063	0.090	0.027	0.023	3.6	1.3	1.7	—	0.035	0.27
	4919	Mean	—	0.24	3.0	1.1	—	0.018	0.17	24	6.9	18	—	0.023	0.15
		Std dev	—	0.023	0.58	0.052	—	0.011	0.11	5.6	0.65	1.4	—	0.013	0.20

Věžná*	Věž1	Mean	14	0.066	0.65	0.78	0.088	0.15	0.11	0.15	72	5.6	29	0.23	0.54	3.7
		Std dev	6.5	0.022	0.15	0.056	0.037	0.12	0.077	0.19	18	1.9	2.4	0.16	0.23	2.2
	Věž2	Mean	14	0.067	0.65	0.73	0.070	0.21	0.11	0.19	114	5.3	25	0.21	0.45	3.7
		Std dev	3.3	0.036	0.18	0.051	0.023	0.20	0.046	0.081	152	1.2	2.5	0.043	0.14	0.79
Věžná*	Věž3	Mean	20	0.85	3.2	1.2	0.17	0.41	0.18	0.21	140	9.9	39	0.17	0.14	2.6
		Std dev	6.2	0.15	0.56	0.10	0.21	0.24	0.11	0.12	21	2.3	3.8	0.063	0.092	2.4
	Věž5	Mean	24	5.5	5.4	2.6	1.7	3.8	3.5	1.5	211	10	43	2.3	2.7	52
		Std dev	13	4.2	3.6	0.67	0.96	2.3	2.3	0.45	65	2.5	41	0.99	1.1	33

– mostly falling below the limit of detection;

* for raw analytical data see Breiter *et al.* (2012a).

increase in Al throughout pegmatite fractionation. In Věžná, Al and Ti contents are positively correlated and increase with increasing fractionation. In contrast, Al/Ti in Znětínek also exhibit a similar positive correlation but show a decrease in both elements from the border unit to crystals of smoky quartz I and II in pockets. Quartz from the Vladislav pegmatite is Al-poor and exhibits no apparent correlation with Al/Ti (Fig. 2a). Consequently, quartz from each pegmatite is characterized by its own particular trend of the Al/Ti-ratio.

Germanium accompanies Si in all silicates because of similar crystallochemical parameters, although its content in quartz is generally small (Breiter *et al.*, 2013). The largest abundances of Ge were found in the albite unit and quartz core of the Rožná pegmatite (averages of 9.6 and 10 ppm Ge). Smaller contents were found in the coarse-grained and graphic units at Rožná (averages of 2.6–4.2 ppm Ge) and in the blocky zone in Věžná (average of 2.6 ppm). Other samples contain <2.2 ppm Ge on average. The abundance of Ge shows a good positive correlation with the Al/Ti-ratio at all localities except for Znětínek, where Ge has no apparent correlation with Al/Ti (Fig. 2b).

The Li abundances vary over a wide range from <0.05 to >50 ppm (Fig. 2c). The highest average concentrations were found in the Rožná LCT pegmatites (coarse-grained unit and quartz core, 32 and 23 ppm Li, respectively) and the blocky zone of Věžná (24 ppm Li). The Li contents show a positive correlation with Al/Ti ratios. In these pegmatite units (zones) abundant (Rožná) to sporadic (Věžná) Li mineralization was encountered (Černý *et al.*, 1995; Novák and Cempírek, 2010; Teertstra *et al.*, 1995). In contrast, all samples from the Vladislav NYF pegmatite contain <0.05 ppm Li. Other samples have Li contents in the range 4–14 ppm and quartz from Znětínek anatectic pegmatite yielded a negative correlation between Li and Al/Ti.

The amounts of Be are generally very small (<1 ppm; Fig. 2d) with means in the range of 0.05–0.85 ppm. Only quartz from the blocky zone in the Věžná beryl-columbite pegmatite with common beryl and Be-enriched cordierite is enriched slightly containing 5.5 ppm Be on average.

The abundance of B in most samples (tourmaline is a typical accessory to minor mineral at all localities) lies in the range of 2–6 ppm. Slightly larger amounts were encountered in the coarse-

grained graphic zone in Vladislav, with an average concentration of 11 ppm. Two generations of crystals of smoky quartz from pockets in Znětínec and the granitic zone of Věžná contain only 1.5, 0.53 and 0.65 ppm B on average, respectively (Fig. 2e).

The P abundances in pegmatitic quartz vary between <0.25 and 13 ppm with most averaging 5.6–7.3 ppm and no well defined trends at individual localities (Fig. 2f). The highest concentrations were found in the graphic and blocky zones at Věžná (average 9.9 and 10 ppm P), while the lowest were found in the granitic, graphic, albite and quartz-core zones of Rožná (≤ 2.8 ppm P). Primary phosphates (fluor-apatite, amblygonite–montebrasite, Novák and Cempírek, 2010) are more abundant in the latter than at any of the other localities examined.

The quartz contains very small amounts of Sn, mostly <0.3 ppm Sn, with individual larger values up to 6.3 ppm Sn (Fig. 2g). Only quartz from the graphic zone in Znětínec and from the blocky zone at Věžná is distinctly Sn-enriched (averages of 1.2 and 3.5 ppm, respectively). Surprisingly, the Rožná pegmatite, with common cassiterite, has quartz with very little Sn content.

The Fe contents in quartz vary widely from trace to 99 ppm (Fig. 2h), but the averages usually do not exceed 2 ppm Fe. Only quartz from the graphic and blocky zones at Znětínec, graphic zone in Rožná and blocky zone in Věžná are Fe-enriched (means of 9.7, 7.2, 10 and 52 ppm Fe, respectively).

The amount of Mn is generally small with averages <0.7 ppm. Slightly elevated means were found in the graphic and albite zones at Rožná (1.1 and 2.6 ppm), in the graphic zone at Znětínec (2 ppm) and in the blocky zone of Věžná (2.7 ppm). Although geochemically similar to Fe, the Mn contents of quartz do not correlate with Fe.

Rubidium, Sr, Ba and Cr are present in quartz, usually in very low concentrations: Rb <0.2 ppm, Sr <0.1 ppm, Ba <0.2 ppm, Cr <0.1 ppm. The largest amounts of all these elements were found in the blocky zone of the Věžná pegmatite with averages of 1.7 ppm Rb, 3.8 ppm Sr, 1.5 ppm Ba and 2.3 ppm Cr, where elevated contents of Ba were found in late zeolites and subsolidus feldspars (Černý *et al.*, 1984; Teertstra *et al.*, 1995; Dosbaba and Novák, 2012). The Cr might originate from the host serpentinite containing Cr-enriched actinolite, which is in direct contact with this pegmatite.

Discussion

Compositional trends during pegmatite melt differentiation

Compositional evolutionary trends of trace elements in quartz from granites of different age and geochemical types are generally the same: i.e. a decrease in Ti is followed by an increase in Al, Li and Ge (Müller *et al.*, 2010; Breiter *et al.*, 2013). The distribution of other elements is either random (B, Fe, Mn) or has been poorly documented. However, the trends for pegmatites investigated in more detail (this work; Beurlen *et al.*, 2011) are more complex.

A generally ‘granitic’ evolutionary trend has been found in the Rožná LCT pegmatite (Fig. 3): Ti decreases from 22 ppm in the granitic border zone to 1.4 ppm in the quartz core. Similarly, Al increases from 109 to 235 ppm, Li from 4.9 to 23 ppm and Ge from 1.3 to 10 ppm (average contents in all cases). The only exception to this trend is the composition of the coarse-grained intermediate zone, which contains the greatest amounts of Al (320 ppm) and Li (32 ppm), within the whole pegmatite; although this unit contains only minor Li mineralization (Fe-rich elbaite, Li-rich muscovite, rare amblygonite–montebrasite). In the case of the Rožná pegmatite, Ge is distributed more evenly in quartz than are Al and Li. The increase in Ge content is the most robust indicator of magma fractionation from the border zone to the quartz core (Fig. 3b). The exceptionally large amounts of Al and Li in the albite (+lepidolite) units may be influenced by Li-rich fluid/melt from which the lepidolite and Li-tourmalines crystallized.

In the Věžná pegmatite, the abundances of Al, Li, Ge, Be and B increase systematically from the wall zone to the core, although Ti is highly scattered with maximum concentrations in the blocky zone. A similar trend was noted for the Borborema beryl-columbite pegmatite by Beurlen *et al.* (2011).

In the Znětínec pegmatite, contents of Al, Ti, B, Rb, Sn, Mn and Fe) decrease slightly from the graphic to the blocky zone and then decrease further in the two generations of smoky quartz crystals in pockets. This reverse compositional trend is unique in granitic rocks.

In the Vladislav pegmatite, the Ti content decreases systematically from the wall zone to the core (44 to 18 ppm), whereas Al increases slightly from the wall-zone to the coarse-grained

TRACE-ELEMENT COMPOSITION OF QUARTZ

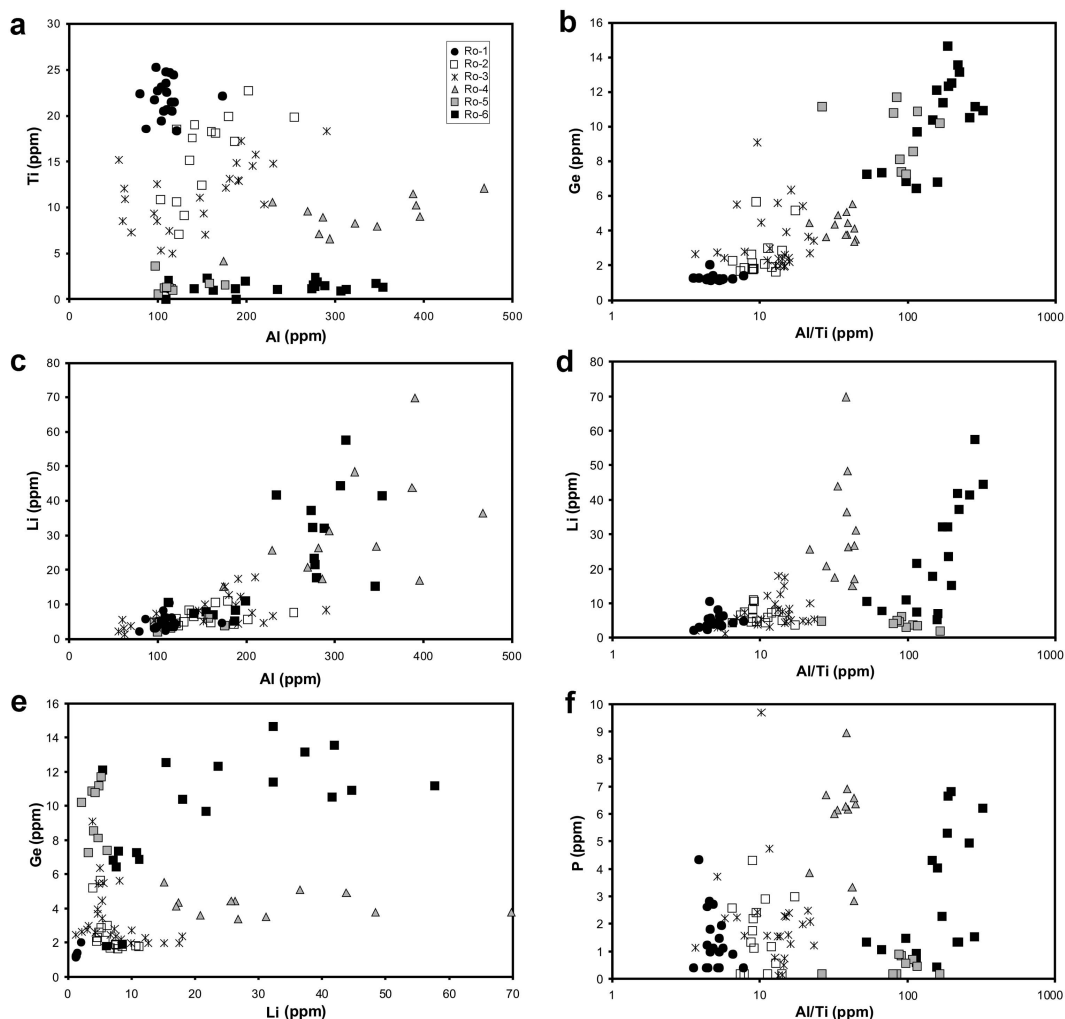


FIG. 3. Trace-element contents in quartz from particular zones of the Li-rich Rožná LCT pegmatite (for sample details see Table 1): (a) Al vs. Ti; (b) Al/Ti vs. Ge; (c) Al vs. Li; (d) Al/Ti vs. Li; (e) Li vs. Ge; (f) Al/Ti vs. P.

graphic zone (30 to 65 ppm) and decreases in the core (24 ppm). The trend of Ge is similar to that of Al. The Li contents of all samples are negligible (<0.1 ppm) and the very small amount in quartz from Vladislav corresponds to the small amounts of Li in the bulk-rock content in the surrounding parental durbachite (20–35 ppm Li; Breiter, 2008) and in beryl from the nearby Kožichovice pegmatite (37 ppm Li; Novák and Filip, 2010).

The ability of late-crystallizing quartz from the core of some pegmatites (e.g. Věžná) to contain unusually large amounts of a number of

trace elements could support the hypothesis that this type of quartz is derived from silica gel (Williamson *et al.*, 1997). The hypothetical considerations of the possible role of silica gel at the end of crystallization of pegmatite melts (Taylor *et al.*, 2004), were recently supported by the discovery of inclusions of silica gel in quartz from a simple pegmatite (Thomas and Davidson, 2012). Our data do not provide sufficient support for this hypothesis; however, a more thorough study of quartz from the cores of one of the latest primary pegmatite units is required.

Comparison of quartz from Moravian pegmatites and pegmatites worldwide

The trace-element signature of quartz from the blocky and core zones of the Vladislav NYF pegmatite is comparable with Norwegian NYF-related pegmatites from the Froland, Evje and Tysfjord fields (Müller *et al.*, 2013) in terms of its contents of Al (24–65 ppm vs. 21–94 ppm Al), Ti (18–34 ppm vs. 2–20 ppm Ti) and Ge (1.1–1.6 ppm vs. 2–3 ppm Ge, averages in all cases). However, quartz from the Norwegian pegmatites contains more Li (6–12 ppm Li).

The evolution of the Rožná LCT lepidolite pegmatite is similar to those of spodumene- and lepidolite-bearing Borborema LCT pegmatites (Fig. 4), as the late-stage quartz is relatively enriched in Al, Li and Ge, whereas the Ti content decreases from the outer zones inward and becomes negligible in the central units (1–2 ppm). However, the Al and Li contents of the Borborema pegmatites are somewhat larger than in Rožná. In contrast, quartz from Rožná is more enriched in Ge. The anatectic pegmatite from Znětín differs from all of the pegmatites examined in terms of a systematic decrease of both Al and Ti contents from the graphic zone through the blocky unit to the two generations of smoky quartz in pockets. Crystallization of feldspars, muscovite and quartz in these pockets represents the transition from magmatic to hydrothermal processes, where smoky quartz II is evidently of hydrothermal origin. A similar decrease in Al and Ti contents during transition from magmatic to hydrothermal crystallization of quartz was described by Larsen *et al.* (2009) from granites along the Oslo Rift.

Comparison of quartz from pegmatites and granites

The compositions of quartz from the less-fractionated pegmatites (Znětín, Věžná and Vladislav) are similar to those of quartz from the two-mica granites of the Moldanubian Pluton (Breiter *et al.*, 2013), with Al contents <250 ppm and Li <40 ppm (Fig. 5). The pegmatites are comparatively poor in Ti (most commonly 1–25 vs. 20–100 ppm) and enriched in Ge (1–6 vs. 0.4–0.8 ppm).

Quartz from the complex LCT-pegmatites exhibits evolutionary trends similar to the quartz from the S-type rare-metal granites of Krušné Hory/Erzgebirge but never reaches such large Al

and Li contents (>1000 ppm Al and >120 ppm Li; Breiter *et al.*, 2013). However, quartz from the Borborema lepidolite- and spodumene-subtype pegmatites contains up to 115 ppm Li (sample average) and is thus similar to quartz in the Podlesí rare-metal granite (Breiter and Müller, 2009). However, in this case, the Al content (sample average max. 650 ppm) is substantially smaller than the typical Al content of the late facies of the rare-metal Krušné Hory/Erzgebirge granites (600–1100 ppm, Breiter and Müller, 2009). In contrast, quartz from complex pegmatites is able to accommodate more Ge than the quartz from the rare-metal granites (sample means 6–10 vs. 2–3 ppm, Fig. 5b).

The Ti–Al–Ge ternary diagram proposed by Schrön *et al.* (1988), utilized this specific feature of pegmatitic melts for discrimination between normal and evolved granites and pegmatites (Fig. 6). Whereas granite melts evolve generally from the Ti to the Al corner of the diagram, pegmatite melts evolved towards the Ge corner.

Note that the samples from quartz cores are largely heterogeneous with domains which have very few trace elements (see Supplementary Table); thus a relatively large number of point-analyses is necessary to obtain a reliable mean value. Trace-element-poor quartz may represent the product of hydrothermal recrystallization. In the Věžná pegmatite in particular, the core quartz is enriched in all analysed elements including Rb, Sr, Ba and Cr.

Substitutions and the role of associated minerals

Of the trace elements in quartz, only Ti, Al and Li are systematically present and more or less homogeneously distributed in the range of tens to 100s of ppm in the majority of samples investigated. Titanium as Ti^{4+} is capable to a limited extent of replacing Si in SiO_4 tetrahedra and the equilibrium between rutile and the Ti content of associated quartz can be used as a thermobarometer (Huang and Audétat, 2012). Aluminium is the most abundant trace element, with different valences to that of Si, and in common granites and pegmatites is usually in the range 100–400 ppm, whereas in evolved rare-metal granites and complex pegmatites it is in the range 400–1000 ppm Al (Breiter *et al.*, 2013). There is no correlation between the ASI (aluminium saturation index) of melt and the Al content of crystallizing quartz (Breiter and

TRACE-ELEMENT COMPOSITION OF QUARTZ

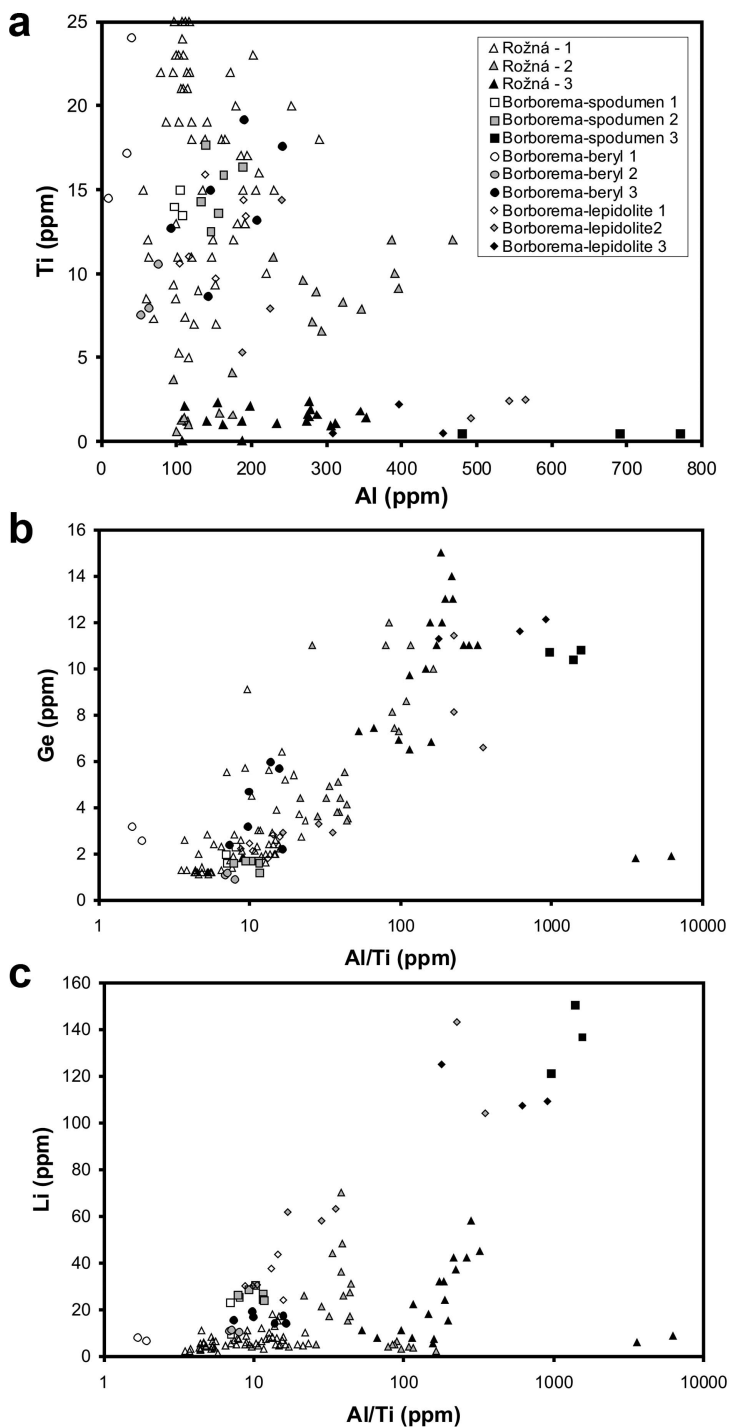


FIG. 4. Comparison of compositional trends of trace elements in quartz from the Rožná LCT pegmatite with the Borborema pegmatites (data from Beurlen *et al.*, 2011): (a) Al vs. Ti; (b) Al/Ti vs. Ge; (c) Al/Ti vs. Li. All the data for each pegmatite has been grouped into three zones representing the border (1), intermediates (2) and core (3).

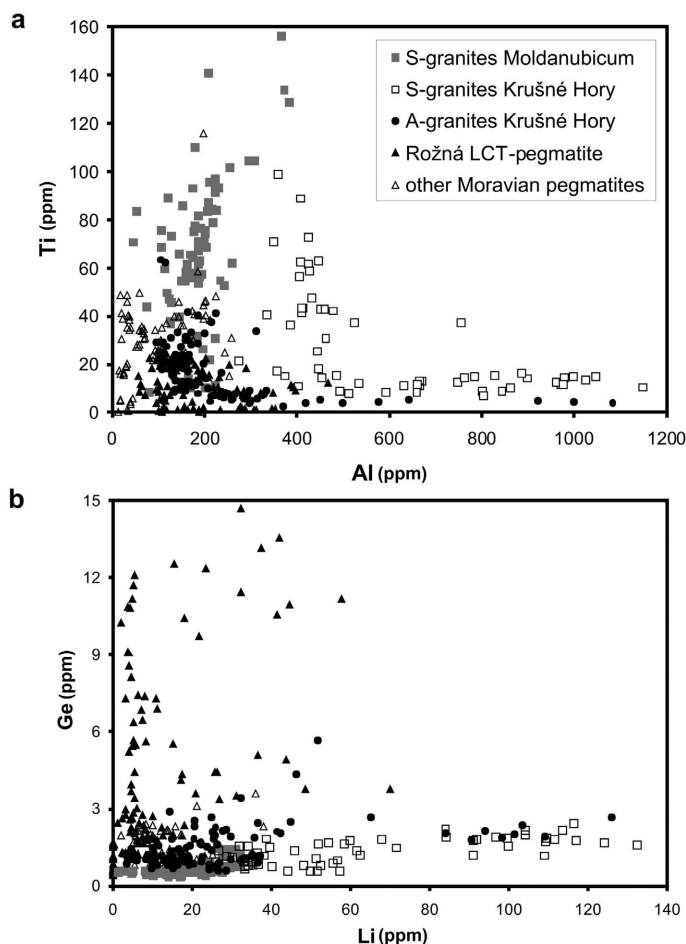


FIG. 5. Comparison of trace-element compositions of quartz during granitic and pegmatitic differentiation: (a) Al vs. Ti; (b) Li vs. Ge (data from Breiter and Müller, 2009; Breiter *et al.*, 2012a, 2012b, 2013).

Müller, 2009). Thus, the entry of Al into the quartz lattice is not determined by the activity of Al in the melt, but by the activities of the available ions for valence compensation. In most cases, substitution of Si^{4+} by Al^{3+} in the quartz structure is essentially compensated by the interstitial ions H^+ , Li^+ , Na^+ and K^+ . The berlinite substitution ($\text{Al}+\text{P} \leftrightarrow \text{Si}+\text{Si}$), which is common in feldspars (London, 1992), garnet (Breiter *et al.*, 2005b) and topaz (Breiter and Kronz, 2004), is expected to be negligible in quartz as its P content is typically >10 ppm. According to Müller and Koch-Müller (2011), igneous quartz preferentially incorporates H^+ as $(\text{OH})^-$ in lieu of Li, K and P and this is reflected by the relatively large $\text{H}/(\text{Li}+\text{K}+\text{P})$ ion ratio compared to hydrothermal

and metamorphic quartz. Note that Müller and Koch-Müller (2011) analysed quartz from Li-poor granites and pegmatites and found only 38–98 ppm Al and 4–11 ppm Li. In contrast, Perny *et al.* (1992) and Götze *et al.* (2004) stressed the importance of Li^+ , mainly in the relative Al-rich igneous quartz. Recently, Beurlen *et al.* (2011) showed, that 60–100% of Al ions in quartz from the Borborema Li-pegmatites are compensated with Li^+ ions. In the pegmatite samples investigated from the Bohemian Massif, $\sim 1/4$ – $3/4$ of the Al ion substitution is compensated with Li (Fig. 3c). It can be assumed that the remainder of the Al is compensated with other alkalis (Na, K) in interstitial positions and/or *via* the coupled substitution $\text{Si}^{4+} + \text{O}^{2-} \leftrightarrow \text{Al}^{3+} + (\text{OH})^-$.

TRACE-ELEMENT COMPOSITION OF QUARTZ

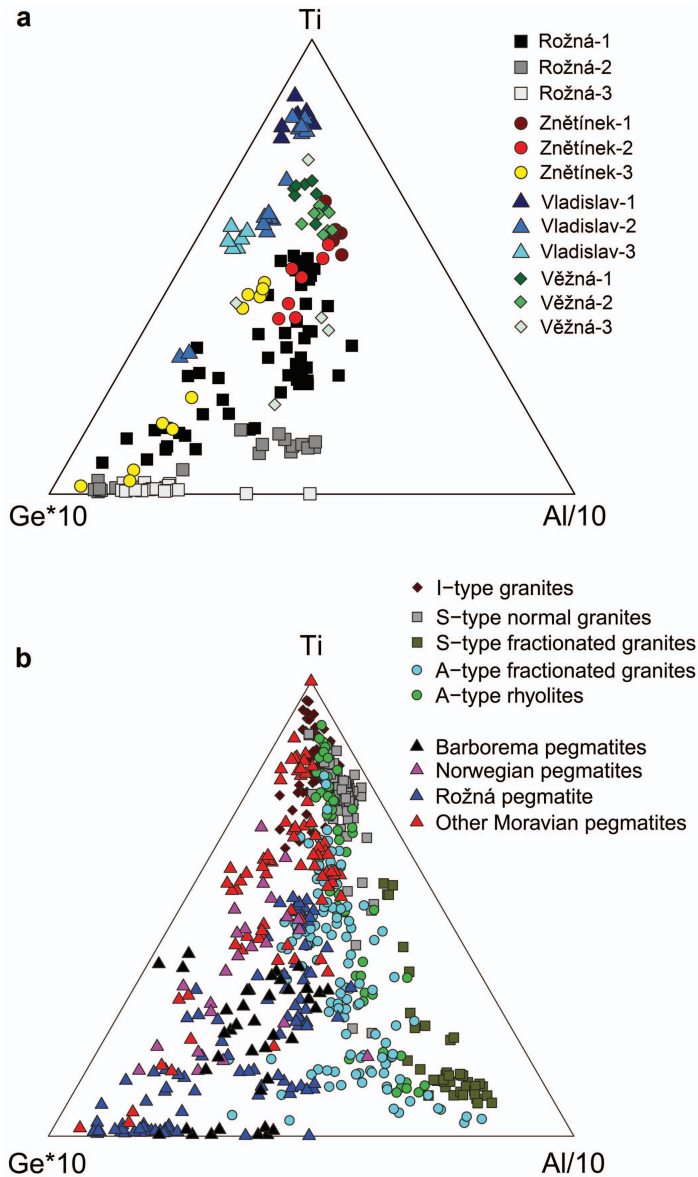


FIG. 6. Ti–Al–Ge-ternary diagram: (a) evolution of quartz within the pegmatite investigated from the border to the core zone (1 to 3); (b) comparison of quartz from pegmatites and the main types of granites (data from Larsen *et al.*, 2004; Breiter and Müller, 2009; Beurlen *et al.*, 2011; Breiter *et al.*, 2012a,b, 2013).

The combination of $\text{Al}^{3+} + \text{Li}^+ \leftrightarrow \text{Si}^{4+}$ and $\text{Al}^{3+} + \text{OH}^- \leftrightarrow \text{Si}^{4+} + \text{O}^{2-}$ substitutions may explain why the largest Al contents of quartz were found in evolved granites and pegmatites strongly enriched in Li and water (complex LCT pegmatites, S- and A-type rare-metal granites) without direct relation to their ASI. This is

supported by the composition of quartz from Vladislav, where very small amounts of Li (below detection limits) are accompanied by small amounts of Al (24–65 ppm).

The role of associated minerals in the concentrations of Li, P and B in quartz is not clear and has not been investigated to date. The behaviour of Li

is unexpected as most quartz from the Li-rich Rožná lepidolite pegmatite contains relatively little Li (averages of the border graphic and albite units are 4–7 ppm Li), whereas quartz from the Li-poor Znětín pegmatite contains 5–14 ppm Li and quartz from Věžná pegmatite (with only minor amounts of Li-bearing minerals, Teerstra *et al.*, 1995) contains 14–24 ppm Li. Phosphorus also displays a similar unexpected behaviour, e.g. in the Rožná pegmatite, which contains the largest number of phosphate minerals among the pegmatites investigated (Novák and Cempírek, 2010). The concentrations of P are mostly very low (0.7–2.8 ppm) except for the sample Ro4. In contrast, in the Vladislav pegmatite the P contents in quartz are among the highest (6.7–7.3 ppm), disregarding very small amounts of P in feldspars and almost an entire absence of primary phosphates, including apatite, in the NYF pegmatites of the Třebíč Pluton (Novák *et al.*, 2011, 2012). All pegmatites examined contain tourmaline as an accessory (Znětín, Vladislav, Věžná) or as a minor mineral (Rožná). However, the highest concentrations of B (5.8–11 ppm) were obtained from the outer units in the Vladislav quartz, where tourmaline is absent. The quartz core with common tourmaline at the same locality yielded a small amount of B (3.0 ppm). It can be assumed that crystallization of associated minerals prior to quartz decreased the concentration of particular elements in the melt and, thus, in the slightly later-crystallizing quartz. Further investigations are required to explain this problem.

Thermobarometry

The Ti-in-quartz thermobarometer (Huang and Audetat, 2012) permits determination of the rock-crystallization temperature when the Ti content in quartz and an appropriate pressure are known. The presence of rutile or ilmenite in association with analysed quartz is the necessary condition for achieving chemical equilibrium and the applicability of this thermobarometer. The pressure in the Strážek Unit and other Moldanubian regions during rare-element pegmatite emplacement was estimated to be 0.2–0.3 GPa (Novák *et al.*, 2013) and 0.3–0.4 GPa (Ackerman *et al.*, 2007). For the model conditions of 0.3 GPa, quartz from the outer zones of the Znětín and Vladislav pegmatites (45 and 44 ppm Ti) indicates a temperature of 670°C, while blocky zones of both pegmatites (35 and 34 ppm Ti, respectively) give 645°C. The border zone in the

Rožná Li-pegmatite (22 ppm Ti in quartz) yields a temperature of 610°C. These temperatures should be considered as maxima, as the real activity of Ti in the melt was probably less than unity.

Conclusions

This study demonstrates:

(1) Quartz from simple anatectic and NYF pegmatites is poor in all trace elements. Compositional evolution is marked by a decrease in Ti and minor increases in Ge. There are only small amounts of Al and Li and they show no systematic changes with pegmatite evolution; usually Al <100 ppm, Ti <30 ppm, Li <12 ppm and Ge <3 ppm.

(2) Quartz from complex LCT pegmatites has similar evolutionary trends to quartz from fractionated granites: a decrease in Ti in the initial stage of melt evolution is followed by an increase in Al, Li and Ge. In comparison with the most fractionated rare-metal granites, pegmatitic quartz is relatively depleted in Al and Li, but strongly enriched in Ge.

(3) The limiting factor for the entry of Al into the quartz lattice appears to be the presence of a sufficient amount of ions for charge compensation, mainly Li ($\text{Al}^{3+} + \text{Li}^+ = \text{Si}^{4+}$) and H ($\text{Al}^{3+} + \text{OH}^- = \text{Si}^{4+} + \text{O}^{2-}$).

(4) The temperature of crystallization of the border zones of the Znětín and Vladislav pegmatites using the Ti-in-quartz thermometer at assumed pressures of 0.3 GPa was ~670°C; the border zone in Rožná crystallized near 610°C.

(5) The trace element content of quartz is a useful tool for obtaining a better understanding of magmatic evolution of complex pegmatites.

Acknowledgements

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References

- Ackerman, L., Zachariáš, J. and Pudilová, M. (2007) P-T and fluid evolution of barren and lithium

- pegmatites from Vlastějovice, Bohemian Massif, Czech Republic. *International Journal of Earth Sciences*, **96**, 623–638.
- Beurlen, H., Müller, A., Silva, D. and Silva, M.R.R.D. (2011) Petrogenetic significance of LA-ICP-MS trace-element data on quartz from the Borborema pegmatite province, northeast Brazil. *Mineralogical Magazine*, **75**, 2703–2719.
- Breiter, K. (2008) Durbachites of the Třebíč pluton within the borehole Požd'átky V-5 – genetic interpretation. Pp. 143–147 in: *Zprávy o geologických výzkumech v roce 2007*. Česká geologická služba, Prague [in Czech].
- Breiter, K. and Kronz, A. (2004) Phosphorus-rich topaz from fractionated granites (Podlesí, Czech Republic). *Mineralogy and Petrology*, **81**, 235–247.
- Breiter, K. and Müller, A. (2009) Evolution of rare metal-specialised granite melt documented by quartz chemistry. *European Journal of Mineralogy*, **21**, 335–346.
- Breiter, K., Müller, A., Leichmann, J. and Gabašová, A. (2005a) Textural and chemical evolution of a fractionated granitic system: the Podlesí stock, Czech Republic. *Lithos*, **80**, 323–345.
- Breiter, K., Novák, M., Koller, F. and Cempírek, J. (2005b) Phosphorus – an omnipresent minor element in garnet of diverse textural types from leucocratic granitic rocks. *Mineralogy and Petrology*, **85**, 205–221.
- Breiter, K., Svojtka, M., Ackermann, L., Ďurišová, J., Matoušková, Š., Švecová, K. and Loun, J. (2012a) Trace elements in quartz from pegmatite Věžná I (Česká republika). *Bulletin Národního muzea*, **20**, 218–222 [in Czech].
- Breiter, K., Svojtka, M., Ackerman, L. and Švecová, K. (2012b) Trace element composition of quartz from the Variscan Teplice caldera (Krušné hory/Erzgebirge Mts., Czech Republic/Germany): Insights into the volcano-plutonic complex evolution. *Chemical Geology*, **326–327**, 36–50.
- Breiter, K., Ackerman, L., Svojtka, M. and Müller, A. (2013) Behavior of trace elements in quartz from plutons of different geochemical signature: A case study from the Bohemian Massif, Czech Republic. *Lithos*, **175–176**, 54–67.
- Cempírek, J. and Novák, M. (2006) Mineralogy of dumortierite-bearing abyssal pegmatites at Starkoč and Běstvina, Kutná Hora Crystalline Complex. *Journal of Geosciences*, **51**, 259–270.
- Cempírek, J., Novák, M., Ertl, A., Hughes, J.M., Rossman, G.R. and Darby, M.D. (2006) Fe-bearing olenite with tetrahedrally coordinated Al from an abyssal pegmatite at Kutná Hora, Czech Republic: structure, crystal chemistry, optical spectra and Xanes spectra. *The Canadian Mineralogist*, **44**, 23–30.
- Cempírek, J., Novák, M., Dolníček, Z., Kotková, J. and Škoda, R. (2010) Crystal chemistry and origin of grandidierite, ominelite, boralsilite and werdingite from the Bory Granulite Massif, Czech Republic. *American Mineralogist*, **95**, 1533–1547.
- Černý, P., Smith, J.V., Mason, R.A. and Delaney, J.S. (1984) Geochemistry and petrology of feldspar crystallization in the Věžná pegmatite, Czechoslovakia. *The Canadian Mineralogist*, **22**, 631–651.
- Černý, P., Staněk, J., Novák, M., Baastgaard, H., Rieder, M., Ottolini, L., Kavalová, M. and Chapman, R. (1995) Chemical and structural evolution of micas at the Rožná and Dobrá Voda pegmatites, Czech Republic. *Mineralogy and Petrology*, **55**, 177–202.
- Černý, P., Chapman, R., Teertstra, D.K. and Novák, M. (2003) Rubidium- and cesium-dominant micas in granitic pegmatites. *American Mineralogist*, **88**, 1832–1835.
- Černý, P., London, D. and Novák, M. (2012) Granitic pegmatites as reflections of their sources. *Elements*, **8**, 289–294.
- Cháb, J., Breiter, K., Fatka, O., Hladil, J., Kalvoda, J., Šimůnek, Z., Štorch, P., Vašíček, Z., Zajíc, J. and Zapletal, J. (2010) *Outline of the geology of the Bohemian Massif: the Basement Rocks and their Carboniferous and Permian Cover*. Czech Geological Survey, Prague. 295 pp.
- Charoy, B., Chaussidon, M. and Noronha, F. (1995) Lithium zonation in white micas from Argemela microgranite (central Portugal): an in-situ ion-, electron-microprobe and spectroscopic investigation. *European Journal of Mineralogy*, **7**, 335–352.
- Čopjaková, R., Škoda, R., Vašinová Galiová, M. and Novák, M. (2013) Distributions of Y + REE and Sc in tourmaline and their implications for the melt evolution; examples from NYF pegmatites of the Třebíč Pluton, Moldanubian Zone, Czech Republic. *Journal of Geosciences*, **58**, 113–131.
- Deans, J.R.L. (2010) *Trace element and calculated temperature variation in quartz and titanite in the 36 Ma Harrison Pass pluton, Ruby Mountains NE Nevada*. Unpublished MSc Thesis, Texas Tech University, Texas, USA.
- Dennen, W.H. (1967) Trace elements in quartz as indicators of provenance. *Geological Society of America Bulletin*, **78**, 125–130.
- Dosbaba, M. and Novák, M. (2012) Quartz replacement by "kerolite" in graphic quartz-feldspar intergrowths from the Věžná I pegmatite, Czech Republic; A complex desilicification process related to episyenitization. *The Canadian Mineralogist*, **50**, 1609–1622.
- Flem, B. and Bédard, P.L. (2002) Determination of trace elements in bcs crm 313/1 (bas) and nist srm 1830 by inductively coupled plasma-mass spectrometry and

- instrumental neutron activation analysis. *Geostandards Newsletter*, **26**, 287–300.
- Flem, B., Larsen, R.B., Grimstvedt, A. and Mansfeld, J. (2002) In situ analysis of trace elements in quartz by using laser ablation inductively coupled plasma mass spectrometry. *Chemical Geology*, **182**, 237–247.
- Gadas, P., Novák, M., Staněk, J., Filip, J. and Vašinová-Galiová, M. (2012) Compositional evolution of zoned tourmaline crystals from pockets in common pegmatites, the Moldanubian Zone, Czech Republic. *The Canadian Mineralogist*, **50**, 895–912.
- Gao, S., Liu, X., Yuan, H., Hattendorf, B., Gunther, D., Chen, L. and Hu S. (2002) Determination of forty-two major and trace elements in USGS and NIST SRM glasses by laser ablation-inductively coupled plasma-mass spectrometry. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, **26**, 181–196.
- Götze, J., Plötze, M., Graupner, T., Hallbauer, D.K. and Bray, C.J. (2004) Trace element incorporation into quartz: A combined study by ICP-MS, electron spin resonance, cathodoluminescence, capillary ion analysis, and gas chromatography. *Geochimica et Cosmochimica Acta*, **68**, 3741–3759.
- Götze, J., Plötze, M. and Trautmann, T. (2005) Structure and luminescence characteristics of quartz from pegmatites. *American Mineralogist*, **90**, 13–21.
- Holub, F.V. (1997) Ultrapotassic plutonic rocks of the durbachite series in the Bohemian Massif: petrology, geochemistry and petrogenetic interpretation. *Sborník geologických Věd, Ložisková Geologie a Mineralogie*, **31**, 5–26.
- Horn, I., Rudnick, R.L. and McDonough, W.F. (2000) Precise elemental and isotope ratio determination by simultaneous solution nebulization and laser ablation-icp-ms: Application to U–Pb geochronology. *Chemical Geology*, **164**, 281–301.
- Huang, R. and Audétat, A. (2012) The titanium-in-quartz (TitanQ) thermobarometer: A critical examination and re-calibration. *Geochimica et Cosmochimica Acta*, **84**, 75–89.
- Jacamon, F. and Larsen, R.B. (2009) Trace element evolution of quartz in the charnockitic Kleivan granite, SW-Norway: The Ge/Ti ratio of quartz as an index of igneous differentiation. *Lithos*, **107**, 281–291.
- Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Gunther, A. and Enzweiler, J. (2011) Determination of Reference Values for NIST SRM 610-617 Glasses Following ISO Guidelines. *Geostandards and Geoanalytical Research*, **35**, 397–429.
- Kotková, J., Schaltegger, U., Leichmann, J. (2010) Two types of ultrapotassic plutonic rocks in the Bohemian Massif - Coeval intrusions at different crustal levels. *Lithos*, **115**, 163–176.
- Kusiak, M.A., Dunkley, D.J., Suzuki, K., Kachlík, V., Kędzior, A., Lekki, J., Opluštil, S. (2010) Chemical (non-isotopic) and isotopic dating of Phanerozoic zircon. A case study of durbachite from the Třebíč Pluton, Bohemian Massif. *Gondwana Research*, **17**, 153–161.
- Larsen, R.B. (2002) The distribution of rare elements in K-feldspar as an indicator of petrogenic processes in granitic pegmatites: examples from two pegmatite fields in southern Norway. *The Canadian Mineralogist*, **40**, 137–151.
- Larsen, R.B., Polvé, M. and Juve, G. (2000) Granite pegmatite from Evje-Iveland: trace element chemistry and implications for the formation of high-purity quartz. *NGU Bulletin*, **436**, 57–65.
- Larsen, R.B., Henderson, I., Ihlen, P.M. and Jacamon, F. (2004) Distribution and petrogenetic behaviour of trace elements in granitic pegmatite quartz from South Norway. *Contributions to Mineralogy and Petrology*, **147**, 615–628.
- Larsen, R.B., Jacamon, F. and Kronz, A. (2009) Trace element chemistry and textures of quartz during the magmatic hydrothermal transition of Oslo Rift granites. *Mineralogical Magazine*, **73**, 691–707.
- London, D. (1992) Phosphorus in S-type magmas: The P₂O₅ content of feldspars from peraluminous granites, pegmatites, and rhyolites. *American Mineralogist*, **77**, 126–145.
- Lyakhovich, V.V. (1972) *Trace Elements in Rock-forming Minerals of Granitoids*. Izd. Nedra, Moscow. 200 pp, [in Russian].
- Melleton, J., Gloaguen, E., Frei, D., Novák, M., Breiter, K. (2012) Timing relationships between emplacement of rare-element pegmatites, metamorphism and magmatism: Example from the Variscan Bohemian Massif (Czech Republic). *The Canadian Mineralogist*, **50**, 1751–1773.
- Monecke, T., Kempe, U. and Götze, J. (2002) Genetic significance of the trace element content in metamorphic and hydrothermal quartz: a reconnaissance study. *Earth and Planetary Science Letters*, **202**, 709–724.
- Müller, A. and Ihlen, P.M. (2012) Trace elements of pegmatite quartz and their regional distribution in two pegmatite fields of southern Norway. Pp. 445–451 in: *Proceedings of the 10th International Congress of Applied Mineralogy (ICAM)* (M.A.T.M. Broekmans, editor). Springer-Verlag, Berlin, Heidelberg.
- Müller, A. and Koch-Müller, M. (2009) Hydrogen speciation and trace element contents of igneous, hydrothermal and metamorphic quartz from Norway. *Mineralogical Magazine*, **73**, 569–583.
- Müller, A., Kronz, A. and Breiter, K. (2002) Trace elements and growth patterns in quartz: a fingerprint

- of the evolution of the subvolcanic Podlesi Granite System (Krušné Hory, Czech Republic). *Bulletin of the Czech Geological Survey*, **77**, 135–145.
- Müller, A., Ihlen, P.M. and Kronz, A. (2008a) Quartz chemistry in polygeneration Sveconorwegian pegmatites, Froland, Norway. *European Journal of Mineralogy*, **20**, 447–463.
- Müller, A., Seltmann, R., Kober, B., Eklund, O., Jeffries, T. and Kronz, A. (2008b) Compositional zoning of rapakivi feldspars and coexisting quartz phenocrysts. *The Canadian Mineralogist*, **46**, 1417–1442.
- Müller, A., Wiedenbeck, M., Flem, B. and Schiellerup, H. (2008c) Refinement of phosphorus determination in quartz by LA-ICP-MS through defining new reference material values. *Geostandards and Geoanalytical Research*, **32**, 361–376.
- Müller, A., van den Kerkhof, A.M., Behr, H.-J., Kronz, A. and Koch-Müller, M. (2010) The evolution of late-Hercynian granites and rhyolites documented by quartz – a review. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **100**, 185–204.
- Müller, A., Snook, B., Ihlen, M.P., Beurlen, H. and Breiter, K. (2013) Diversity of the quartz chemistry of NYF- and LCT-type pegmatites and its economic implications. Pp. 1774-1776. *Mineral deposit research for a high-tech world. Proceedings of the 12th Biennial SGA Meeting, 12–15 August 2013. Vol. 4*, Uppsala, Sweden.
- Novák, M. and Cempírek, J. (Editors) (2010) Granitic pegmatites and mineralogical museums in Czech Republic. IMA 2010, Budapest, Hungary. *Acta Mineralogica-Petrographica, Field guidebook serie*, **6**, 1–56.
- Novák, M. and Filip, J. (2010) Unusual Na,Mg enriched beryl and its breakdown products (beryl II, bazzite, bavenite) from euxenite type NYF pegmatite related to the orogenic ultrapotassic Třebíč Pluton, Czech Republic. *The Canadian Mineralogist*, **48**, 3, 615–628.
- Novák, M., Černý, P., Kimbrough, D.L., Taylor, M.C., Ercit, T.S. (1998) U-Pb Ages of monazite from granitic pegmatites in the Moldanubian Zone and their geological implications. *Acta Universitatis Carolinae Geologica*, **42**, 309–310.
- Novák, M., Povondra, P. and Selway, J.B. (2004) Schorl-oxy-schorl to dravite-oxy-dravite tourmaline from granitic pegmatites; examples from the Moldanubicum, Czech Republic. *European Journal of Mineralogy*, **16**, 323–333.
- Novák, M., Škoda, R., Filip, J., Macek, I. and Vaculovič, T. (2011) Compositional trends in tourmaline from the intragranitic NYF pegmatites of the Třebíč Pluton, Czech Republic; electron microprobe, LA-ICP-MS and Mössbauer study. *The Canadian Mineralogist*, **49**, 359–380.
- Novák, M., Škoda, R., Gadas, P., Krmíček, L. and Černý, P. (2012) Contrasting origins of the mixed signature in granitic pegmatites; examples from the Moldanubian Zone, Czech Republic. *The Canadian Mineralogist*, **50**, 1077–1094.
- Novák, M., Kadlec, T. and Gadas, P. (2013): Geological position, mineral assemblages and contamination of granitic pegmatites in the Moldanubian Zone, Czech Republic; examples from the Vlastějovice region. *Journal of Geosciences*, **58**, 21–47.
- Perny, B., Eberhardt, P., Ramseier, K., Mullis, J. and Pankrath, R. (1992) Microdistribution of aluminium, lithium and sodium in a quartz: possible causes and correlation with short lived cathodoluminescence. *American Mineralogist*, **77**, 534–544.
- Povondra, P., Staňková, J. and Staněk, J. (1992) CO₂-bearing cordierite of Moldanubian leptynite rock series from Horní Bory, Czech Republic. *Acta Universitatis Carolinae Geologia*, **1992**, 331–349.
- Schrön, W., Schmädicke, E., Thomas, R. and Schmidt, W. (1988) Geochemische Untersuchungen an Pegmatitquarzen. *Zeitschrift für geologische Wissenschaften*, **16**, 229–244.
- Selway, J.B., Novák, M., Černý, P. and Hawthorne, F.C. (1999) Compositional evolution of tourmaline in lepidolite-subtype pegmatites. *European Journal of Mineralogy*, **11**, 569–584.
- Škoda, R. and Novák, M. (2007) Y,REE,Nb,Ta,Ti-oxide (AB₂O₆) minerals from REL-REE euxenite-subtype pegmatites of the Třebíč Pluton, Czech Republic; substitutions and fractionation trends. *Lithos*, **95**, 43–57.
- Suttner, L.J. and Leininger, R.K. (1972) Comparison of the trace element content of plutonic, volcanic, and metamorphic quartz from southwestern Montana. *Bulletin of the Geological Society of America*, **83**, 1855–1862.
- Taylor, M.C., Sheppard, J.B., Walker, J.N., Kleck, W.D. and Humiston, L.E. (2004) Magmatic hydrogels and hydrosols in the petrogenesis of rare-element pegmatites and other ore deposits. *Geological Association of Canada. – Mineralogical Association of Canada Program Abstracts*, **29**, 198.
- Teertstra, D.K., Černý, P. and Novák, M. (1995) Compositional and textural evolution of pollucite in rare-element pegmatites of the Moldanubicum. *Mineralogy and Petrology*, **55**, 37–52.
- Thomas, R. and Davidson, P. (2012) Evidence of a water-rich silica gel state during the formation of a simple pegmatite. *Mineralogical Magazine*, **76**, 2785–2801.
- van Achterbergh, E., Ryan, C.G., Jackson, S.E. and Griffin, W.L. (2001) Data reduction software for LA-ICP-MS. Pp. 239–243 in: *Laser ablation-ICPMS in the Earth Sciences: Principles and Application* (P.J. Sylvester, editor) Mineralogical Association of

- Canada Short Course Series, **29**. Mineralogical Association of Canada, Québec, Canada.
- Williamson, B.J., Stanley, C.J. and Wilkinson, J.J. (1997) Implications from inclusions in topaz for greisenisation and mineralisation in the Hensbarrow topaz granite, Cornwall, England. *Contributions to Mineralogy and Petrology*, **127**, 119–128.