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Teze disertace k získání vědeckého titulu „doktor věd“ ve skupině věd geofyzikálně-geologických (vědy o Zemi)

# A-TYPE GRANITOIDS IN THE BOHEMIAN MASSIF

## Granitoidy A-typu v Českém masívu

Komise pro obhajoby doktorských disertací v oboru věd geologických

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**Abstract of the DSc. Thesis**

**A-type granitoids in the Bohemian Massif**

The chemical character of igneous rocks results from many factors, of which the most important are: the composition of protolith, the tectonic setting in which melting took place, and the degree of fractionation of the magma. That applies to all types of magmas, although in the case of acidic rocks (granitoids) the relationship between environmental parameters and the resulting magma is less obvious than in the basic rocks.

Nevertheless, a few principal types of granite occupy a specific position during the temporal-spatial evolution of an orogeny. When classifying, in a first approach, the granites into the I, S and A groups (in terms of Chappell and White, 1974; Loiselle and Wones, 1979), the I-type granites are believed to have been extracted from igneous protoliths, whereas S-type granites originated from sedimentary protoliths, both in temporal-spatial relationship to collisional tectonics and metamorphism. The A-type rocks (Bonin, 2007) can be derived from water-undersaturated felsic continental crust or straight through fractionation of basaltic magma, typically in tensional tectonic setting.

The granites of Krušné Hory/Erzgebirge have been, for their obvious association with tin mineralization, investigated in detail petrographically and chemically since the mid-19$^{th}$ century and belong to one of the classical regions of ore-bearing granites (rare-metal granites) in the world (Hochstetter, 1856; Laube, 1876). Geochemical studies after 1970 brought forth new ideas on the nature of granitic plutons of Krušné Hory/ Erzgebirge Mts. Breccias

cemented by granites were found at many localities (Seltmann et al., 1987; Jarchovsky and Pavlů, 1991) and their magmatic origin was proven. Geochemically, two types of tin-bearing granites were distinguished, namely high-phosphorus, strongly peraluminous, typical S-type granites, and low-phosphorus, HFSE-enriched, weakly peraluminous, A-type granites (Breiter et al., 1991).

The A-type granitoides are relatively rare within the Variscan Europe. Except the ore-bearing A-type granites in the Krušné Hory/Erzgebrge, only a few minor occurrences are incorporated into the Alpine orogene in Western Carpathians (Uher and Broska, 1996) and Corsica (Bonin, 2007)) were found and described during last 20 years. A-type granites of the Krušné Hory/Erzgebirge are unique because of its close relationship to roughly the same old S-type granites, with who bear in essentially the same Sn-W mineralization.

The present dissertation is a summary of the author's research of A-type rocks in the Krušné Hory since 1990, especially in the last 10 years. A-type granites and rhyolites in the Krušné Hory/Erzgebirge have never been investigated systematically.  Existing and here presented textural, geochemical and mineralogical data were obtained during various projects aimed primarily to applied geology (prospecting of mineral deposits, hydrogeology). Therefore, the existing knowledge about various aspects of A-granitoids is unbalanced. However, in summary, has served a fairly detailed picture of the geology, geochemistry and mineralogy of this interesting group of rocks.

## Abstrakt předkládané DSc. disertace

## Granitoidy A-typu v Českém masívu

Chemický charakter magmatických hornin je výsledkem mnoha faktorů, z nichž nejdůležitější jsou: složení protolitu, geotektonické prostředí v němž k tavení došlo, a stupeň frakcionace magmatu. To platí pro všechny typy magmat, i když v případě kyselých hornin (granitoidů) je vztah mezi parametry prostředí a výsledným složením magmatu méně zřetelný než v případě hornin bazičtějších.

Nicméně, několik základních typů magmat zaujímá během časoprostorového vývoje orogénu specifické postavení. Použijeme-li v prvním přiblížení klasifikaci granitů na I-, S- a A- typy (z hlediska Chappell a White, 1974; Loiselle and Wones, 1979), granity I-typu vznikly přetavením převážně magmatických zdrojových hornin, kdežto granity S-typu přetavením původních sedimentů, oba typy v časoprostorovém vztahu ke kolizní tektonice a metamorfóze. Granitoidy A-typu (Bonin, 2007) lze odvodit suchým tavením spodní kontinentální kůry, vzácně snad i přímou frakcionací bazaltického magmatu, typicky v tenzním tektonickém prostředí.

Granity krušnohorského krystalinika byly pro své zřejmé spojení s cínovou mineralizací detailně petrograficky a chemicky zkoumány od poloviny 19. století a jsou jednou z klasických oblastí rudonosných granitů na světě (Hochstetter, 1856; Laube, 1876). Moderní geochemická studia po roce 1970 přinesla nové představy o povaze granitických plutonů Krušných hor. Byl prokázán magmatický původ brekcií v nadloží granitických intruzí (Seltmann et al., 1987; Jarchovský and Pavlů, 1991) a byl rozpoznán celkově subvulkanický charakter cínonosných granitových pňů. Geochemicky byly odlišeny dva typy

cínonosných granitů: silně peraluminické a fosforem bohaté granity S-typu, a slabě peraluminické, bezfosforové, HFSE-obohacené granityA-typu (Breiter et al., 1991).

Ve variské Evropě jsou horniny A-typu poměrně vzácné. Kromě cínonosných A-granitů východních a středních Krušných hor lze ještě jmenovat několik drobných výskytů zapracovaných do alpínského orogenu v Karpatech (Uher and Broska, 1996) a několik plutonů na Korsice (Bonin, 2007). A-typové granity Krušných hor jsou unikátní svým úzkým vztahem k prakticky stejně starým granitům S-typu, s nimiž nesou v podstatě shodné Sn-W zrudnění. Petrografická i metalogenetická shoda mezi krušnohorskými granity S- a A-typu byla příčinou, proč byly oba geochemicky principiálně odlišné typy granitů rozpoznány až počátkem 90. let (Breiter et al., 1991).

Předkládaná disertace je souhrnem autorových výzkumů hornin A-typu v Krušných horách od roku 1990, zejména však v posledních 10 letech. Krušnohorské granity a ryolity A-typu nebyly nikdy zkoumány systematicky. Prezentovaná data vznikla během různých projektů zaměřených primárně prakticky v rámci ložiskového a hydrogeologického výzkumu. Proto jsou existující poznatky o různých aspektech A-granitoidů nevyvážené. Přesto v souhrnu podávají již dosti podrobný obraz o geologii, geochemii a mineralogii této zajímavé skupiny hornin.

## Thesis of the dissertation

### A-TYPE GRANITOIDS IN THE BOHEMIAN MASSIF

## 1. Introduction

The present dissertation is a summary of the author's research of A-type rocks in the Krušné Hory/Erzgebirge since 1990, especially in the last 10 years. A-type granites and rhyolites in the Krušné Hory area have never been investigated systematically. Existing and here presented geological, textural, and geochemical data were obtained during various projects aimed primarily to applied geology in the Czech Geological Survey (prospecting of mineral deposits, hydrogeology). Presented mineralogical data originated mainly during the last five years at the Geological Institute of the Academy of Science. Therefore, the existing knowledge about various aspects of A-granitoids (e.g. granites and rhyolites) is unbalanced. However, in summary, has served a fairly detailed picture of the geology, geochemistry and mineralogy of this interesting group of rocks.

## 2. Geochemical classification of granites

The chemical character of igneous rocks is the result of many factors, of which the most important are: the composition of protolith, the tectonic setting in which melting took place, and the degree of fractionation of the magma. That applies to all types of magmas, although in the case of acidic rocks (granitoids) the relationship between environmental parameters and the resulting magma is less obvious than in the basic rocks. There is general consensus, that principal types of granitoids occupy a specific position during the temporal-spatial evolution of an orogene. When classifying, in a first approach, the granites into the I, S and A groups (in terms of Chappell and White, 1974; Loiselle and Wones, 1979), the I-type granites are believed to have been extracted from igneous protoliths, whereas S-type granites originated from sedimentary protoliths, both in temporal-spatial relationship to collision tectonics and metamorphism. The A-type rocks (Bonin, 2007) can be derived from water-undersaturated felsic continental crust or straight through fractionation of basaltic magma, typically in tensional tectonic setting.

## 3. Brief history of the investigation of granites in the Krušné Hory/Erzgebirge area

The granites of Krušné Hory area have been, for their obvious association with tin mineralization, investigated in detail petrographically and chemically since the mid-19th century and belong to one of the classical regions of ore-bearing granites (rare-metal granites) through the world. Hochstetter (1856) and Laube (1876) had already distinguished two fundamental granite types in the Krušné hory Mts. and the nearby Slavkovský Les area - the older barren "Gebirgsgranit" (today usually termed as “older intrusive complex” – OIC) and the younger ore-bearing "Erzgebirgsgranit" (“younger intrusive complex” – YIC). A detailed microscopic study of granites of the Nejdek Massif led Teuscher (1936) to the concept of "autometasomatism", in other words an alteration of granites in their postmagmatic development stages by their own cogenetic hydrothermal fluids. This theory influenced genetic interpretation of fractionated granites around the world for more than 50 years.

The 1594 m long borehole CS-1 at Cínovec in 1961-63 provided the first data about vertical evolution of highly fractionated Sn-bearing granite worldwide (Štemprok and Šulcek, 1969).

Regional prospecting (Absolonová and Matoulek, 1971; Breiter et al., 1987) and geochemical studies (Čadková and Mrázek, 1987) after 1970 brought forth new ideas on the nature of granitic plutons of Krušné Hory Mts.

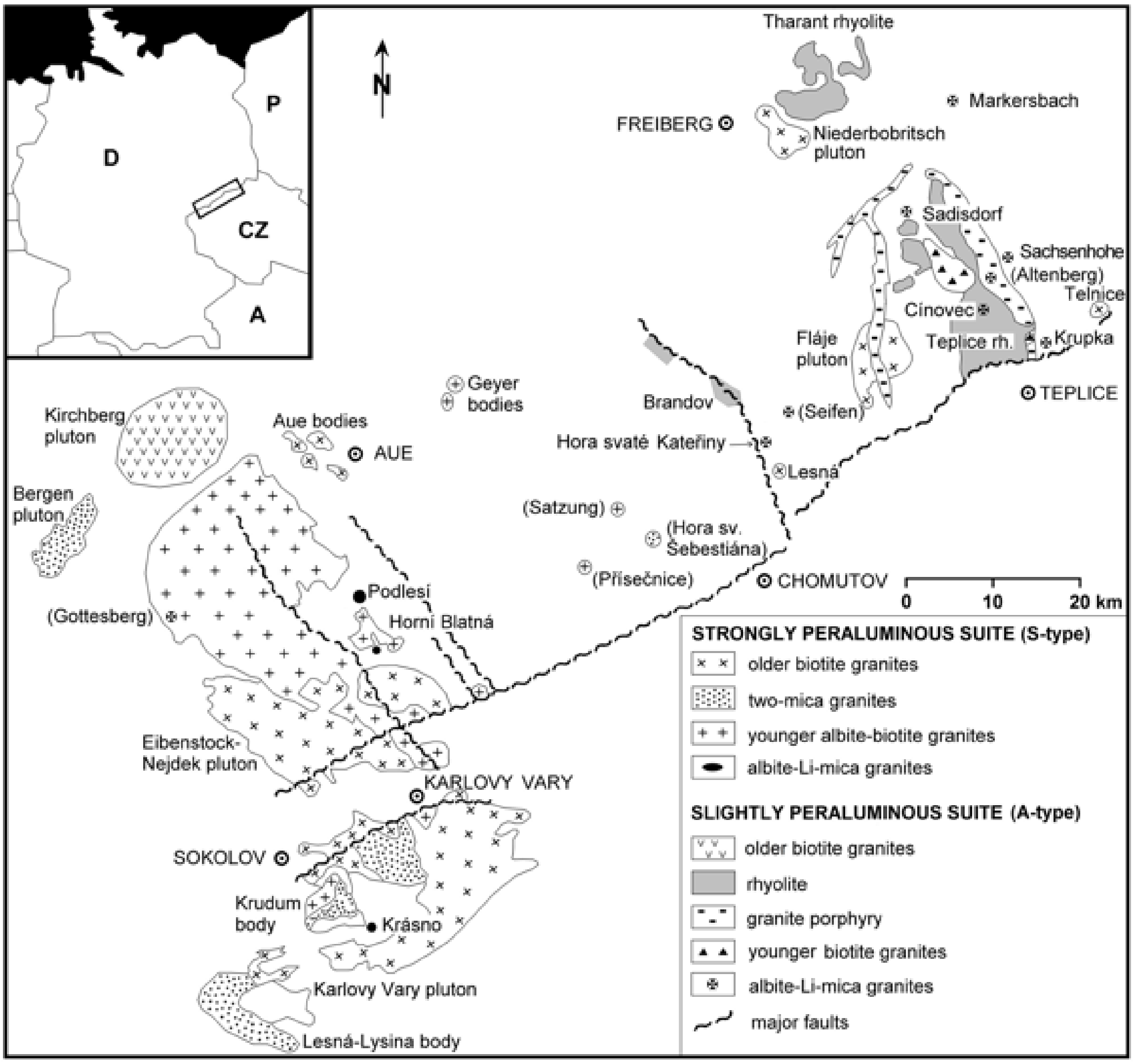


Fig. 1 Localization of studied A-type granitoids within the Krušné Hory/Erzgebirge area

Magmatic breccias cemented by granites were found at many localities and their primary magmatic origin was proven (Seltmann et al., 1987; Jarchovský and Pavlů, 1991). Geochemically, two types of tin-bearing granites were distinguished, namely high-phosphorus, strongly peraluminous, typical S-type granites, and low-phosphorus, HFSE-enriched, weakly peraluminous, A-type granites (Breiter et al., 1991).

## 4. A-type granitoids in the Krušné Hory area

### *4.1 Altenberg-Teplice caldera*

The Altenberg-Teplice Caldera (ATC) is located in the eastern Krušné Hory Mts. (Hoth et al., 1995). ATC has an elliptical shape elongated in north-south direction with dimensions of about 35x18 km (500 $km^2$). Its basement and adjacent rocks are mainly Lower Paleozoic metagranitoids and gneisses intruded by Carboniferous Fláje granite. The crystalline basement of the caldera dips at 20° to the east. The basal units of the caldera fill are exposed on the surface in the NW part of the ATC - Schönfeld Unit paleontologically dated as Westphalian B/C (=Duckman-tian/Bolsovian) with rhyolite and dacite volcanism. The eastern third of ATC is covered by the so-called Teplice Rhyolite (TR). The preserved volume of TR exceeds 250 $km^3$ (Jiránek et al., 1987). The eastern contact of ATC is strongly affected and modified by north-south trending faults intruded by granite porphyry dykes up to 1 km thick and post-caldera intrusions of Preiselberg and Cínovec granite. The western contact is flat and therefore it is possible there to study an uninterrupted volcanic sequence unaffected by younger faults. The southern part of the

Caldera is covered by Tertiary sediments; its perimeter was defined by Mlčoch and Skácelová (2010).

Structural borehole Mi-4, drilled in 1984 in the central part of the ATC, revealed a stratigraphic cross-section with six clearly distinct magmatic phases (Breiter, 1997):

1. basal rhyolite tuff (**BR**) at a depth of 924.5–871 m;
2. dacite tuffs and ignimbrites (**DC**) at a depth of 870–603 m;
3. rhyolite tuffs (**TR1**) at a depth of 601–493 m;
4. rhyolite tuffs to ignimbrites (**TR2**) at a depth of 491–192 m;
5. rhyolite ignimbrites to lavas (**TR3**) at a depth of 192–0 m. This unit also makes up the vast majority of the outcrops of the Czech part of the Caldera;
6. Post-Caldera granite porphyries (**GP**) form thick dykes of NW-SE to N-S direction and are chemically closely related to the TR3 phase.

*Reversal zoning of the Teplice rhyolite*

All three units of Teplice rhyolite (TR1 to TR3) show a strong reverse development. Tuffs, relatively rich in lithofile elements (Si, Rb, Na), Y and Th, are at the base of each eruptive unit, while superposed ignimbrites and rhyolite lavas are relatively enriched in Fe, Mg, K, Sr and Zr. Among the phenocrysts, the replacement of a mineral assemblage of albite + pure K-feldspar in the basal tuffs by an assemblage consisting of oligoclase + Na-rich sanidine in the upper lavas indicate increase in temperature of phenocrysts crystallization during each volcanic event. These observations can be explained by the model of repeatedly exhausted magmatic reservoir (Breiter, 1997): the melt produced in the lower crust interrupted its ascent in a transition reservoir where thermogravitational differentiation took place – the early crystallized minerals like amphibole, biotite, K-feldspar and zircon (carriers of Zr, Fe, Mg, K, Sr) accumulated dominantly at the bottom of the reservoir, whereas the relatively light Si-rich melt enriched in incompatible elements, e.g. Rb, Na, Y, and Th, prevailed in the upper part of the reservoir. Thorium and yttrium exhibit an incompatible behavior in the melts of A-type, and become enriched during fractionation. The subsequent eruption produced first the acid tuffs from the upper part of the reservoir, then intermediate ignimbrites, and finally the relatively less differentiated lavas with numerous phenocrysts and accessories from the bottom of the reservoir. This process was repeated three times during the development of the volcano. After the third eruption, the rhyolite caldera subsided and granite porphyry dykes intruded. Some authors explain their relatively less differentiated character by mixing of rhyolite magma with more basic mantle magma which penetrated the bottom part of the rhyolite reservoir. Indications of this process are seen, for instance, in the zonal development of phenocrysts of alkali feldspars ("rapakivi texture", Müller et al., 2005).

### *Post-caldera granites*

The late Variscan Cínovec granite lies on both sides of the Czech-German border in 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 the Upper Proterozoic paragneisses and Upper Carboniferous rhyolites. Only a few small exposures less than 1 $km^2$ in size, in form of small copulas (Cínovec, Altenberg) or vertical stocks (Krupka, Schölerhau), 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 accompanied by Sn-W (Nb, Ta, Mo, Sc) mineralization of greisen type form small separate intrusions. 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 and Breiter, 1993), or intruded in 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 x 0.3 km large was studied to a depth of 1,596 m by borehole CS-1 (Štemprok and Šulcek, 1969). An albite-topaz-zinnwaldite granite was proved to exist in several textural varieties to a depth of 735 m, while an albite-prolithionite granite continues to greater depths. A fractionation *in situ* can be observed in the zinwaldite 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. Common accessory minerals comprise fluorite, topaz, cassiterite, columbite, microlite, pyrochlore, Nb-rutile, zircon, thorite, xenotime, fluorides, oxo-fluorides and carbonates of REE (Rub et al., 1998; Breiter et al., 1999; Förster et al., 1999; Johan and Johan, 2005; Breiter, 2011).

### *4.2 Hory Svaté Kateřiny stock*

The Hora Svaté Kateřiny (St. Katharinaberg) granite is exposed in the form of boulders covering an area of 100x300 m about 2 km to the west of the village of the same name, in the Czech central part of the Krušné Hory/Erzgebirge Mts (Breiter, 2008). The granite was emplaced into the Lower Palaeozoic crystalline basement of the Kateřina Dome in a prominent NNW–SSE-striking tectonic zone ("Brandov deep fault" in Czech, "Flöha-zone" in German literature, Hoth et al., 1995). Remnants of the small Permo-Carboniferous (Duckmantian-Bolsovian) sedimentary Brandov Basin with rhyolitic tuffs and tuffites located 3 km to the north of the granite outcrop are also located within this tectonic zone. Biotite granite belonging to the older intrusive complex of the Krušné Hory Mts. forms a small, fault-bounded outcrop (0.5 $km^2$) about 3 km to the SE from the studied granite.

The granite was forcefully emplaced into the crystalline in two pulses:

1. Equigranular medium-grained biotite granite,
2. Porphyritic fine-grained leucogranite with only scarce grains of dark mica. The younger magma pulse formed several types of unidirectional solidification textures (UST) indicating high contents of fluids and deep undercooling.

### *4.3 Small intrusions in the western Erzgebirge*

Several north-south trending up to 5 m thick rhyolite dykes cropped out about 2 km to SW of Gottesberg (about 10 km to the north of Kraslice) in the slopes of the creek Heroldsbach. The dykes differ in concentration of quartz and K-feldspar phenocrysts. Some of the dykes exhibit distinct zoning with fast cooled fine grained rims and coarsely porphyritic central parts rich in phenocrysts. According to their chemical composition, these rhyolites have distinct A-type character and age of 305–295 Ma (Förster et al., 2007).

The breccia-related tin deposit Gottesberg itself (Gottesmann et al. 1994) is related to the deep-seated rhyolite subvolcanic intrusion of supposed A-type affiliation.

### *4.4 Geochemical differences between the A-type and S-type granitoids*

Due to their economic importance, the geochemical characteristic of the granites from the Krušné Hory Mts. were studied by numerous authors (Štemprok and Šulcek, 1969; Lange et al., 1972; Štemprok, 1986; Tischendorf, 1989; Breiter et al., 1991, 1999; Förster et al., 1999).

Older intrusions of both geochemical types (OIC-S and OIC-A) correspond roughly to high-K calc-alkaline granites. Their fractionation is reflected in the increase of Si content and in the depletion of Ti, Mg, Fe, Ca, Sr, Ba, Zr. Contents of lithofile elements (Li, Rb, F) increase only slightly. The slightly peraluminous Kirchberg pluton (OIC-A) differs from the strongly peraluminous granites (OIC-S) by somewhat lower content of $P_2O_5$ and by enhanced concentrations of REE, Th, U and Zr, for samples with similar $SiO_2$ contents.

Even within the groups of younger intrusions (YIC-S and YIC-A), the contents of major elements and their evolutionary trends in both geochemical granite types are similar: gradual increase in Al, Na and F, and decrease in Si. The contents of Ti, Mg, Fe and Ca are low from the very beginning of fractionation. There is a significant difference in phosphorus levels. In strongly peraluminous granites, the phosphorus content increases systematically (from 0.2 to 1.5 wt% $P_2O_5$) and these granites can thus be simply described as "phosphorous". In slightly peraluminous granites, phosphorus is on the other hand always very low, usually below 0.05 wt% $P_2O_5$. The phosphorus content naturally has an impact on the crystallization of accessory minerals and consequently on the behavior of many trace elements during fractionation. While an increase in the content of lithofile elements (Li, Rb, Cs, Ga, F) and also of Sn, W, Nb and Ta are common for both geochemical types of granites, there is a substantial difference in the behavior of Zr, Th, Y and REE. Their contents decrease in peraluminous (and thus P-rich) S-granites, but increase in slightly peraluminous phosphorus-free A-granites. Among the other elements with different behavior, it is possible to point out boron which reaches much higher levels in S-granites (25 to 100 ppm) than in the A-granites (<30 ppm). On the other hand, Be is clearly concentrated in A-granites (10–40 ppm) rather than in S-granites (<15 ppm). Concentrations of Pb in A-granites increase with increasing fractionation (30 to 80 ppm), while decreasing in S-granites (40 to 5 ppm). The degree of fractionation in granites of Krušné Hory Mts. is very high if commonly used indicators of fractionation are considered: Rb/Sr evolved from 1 to over 100, Zr/Hf from 40 to 10, U/Th from 0.1 to 10. Because the content of $SiO_2$ in the late, highly fractionated granites decreases, traditional Harker diagrams are not suitable for graphical representation of the fractionation. More appropriate are diagrams constructed on the basis of the systematic decrease of $TiO_2$.

## 5. Selected minerals from the A-type rocks

### *5.1 Quartz*

Evolution of quartz chemistry during crystallization of evolved subvolcanic granite was studied in the Hora svaté Kateřiny A-type granite stock. Six populations of igneous quartz were distinguished:

1. anhedral groundmass quartz (0.2–3 mm) in the older biotite granite intrusion,
2. anhedral groundmass quartz in the younger leucogranite intrusion,
3. large (>3 cm) broken, sub-euhedral crystals, which are interpreted as stockscheider quartz presumably originated from the quenched margin of the magma reservoir,
4. layers of comb quartz (0.5–10 mm) developed within the fine-grained leucogranite.
5. drop-like groundmass quartz (0.2–1 mm)
6. comb quartz (0.3–2 cm) in layers with oriented crystallization (UST).

Significant increase of Al, Li, and Be and decrease of Ti are the most important features of quartz evolution (Breiter and Müller, 2009).

Internal structures and appropriate trace-element distributions within quartz grains from rhyolites and granites from the Altenberg-Teplice caldera were investigated using a laser ablation ICP-MS technique combined with a hot-cathode and scanning cathodolumi-nescence (Breiter et al., 2012).

Quartz crystals from rhyolite and granite porphyry exhibit zoned structures, and with one odd exception, their cores are poor in Ti, while their outer zones or rims are enriched in Ti. Aluminum exhibits an opposite trend: the cores of some quartz grains are strongly enriched in Al relative to their rims (350→150 ppm of Al core to rim, typical of sample No. 3198), but other crystals are almost Al-homogeneous (100–120 ppm across the entire quartz grain, with randomly distributed and sporadic slightly enhanced concentrations, typical of sample 3201).

The cores of some quartz crystals in the late rhyolite TR3 have high Al contents corresponding to the strongly fractionated granite, but their rims are rich in Ti, which is typical of rhyolite;

Quartz from granite exhibits no chemical zoning: older BiG shows quartz chemistry similar to the core of crystals from the rhyolite TR2 composition (100–150 ppm Al, 15–40 ppm Ti). In contrast, quartz from the younger ZiG shows a wider scatter in Al contents and also extremely low Ti concentrations (150–300 ppm Al, max. to 10 ppm Ti). However, these contents do not significantly differ from those in the cores of quartz crystals from rhyolites TR3.

Quartz crystals began to crystallize gradually in the deep-seated magma chamber in an environment with an increasing concentration of Al and a decreasing concentration of Ti; this is the standard trend in the fractionation process. The chemistry of the quartz crystal cores indicates that the fractionation of rhyolite magma progressed from TR2 to TR3 and that the same trend repeated in the granite melt from BiG to ZiG in the primary deep-seated magma reservoir (based on the model conditions of 750 °C and 1,000 MPa). These volcanic crystals later underwent an adiabatic ascent into the shallow magma chamber (at the model conditions of 700 °C and 200 MPa), during which the crystal rims rich in Ti originated and then extruded. The quartz crystals in the granite melt directly intruded, and in the environment of a residual melt rich in water and flux agents, later grew in the form of snowball quartz rich in Al and poor in Ti.

The chemistry of quartz in older granite indicates that, between the fractionation of rhyolite and granite, the deep-seated magma chamber became more primitive chemically, perhaps because of the contamination by a new, less developed, but essentially granitic melt;

Granites with quartz grains extremely poor in Ti (10–20 ppm) simultaneously contain Nb-rutile, apparently satisfying the condition for applying the Ti-in-quartz thermobarometer. The low Ti content in these rocks (<0.03 wt% $TiO_2$) and high concentration of flux agents in the melt may be the reason why the real Ti content in quartz is lower than its concentration derived from the relevant pressure and temperature based on experiments.

### *5.2 Alkalifeldspars*

The fundamental difference between feldspars from A- and S-type granites is in their phosphorus content. Both K-feldspar and plagioclase of strongly peraluminous S-type granites contain substantial amounts of phosphorus (0.2 to 1.5 wt% of $P_2O_5$), which enters into the feldspar lattice by means of berlinite substitution (Breiter et al., 2002). Both feldspars in A-type granites are P-free. K-feldspars in highly fractionated facies of both types of granites are enriched in Rb in order of 0.1–0.4 wt% $Rb_2O$ (Breiter et al., 2002; Breiter, 2008).

A significant vertical trend in feldspar composition can be observed in each of the TR1 and TR3 units in the volcanics of ATC. While rhyolites at the base of each unit contain phenocrysts of albite and of pure Kfs, albite-oligoclase and sanidine with 30 % Ab-component coexist in the upper parts of all units.

### *5.3 Li-bearing micas*

The Fe-Li micas are represented by biotite-protolithionite-zinnwaldite (Bt–Protol–Zinw) series in both geochemical types of granites, whereas lepidolite (Lpd) was rarely found only in A-type granites at Cínovec. The content of Si, Li and F in mica increases with the degree of fractionation of granites, while the content of Ti, Fe, and Mg decreases. The content of Al increases from biotite to zinnwaldite, but it slightly decreases in lepidolite. All micas are poor in Mg (Fe/(Mg+Fe) = 0.90 to 0.98). Micas with a higher content of Li (zinnwaldite–lepidolite) have their (OH, F) position usually by more than 90 % saturated with fluorine. Zinnwaldite contains up to 2.5 wt% $Rb_2O$ and 0.2 wt% $Cs_2O$. The occurrence of primary muscovite is restricted to the two-mica facies of S-type granites in Bergen pluton and in the Slavkovský Les area.

### *5.4 Fluorite*

Magmatic fluorite is one of the most important carriers of F in subaluminous granites of A-type. It forms subhedral to anhedral grains up to100 μm in diameter, of magmatic origin. It is rather common in some samples. Some grains are rich in Y (up to 5.1 wt% Y, 0.06 apfu Y) and REE (up to 3.8 wt% Ce and 1.8 wt% Nd, 0.02 apfu Ce, 0.01 apfu Nd). Chondrite-normalized REE patterns are flat, resembling the whole-rock REE pattern. Locally, fluorite is replaced by bastnäsite and REE-oxyfluorides. Another, hydrothermal type of fluorite, poor in REE, was found together with beryl in a Qtz-Kfs vein and in fillings of small cavities in granite

### *5.5 Topaz*

Topaz occurs only in accessory amounts in A-type granites due to lower activity of Al. At Hora Svaté Kateřiny, topaz forms small late interstitial euhedral crystals (100–300 µm) of yellow to brown color. This is a substantial difference to the S-type fractionated F-rich granites which usually contain over 1 vol% of topaz (Breiter et al., 1991; Förster et al., 1999). At contact of late intrusions in the eastern Erzgebirge (e.g. Altenberg), topaz evolved as haulm-like aggregates, locally termed pycnite.

The composition of topaz from Cínovec, Altenberg and Schneckenstein was investigated using electron microprobe analysis and LA-ICP MS. All topaz grains are rich in F (17.9–19.8 wt%, 1.73–1.90 apfu), the most important trace elements being Ge and Ga. Regardless of genetic type, topaz from granites typically contains 50–100 ppm Ge. The greatest amounts (up to 204 ppm Ge) were found in topaz from quartz-topaz-apatite greisen in Krásno. In fractionated granites and greisens, topaz is calculated to contain 23–87 % of the bulk Ge content in the rock. In contrast, topaz does not concentrate Ga. The Ga content of topaz (typically 5–35 ppm in S-type granites, <10 ppm Ga in A-type granites) is usually lower than the bulk Ga-content of the rock. In addition, up to 16 ppm Sc, 23 ppm Sn, and more than 400 ppm Fe may be present (Breiter et al., 2013).

### *5.6 Zircon*

Changes in the chemical composition of zircon in vertical section of fractionated plutons were studied along 1,596 m long borehole CS-1 at Cínovec. Chemical composition of zircon show distinct vertical zoning. Hf shows moderate enrichment from ca 2 wt% $HfO_2$ in the deeper proto-lithionite granite to 5–10 wt% $HfO_2$ in the uppermost part of the zinnwaldite granite. High contents of Th (3–8 wt% $ThO_2$) 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% $ThO_2$. 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 are not considered to be a specific phenomenon characterizing melts of A-type, but reflects a high degree of fractionation of systems rich in Na and F (Breiter and Škoda, 2012).

The assemblage of Zr(Hf)-Th(U)-REE minerals from a subvolcanic A-type granite from Hora Svaté Kateřiny were studied in an effort to distinguish how both magmatic and hydrothermal processes affected the rock system. The primary accessory phases included fluorite, magnetite and zircon with rare xenotime, monazite, and thorite. Complex solid solutions with nearly equal contents of (Th+U)-, (Zr+Hf)- and REE-components usually formed irregular domains within zircon and thorite crystals and are supposed to by also primary. The granite was affected by strong reactions with late- to post-magmatic fluids. Pyrite and arsenopyrite crystallized from the first portion of hydrothermal fluid with low oxygen fugacity. Later, fluid with higher oxygen fugacity altered magnetite to hematite, sulfides to Fe-hydroxides, and dissolved xenotime. During this time, Th and U-bearing zircon and thorite were partially metamictised. Arsenic was oxidized to $As^{5+}$ and intensively metasomatised xenotime, Y-rich zircon and thorite forming chernovite. Even later, fluid rich in $CO_2$ dissolved metamictised thorite and partially dissolved monazite after only short transport at the contact with fluorite crystallized Th-rich bastnäsite.

## 6. Evolutionary model of the simultaneous production of the S- and A-type melts in the Krušné Hory/ Erzgebirge

The difference in geochemical character between the Kirchberg granite (OIC-A) and the peraluminous weakly fractionated granites (OIC-S) indicates that the two types of magma formed already from the beginning of the Variscan magmatic activity in the relatively small area of the Krušné hory Mts. Their difference gradually increased in time. While both groups of strongly peraluminous magma (OIC-S and YIC-S) intruded probably in rapid succession in the course of about 10 Ma (ca 328–318 Ma) across the whole Krušné Hory Mts., the A-type magma intruded in several time-separated and space limited pulses.

The period of around 318 Ma can be considered the end of the formation of S-type magmas and the period of around 310 Ma the beginning of the ascent of the A-type magmas in the central and western Krušné Hory Mts. There was therefore a gap of about 10 Ma between the two types of magmatic activity. A minimum time gap between the two types of magmas is believed to have existed in the eastern Krušné Hory Mts., as evidenced by an almost immediate succession of extrusive units in the ATC. If the paleontological dating is closer to reality, then the A-type magmatism across the Krušné Hory Mts. started almost simultaneously 310 Ma ago. If the isotopic dating is correct, then the ascent of A-magmas began in the east already more than 325 Ma ago, i.e. at the time when the younger phase of S-type plutonism was just starting in the central and western parts of the Krušné Hory Mts. In that case, magmas of both types would have originated in a small area of the Krušné Hory Mts. at the same time.

The existing εNd values for T=325 Ma range from -1.8 to -5.2 for OIC-S granites up to -4.4 to -8.5 for YIC-S granites. The values -1.8 to -4.4 for A-type granites are indistinguishable from the values for the OIC-S (Förster and Romer, 2010). The activity of mantle melts in the Krušné Hory area is documented by the existence of several generations of numerous lamprophyre dykes, insignificant by volume, but widespread throughout the whole duration of the Variscan magmatism. Their material participation in the formation of granitoid magmas is unlikely, because all granites contained minimum levels of elements such as Mg, Ni, Cr, Co and V since the beginning of fractionation. Müller et al. (2005) found evidence of mixing of acidic and basic (mantle?) magma in the ATC volcanics. The εNd values can be explained by crustal melting of stratified subducted crustal slab containing a mix of sedimentary and volcanic rocks of Upper Proterozoic to Ordovician age whose equivalents are known from outcrops in other parts of Saxothuringicum (cf. Linnemann and Romer, 2010). Those sequences of rocks – sources of LILE, metals like Sn, W, U etc., and fluorine (micaceous pelites?) – must have been available throughout the entire Krušné Hory region.

Two basic phenomena are essential for creation of a model of contemporaneous origin of two types of magma in the Krušné Hory Mts: (i) both types of magma were enriched in LILE, F and Sn, W, Nb, Ta; (ii) both types are poor in Mg, Cr, V and Ni, and (iii) εNd values of both magma suites are very similar. Consequently, it is thought that (1) both types of magma originated through melting of a similar protolith, and (2) the involvement of mantle material in the origin of even A-type magma must have been negligible.

In the present level of knowledge, only a very simplified genetic model can be proposed. Generally, the peraluminous S-type granites are considered to be product of melting of metasedimentary (pelitic) source rocks, whereas metaluminous to slightly peraluminous A-type granites are interpreted as product of low-grade melting of quartzo-feldspathic rocks (Patino Douce, 1997; Dall´Agnol and Oliveira, 2007). In the Krušné hory/Erzgebirge, both types of granites are scattered in a small area and occur close each other. In this case, a common protolith for both magma types is probable.

The Krušné Hory/Erzgebirge crystalline is composed of stack of napes of upper Proterozoic to lower Paleozoic lithologies (Cháb et al., 2009), among others of micaceous metapelites enriched in LILE and Sn+W, and quartzo-feldspathic meta-graywakes and gneisses. During Cadomian and early-Variscan deformation and metamorphism, these rocks were mingled in different proportions and underwent different pT-paths connected with different degree of dehydratation. Subsequent late-Variscan partial melting of this layered protolith should give rise to all recognized granite types.

Reasons for the differences in chemical composition of produced melts should be searched in local changes in the proportion of quartzo-feldspathic and pelitic lithologies, slightly different pT-conditions of melting, degree of the melting, and the degree of metamorphic dehydratation of the protolith prior the melting. Relatively higher content of metapelites, higher contents of water and higher pressure in the source area should favor the production of magmas with typical S-type signature, whereas a higher proportion of quartzo-feldspathic rocks, lower water-content, lower pressure (in areas of beginning post-orogenic extension) favored the A-type signature of ascending melt (compare Anderson and Bender, 1989; Patino Douce, 1997).

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## List of publications, which are included into dissertation, and their abstracts

The publication No.1 firstly reported presence of A-type granites in the Krušné Hory Mts. The publication No.2 firstly defined evolutionary stages within the Teplice caldera and suggest model for their antidrome chemical character. Major metallogenic features of S- and A-type granites in Erzgebirge are described and modeled in the publication No.3. Publication No.4 deals with the genetic interpretation of rocks textures on the example of the Hora Svaté Kateřiny A-type granite stock. Publication No.5 track changes in chemical composition of quartz during magmatic evolution of strongly fractionated S- and A-type granites on the example of the Podlesí and Hora Svaté Kateřiny stocks. Publication No.6 studied alteration of the Zr-Th-REE minerals during post-magmatic alteration of an A-type granite. Article No.7 is a summarizing publication on the A-type magmatic rocks in the Krušné Hory area. Publication No.8 interprets the pT-conditions of crystallization of rocks in the Teplice caldera on the basis of Ti-in-Quartz thermobarometer. Publication No.9 compares vertical differentiation of strongly fractionated S- and A-type plutons on the example of chemical composition of zircon. Article No.10 defined topaz as the most important concentrator of Ge during crystallization of evolved S- and A-type granites.

**(1)** Breiter K., Sokolová M., Sokol A. (1991) Geochemical specialization of the tin-bearing granitoid massifs of NW Bohemia. *Mineralium Deposita 26,* 298-306.

**Abstract:** The geochemistry of Variscan tin-bearing granitoid massifs of the Krušné Hory Mts. (Erzgebirge),

Slavkovský Les (Kaiserwald) and Smrčiny (eastern Fichtelgebirge) is compared by statistical processing of 270 analyses including a wide spectrum of major and trace elements. Seven different types of granites are distinguished. Out of these, five types represent the successive differentiation of the largest massif of NW Bohemia: the Karlovy Vary massif. This comprises strongly differentiated peraluminous granites evolving towards extreme Li-Rb-Cs-F-and Sn-enrichment in the youngest members, which are albite-topaz-zinwaldite "lithium" granites. The sixth and seventh types are different from the former by their location in the eastern Krušné hory and tectonic setting, and they display geochemical features of anorogenic granites: they are metaluminous albite-zinwaldite granites with marked enrichment of Nb, Y, and HREE in addition to Li, Rb, Cs, F and Sn, indicating contamination by sub-crustal material. All types of Sn-W mineralizations are intimately associated with the most strongly differentiated granites.

**(2)** Breiter K. (1997) Teplice rhyolite (Krušné hory Mts., Czech Republic) Chemical evidence of a multiply exhausted stratified magma chamber. *Bulletion Czech geological Survey* 72, 205-213.
**Abstract:** The study of a 924 m long Mi-4 drilling log and the areal lithogeochemistry of outcrops of the Czech part of the Teplice rhyolite (TPR) allow to be distinguished four volcanic phases in the volcanogenic fill of the Altenberg-Teplice caldera - 1) the Schönfeld unit; 2) the tuff unit of the TPR1; 3) the explosive-effusive phase of the TPR2 ('western margin' type); and 4) the effusive-intrusive phase of the TPR3 (types Pramenáč, Medvědí vrch, Přední Cínovec, and dykes of granite porphyry). The two youngest

phases show a remarkable antidrome (reversal) evolutionary trend, which is explained by a model based on the step-by-step exhausting of a gravitationally stratified magma chamber.

**(3)** Breiter K., Förster H., Seltmann R. (1999) Variscan silicic magmatism and related tin-tungsten mineralization in the Erzgebirge-Slavkovský les metamollgenic province. *Mineralium Deposita* 34, 505-521.
**Abstract:** Integration of geochemical, mineralogical, isotopic, and geochronological data with geodynamic considerations suggests that the Variscan granites in the Erzgebirge-Slavkovský Les domain originated from repeated melting events and were emplaced over a period of about 40 Ma (330-290 Ma). Several lines of evidence exist supporting the idea that Erzgebirge granites assigned to different types (biotite granites, two-mica granites, strongly peraluminous P-rich Li-mica granites, and slightly peraluminous P-poor granites) are in most cases not genetically related via continuous fractional crystallization from a common magmatic reservoir. The genesis of the Slavkovský Les granites, however, might be discussed in terms of an uninterrupted fractionation series. Geological models of Sn-W deposits based upon geochemical and structural results imply that the main ore depositional events followed immediately the emplacement and solidification processes of melt via fluid-melt immiscibility, breccia-pipe formation and/or pervasive rock-fluid interactions.

**(4)** Breiter K. (2008) Mineral and textural evolution of subvolcanic A-type granite: Hora Svaté Kateřiny stock, Krušné Hory Mts., Czech Republic. *Zeitschrift f. geologische Wissenschaften* 36, 365-382.

**Abstract:** The Hora Svaté Kateřiny granite forms a small stock in the Czech central part of the Krušné Hory/ Erzgebirge Mts. Granite emplacement preceded in two pulses: (i) Equigranular medium-grained biotite granite forms most of the stock; (ii) Fine-porphyritic fine-grained leucogranite with only scarce grains of dark mica cemented fragments of the older granite. The younger magma pulse formed several types of unidirectional solidification textures (UST). Both granite pulses are accompanied by brecciation, which – together with UST – indicates a forceful intrusion into a shallow level. Chemical features correspond to an A-type character of the granite. Rock of both stages are only slightly peraluminous (ASI=1.05), rich in fluorine, Rb, Nb, Ta, Th, Zr, Y and Be (5-19 ppm), and poor in phosphorus (<0.1 wt% $P_2O_5$). Significant differences exist between fresh samples and samples that underwent late magmatic to post-magmatic reactions with fluids. All fluid-influenced samples are depleted in F, Li, Rb, Cs, Sn, W, Be, Ga, Hf, Ho, and LREE, while the contents of Zr, U and Th remained unchanged, and As became enriched. Both granite types contain phenocrysts of perthitic K-feldspar in groundmass composed of quartz, K-feldspar, albite and Li-bearing annite. Magmatic accessory phases comprise fluorite, magnetite, and zircon with less abundant topaz, beryl, xenotime, monazite, thorite, cassiterite, columbite, and other Nb, Ta, U-bearing phases. Chernovite, rhabdo-phane, bastnäsite, and Ce-dominated oxyfluoride are products of intensive hydrothermal alteration. The Th-U-total Pb method yielded the age of 308 ± 14 Ma.

**(5)** Breiter K., Müller A. (2009) Evolution of rare-metal granitic magmas documented by quartz chemistry. *Europian Journal of Mineralogy* 21, 335-346

**Abstract:** The study documents changes in the chemical composition of igneous quartz during evolution of two contrasting late-Variscan granite suites in the Erzgebirge/Krušné Hory Mts., Czech Republic. Six quartz populations were optically distinguished in each of the studied granite suites: a highly peraluminous phosphorus-rich (S-type) from Podlesí, and slightly peraluminous P-poor (A-type) from Hora Svaté Kateřiny. Contents of Li, Be, B, Al, Ge, P, K, Na, Ca, Ti, Mn, and Fe were determined in situ in all quartz types using LA-ICP-MS. Of all the determined elements, only Ti decreases with increasing fractionation. Al reached the highest contents in all samples (100-1200 ppm), followed by Ti, Li, and K (in the range of 10-100 ppm). The Ti vs. Al diagram is the most fitting indicator of the evolution of the melt from which the quartz crystallized. Al enters the quartz lattice according to coupled substitution $Si^{4+} \leftrightarrow Al^{3+} + (Li, K, H)^{+}$. No first-hand correlation between Al in quartz and the peraluminosity of the melt was found. The contents of B, Be, Ge, Fe, Mn, and P in quartz are usually lower than 10 ppm and their abundances are generally positively correlated with whole-rock chemical compositions.

**(6)** Breiter K., Čopjaková R., Škoda R. (2009) The involvement of F $CO_2$-, and As in the alteration of Zr-Th-REE-bearing accessory minerals in the Hora Svaté Kateřiny A-type granite, Czech Republic. *Canadian Mineralogist* 47, 1375-1398

**Abstract:** The Zr(Hf)-Th(U)-REE minerals from a subvolcanic A-type granite from Hora Svaté Kateřiny, in the Czech Republic, were studied in an effort to distinguish how both magmatic and hydrothermal processes affected the rock system. The primary accessory phases include

fluorite, magnetite and zircon, with rare xenotime-(Y), monazite-(Ce), and thorite. Complex solid solutions with nearly equal contents of (Th+U), (Zr+Hf) and REE components usually form irregular domains within zircon and thorite crystals and are supposedly also primary. The granite was affected by strong reactions with late- to postmagmatic fluids. Pyrite and arsenopyrite crystallized from the first phase of hydrothermal activity, with low fugacity of oxygen. Later, fluid with a higher fugacity of oxygen altered magnetite to hematite, sulfides to Fe hydroxides, and dissolved xenotime. At this stage, Th- and U-bearing zircon and thorite became partially metamict. Arsenic in the fluid phase was oxidized to $As^{5+}$, and intensively metasomatized xenotime, Y-rich zircon and thorite, forming chernovite. Even later, fluid rich in $CO_2$ dissolved metamict thorite and partially dissolved monazite; after only a short distance of transport, Th-rich bastnäsite deposited in contact with fluorite.

**(7)** Breiter K. (2012) Nearly contemporaneous evolution of the A- and S-type fractionated granites in the Krušné hory/Erzgebirge Mts., Central Europe. *Lithos* 151, 105-121.
**Abstract:** Variscan magmatic activity in the Krušné Hory area spanned from 330 to 295 Ma. During this time, two types of magma were generated and emplaced in close proximity. Strongly peraluminous P-rich (S-type) melts were formed alongside slightly peraluminous P-poor melts (A-type). Two suites of strongly peraluminous P, F, Li, Rb, Cs, U, Sn-rich and Zr, Th, Y, HREE-poor magmas were intruded in rapid succession over a period of about 10 Ma (about 330-320 Ma) over the entire region. Several peraluminous rhyolitic dykes near Gottesberg mark an isolated event at about 295 Ma. Slightly peraluminous F, Li,

Rb, Cs, Sn, Zr, Y, HREE-rich and P-poor magmas were intruded in several events separated in space and time (325-295 Ma). Both magmatic episodes culminated with strongly fractionated subvolcanic granite intrusions, accompanied by explosive brecciation and followed by Sn+W mineralization. The time difference between the two types ranges from 1 to about 15 Ma. The assumed protolith of all late-Variscan granites in the area of Krušné Hory is a mixture of fertile quartzo-feldspathic rocks with micaceous metapelites enriched in LILE and Sn+W. The differences in chemical composition of S- and A-type melts originated from local changes in the proportion of quartzo-feldspathic and pelitic lithologies, different pT-conditions of melting, the degree of melting, and the degree of metamorphic dehydratation of the protolith prior to the melting.

**(8)** Breiter K., Svojtka M., Ackerman L., Švecová K. (2012) 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.

**Abstract:** The internal structures and appropriate trace-element distributions within quartz grains were investigated using a LA-ICP-MS technique combined with a hot-cathode and scanning cathodoluminescence analysis. The studied Variscan magmatic suite is located in the Altenberg-Teplice Caldera (eastern Krušné Hory/Erzebirge) and composed of co-magmatic rhyolites and granites of A-type. The trace-element distribution in the volcanic quartz demonstrates a distinct zoning in the cathodoluminescence images and chemical compositions: the core is poor in Ti, the outer-rim zones are enriched in Ti, and the trends recorded for Al are opposite to those of Ti. The quartz from granites is either very weakly zoned or homogeneous. Based on the chemical composition of quartz and its zoning, the quartz crystals began to crystallize gradually in the primary deep-seated magma chamber with a P-T condition of 10 kbar and 750 °C and in an environment with an increasing concentration of Al and decreasing concentration of Ti. The early stage was followed by the subsequent adiabatic ascent into a shallow magma chamber (approximately 700 °C, 2 kbar), during which crystal rims rich in Ti formed and then extruded. After the caldera collapse, part of the magma intruded as granite, and in the environment of the residual melt rich in water and flux agents, late quartz grew in the form of snowball quartz with an increased Al content and decreased Ti content.

**(9)** Breiter K., Škoda R. (2012) Vertical zonality of fractionated granite plutons reflected in zircon chemistry: the Cínovec A-type versus the Beauvoir S-type suite. *Geologica Carpathica* 63, 383-398.
**Abstract**: Vertical changes in the chemical composition of zircon from two contrasting Variscan granite systems, the S-type Beauvoir system (France), and A-type Cínovec system (Krušné Hory Mts/Erzgebirge) were studied. Samples from Beauvoir represent an 800 m long vertical section through the entire granite stock, while CS-1 borehole (Cínovec) reached a depth of 1600 m. In both localities, the most fractionated intrusions are located on the top of the system. Chemical compositions of zircons from both granite systems show distinct vertical zoning, but their elemental speciation is highly contrasting. At Beauvoir, zircon shows a remarkable increase in Hf-content from 2-4 wt% $HfO_2$ in the deepest B3-unit to 15-19 wt% $HfO_2$ 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% $HfO_2$ in the deeper protolithionite granite to 5-10 wt% $HfO_2$ in the uppermost part of the zinnwaldite granite. High contents of Th (3-8 wt % $ThO_2$) 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% $ThO_2$. 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, and Nb is not 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.

**(10)** Breiter K., Gardenová N., Vaculovič T., Kanický V. (2013) Topaz as an important host for Ge in granites and greisens. *Mineralogical Magazine* 77, 403-417.

**Abstract:** The composition of topaz from different granites and greisen in the Krušné Hory/Erzgebirge area was investigated using electron microprobe analysis (EMPA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometery (LA-ICP MS). All topaz grains are rich in F (17.9-19.8 wt%, 1.73-1.90 apfu), the most important minor/trace elements being P, Ge and Ga. Contents of P up to 1 wt.% $P_2O_5$ (0.025 apfu) were found in topaz from the strongly peraluminous P-rich magmatic systems at Podlesí. Regardless of genetic type, topaz from granites typically contains 50-100 ppm Ge. The greatest amounts (up to 204 ppm Ge) were found in topaz from quartz-topaz-apatite

greisen in Krásno. In fractionated granites and greisens, topaz is calculated to contain 23-87 % of the bulk Ge-content in the rock. In contrast, topaz does not concentrate Ga. The Ga content of topaz (typically 5-35 ppm in S-type granites, <10 ppm Ga in A-type granites) is usually lower than the bulk Ga-content of the rock. In addition, up to 16 ppm Sc, 23 ppm Sn, and more than 400 ppm Fe may be present.