Chemistry of quartz related to the Zinnwald/Cínovec Sn-W-Li greisen-type deposit, Eastern Erzgebirge, Germany

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Abstract

Magmatic and hydrothermal quartz populations related to the Late-Variscan Zinnwald/Cínovec Sn-W-Li greisen-type deposit in the Eastern Erzgebirge/Krušné Hory (German/Czech Republic) were studied in terms of trace element contents and growth structures visualized by cathodoluminescence. The sample suite represents different populations of hydrothermal greisen quartz and magmatic quartz of the granitic host collected at a 600-m long, lateral section crosscutting the northern part of the deposit at the 750-m level.

The studied quartz populations are characterized by generally low concentrations and low variation of Al and Ti indicating relatively constant crystallization conditions (temperature, pressure and fluid chemistry) during ore precipitation. Magmatic and hydrothermal quartz are distinguished by their Al, Ti, Li and Ge concentrations and ratios. Magmatic quartz has commonly higher Al (>100 ppm) and Ti (>3 ppm) compared to hydrothermal quartz. The Ge/Al ratio in quartz increases systematically from high to low formation temperatures (664 to ~400°C = temperature range including published data and our estimates) whereas Ti decreases. The Zinnwald albite granite (mineralization host), an albite-rich alkali granite, and massive quartz-zinnwaldite greisen contain both magmatic and hydrothermal quartz populations which are distinguishable by their Ge/Al weight ratio: magmatic quartz has a Ge/Al ratio of <0.008 whereas hydrothermal quartz a ratio of >0.008.

Hydrothermal vein quartz related to the Sn-W mineralization (Flöze=flat veins and Morgengänge=steep veins) does not show systematic trace element variations along the sampling profile indicating that no significant chemical gradients (in lateral direction) in the ore forming fluid existed. The uptake of Li in the quartz lattice is limited by the incorporated Al although the Zinnwald/Cinovec magmatic-hydrothermal system was strongly enriched in Li. The calculated crystallization temperatures of quartz of the Sn-W mineralization applying the TitaniQ thermobarometer reveal crystallisation temperatures ranging from 575 ± 48 °C (albite granite), 612 ± 12 °C (stockscheider), 610 ± 23 (massive greisen), 536 ± 77 °C (flat veins), to 516 ± 58 °C (steep veins) confirming in general early estimations based on fluid and melt inclusion studies . In economic terms, the hydrothermal quartz (flat and steep veins) with an average total trace element content of 128 ± 56 ppm has intermediate chemical quality and can serve as a by-product if colour sorting and other processing steps are applied. Rock-forming quartz of albite granite and massive greisen with an average total trace element content of 233 ± 127 ppm has medium quality and the disadvantage that quartz contains a high amount of contaminating mineral inclusion, which will be challenging to remove by processing.

1. Introduction

Quartz forms under a wide range of temperature and pressure conditions from aqueous fluids and silicate-rich magmas of diverse origin and composition. The diversity results in a great variability of its trace element chemistry reflecting the conditions of the crystal growth environment. For that reason and because of technical developments of microanalytical methods (LA-ICP-MS, SIMS etc.) quartz is more and more utilized to study crystallization processes and parameters in hydrothermal and silica-rich magmatic systems and their transitions (Müller et al., 2002; Breiter et al., 2005, 2012; Rusk 2012). The advantages of using quartz as genetic pathfinder mineral are its almost omnipresence in these environments and its relative strong resistance to post-crystallization alteration (Müller et al., 2000; Monecke et al., 2002; Götze et al., 2004). Variability of concentrations of Al, Ti, Ge, and Li are commonly used for discrimination, classification and genetic interpretations in igneous quartz and to some extent in hydrothermal quartz as well (Lyakhovich, 1972; Suttner and Leininger, 1972; Schrön et al., 1988; Gurbanov et al., 1999; Larsen et al., 2000, 2004; Götze et al., 2004; Jacamon and Larsen, 2009; Müller et al.,

2010a, 2010b; Rusk, 2012). The concentrations of these trace elements are generally controlled by their abundance in the melt, pressure and temperature, physico-chemical conditions of the system, and the partitioning between the co-genetic mineral phases (Gurbanov et al., 1999; Larsen et al., 2004; Jacamon and Larsen, 2009). The parameters controlling the uptake of Ti into the quartz lattice are crystallization temperature and pressure (Huang and Audétat, 2012), whereas Al, Ge and Li generally increases with progressing fractionation of the melt. However, parameters controlling the uptake of these elements under transitional magmatic-hydrothermal and purely hydrothermal conditions are less explored and understood (e.g., Rusk, 2012). Analytical methods used for the *in situ* determination of trace elements in quartz include electron probe microanalysis (EPMA; Müller et al., 2002, 2005; Donovan et al., 2011), secondary ion mass spectrometry (SIMS; Watt et al., 1997; Müller et al., 2003) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; Flem et al., 2002; Götze et al., 2004; Larsen et al., 2004; Breiter and Müller, 2009; Müller and Koch-Müller, 2009). These analytical techniques have various benefits and drawbacks and they offer most value when integrated with one another and with cathodoluminescence (CL) textural analyses (Rusk, 2012). The advantages of LA-ICP-MS over EPMA are lower detection limits in the range of 0.01 ppm to a few ppm for many elements and those of LA-ICP-MS over SIMS the quantification of up to 30 elements simultaneously.

In this study LA-ICP-MS combined with scanning electron microscope cathodoluminescence (SEM-CL) has been applied to study of different igneous and transitional magmatic-hydrothermal quartz populations related the late Variscan granite-hosted Zinnwald/Cínovec Sn-W-Li greisen-type deposit in the eastern Erzgebirge/Krušné Hory across the German/Czech border (Štemprok, 1960, 1961; Bolduan et al., 1967; Čada and Novák, 1974; Dahm and Thomas, 1985; Dolejš and Štemprok, 2001; Seifert et al., 2011; Neßler et al., 2013, 2015). The aim of the study is to evaluate the variability of the trace element concentrations in quartz of different rock types related to the mineralization along a 600-m long section intersecting the northern part of the deposit at the 750-m level. Our study complements the data set of Breiter et al. (2012) and Breiter et al. (2017) which provide a vertical 1600-m section (drill hole CS-1) through the central part of the deposit. The results are used to better understand the parameters which control the trace element distribution in quartz and how this information contributes to a better understanding of the deposit formation in terms of pressure-temperature-

composition (P-T-X) conditions. In addition, the data are also utilized to evaluate if the quartz of the mineralized veins and the granite host can be used as economic by-product during future exploitation of the Sn-W-Li Zinnwald/Cínovec deposit.

2. Regional geology

The Eastern Erzgebirge/Krušné Hory is part of the Saxothuringian Zone of the Variscan orogeny where late- to post-collisional Variscan uplift and exhumation processes accompanied intense felsic (rhyolitic and granitic) magmatism and formed the eastern Erzgebirge volcano-plutonic complex with the Altenberg-Teplice caldera as the major magmatic structure (Seltmann et al., 1996; Štemprok et al., 2003; Figure 1). The pre-Variscan basement of the area, referred to as the Krušné Hory/Erzgebirge Crystalline Complex, comprises various tectonic units of different metamorphic grades that experienced their last metamorphic and deformation imprint during Lower Carboniferous (e.g., O'Brien and Carswell, 1993; Willner et al., 1997; Rötzler et al., 1998; Rötzler and Plessen, 2010). The Eastern Erzgebirge volcano-plutonic complex developed over a period of about 15 Ma (Romer et al., 2007; 2010) during Variscan post-collisional collapse, beginning with the intrusion of the Niederbobritzsch granites at 328-314 Ma (Tichomirowa, 1997; Förster, 1998) and ending with intrusions of topaz-bearing rare metal granites at 326-308 Ma and related Sn-W mineralization (Romer et al., 2007; Seifert et al., 2011; Seifert and Pavlova, 2016). According to Jiránek et al. (1987), Breiter (1997), Breiter et al. (2001) the magmatic history of the Eastern Erzgebirge volcano-plutonic complex includes the following main stages (in the order from old to young):

- (I) the emplacement of the Niederbobritzsch and Flaje granite massifs and Telnice granite classified as low-F biotite granites of the Erzgebirge/Krušné Hory (Förster et al., 1998, 1999, Štemprok et al., 2003);
- (II) the formation of the 50-km² Tharandter Wald caldera at 320 ± 4 Ma (Breitkreuz et al. 2009) comprising rhyolitic ignimbrites;
- (III) the formation of the 630-km² Altenberg-Teplice caldera comprising the extrusion of the Schönfeld rhyolitic/dacitic ignimbrites, Mikulov rhyolitic ignimbrites (Mikulov beds), Teplice rhyolitic ignimbrites and the intrusion of the Altenberg-Frauenstein microgranite into the caldera collapse structures. The pear-shaped, N–S elongated ring of collapse fractures of the caldera

were filled by multiple intrusions of the rapakivi-textured porphyritic microgranite of Altenberg-Frauenstein (Benek, 1991; Müller and Seltnann, 2002). Hoffmann et al. (2013) acquired a U/Pb zircon age of 326.8 ± 4.3 Ma for the Mikulov ignimbrite, the initial stage of the Altenberg-Teplice caldera suite. The same authors yielded an age of 308.8 ± 4.9 Ma for the Teplice ignimbrite TR1 but stated that the age is not well constrained;

(IV) the youngest stage is represented by the intrusions of topaz-bearing rare-metal granites comprising the Schellerhau granite complex and other small intrusions (Zinnwald-Cínovec, Altenberg, Sadisdorf, Schenkenshöhe, Hegelshöhe, Loupežný, Preisselberg, Knötl). All these intrusions belong to the high-F, low-P Li-mica granites of the Krušné Hory/Erzgebirge which show A-type affinity (Förster et al., 1995; Breiter et al., 1999; Štemprok et al., 2003). Ar-Ar ages of Li-mica of Zinnwald/Cínovec intrusion between 312.6 ± 2.1 to 314.9 ± 2.3 Ma which are interpreted as near-formation ages of Li-mica (Seifert et al., 2011).

Ages of the Sn-W mineralization related to the Altenberg-Teplice caldera overlap with the granite ages. Recent Ar-Ar dating of the greisen mineralization at Zinnwald/Cínovec revealed ages of 311.4 ± 3.0 Ma and 312.5 ± 3.1 Ma (Seifert and Pavlova, 2016). Romer et al. (2007) obtained ages of 323.9 ± 2.5 and 317.9 ± 2.4 Ma (2σ ; Re-Os molybdenite) for the Sn-W mineralization related to the Altenberg granite. The deposit is considered as co-genetic with the Zinnwald/Cínovec granite intrusion. The Sn-W-Li Zinnwald/Cínovec deposit is in the central eastern part of the Altenberg–Teplice Caldera and hosted by the Zinnwald/Cínovec albite granite. The term Zinnwald/Cínovec albite granite, referred to Zinnwald albite granite in the following, was introduced by Štemprok (1965) and represents an alkali granite with high abundance of magmatic albite.

The Zinnwald/Cínovec Sn-W-Li deposit

The greisen massive and vein Sn-W-Li mineralization of Zinnwald/Cínovec is situated in the apical part of the Zinnwald pluton beneath the village of Zinnwald-Georgenfeld/ Cínovec at the German-Czech border, ~35 km S of Dresden (Figure 2). The Zinnwald granite intrusion forms a multiply composed, elliptical granite cupola outcropping 1.3 km in N-S direction and 0.3 km in E-W direction between the German village of Zinnwald-Georgenfeld and the Czech village of Cínovec (Figure 2). The western contact of the intrusion is steep whereas the southern and

eastern contact plunges gently with 10 to 30°. The host rock is the Teplice rhyolite. The upper part of the intrusion is formed by Li-F-enriched albite granite (sampled facies) which has in part been strongly greisenized by high-temperature fluids (e.g., Štemprok 1960) and which is underlain by medium-grained protolithionite granite at a depth of 730 m (beneath Cínovec; Štemprok and Šulcek, 1969, Rub et al., 1983). The Zinnwald pluton is composed of strongly fractionated, slightly peraluminous A-type granites (Seltmann et al., 1998; Štemprok, 1989). In the cupola the Zinnwald albite granite consists of two textural varieties: an older porphyritic and younger medium-grained seriate granite which contains enclaves of the porphyritic granite. Minor dykes of aplite albite granite (albite microgranite), marginal pegmatite (Stockscheider) separate the granite from its host rocks. The stockscheider forms an up to 1.5 m wide sequence at the contact to the Teplice rhyolite. It has a layered structure consisting of one or several megacrystic bands of K-feldspar and quartz with crystal sizes of up to 20 cm which alternate with fine-grained, aplitic layers. The comb-like, pluton-inward orientated megacrysts display unidirectional solidification textures. Zinnwaldite is the predominant mica in the albite granite. Feldspars are represented predominantly by albite with low anorthite content ($An_{<3}$; Seltmann et al., 1998) and minor K-feldspar. Main accessories are cassiterite, fluorite, topaz and columbite-tantalite in addition to rare bastnaesite, uranpyrochlor, uranmicrolite, strueverite and synchisite (Johan and Johan, 1994; Rub et al., 1998). The protolithionite granite contains on average 0.05 wt.% Li_2O and 5.34 wt.% K_2O . Main accessories are zircon, columbite, monazite, xenotime and rutile; apatite is very rare (Johan and Johan, 2005).

The Sn-W-Li mineralization, which was described in detail by Štemprok (1960, 1961), Bolduan et al. (1967) and Čada and Novák (1974), is spatially and genetically associated with the Zinnwald granite cupola. The deposit consists of three structural types of Sn-W ores:

(I) Irregular and massive greisen bodies up to several tens of meters in size within the Zinnwald albite granite (Figures 2B and 4A). The massive greisens are the result of a intense fluid-rock-interaction which affected parts of the Zinnwald albite granite cupola. The commonly sheet-like greisen bodies follow the shape of the granite contact, are most common in the in the apical part of the granite intrusion with decreasing intensity to the flanks but do not extend into the Teplice rhyolite. There are several types of greisens and greisenized granites. The predominant greisens consist of quartz and zinnwaldite or zinnwaldite-quartz-topaz. The greisens contain irregular

admixtures of sericite, fluorite and potassium feldspar (adularia). Some of the greisens are intensely hematitized. Cassiterite is finely, irregularly dispersed in the greisens and formed co-genetically with the greisens (Štemprok and Šulcek, 1969). Based on field observations the major greisen bodies are considered, in general, to be older than the mineralized quartz-zinnwaldite veins described in the following.

(II) Flat-dipping, coarse- to megacrystic quartz-zinnwaldite veins (historically called Flöze) with a thickness of up to 2 m in the central upper part of the granite cupola (Figures 4B-F). In the Tiefer Bünaustolln the flat veins dip 15 to 40° NE. The vertical spacing between the individual flat veins varies between 1 and 40 m. Occasionally the veins extend for several tens of meters out of the granite into surrounding the Teplice rhyolite and contain cavities 5 to 20 cm in size. The quartz veins are commonly accompanied by greisen selvages extending normally not more than 20 cm into the wall rock. Where the quartz veins cross-cut the massive greisen (type I) these selvages clearly superimpose the massive greisen and are commonly richer in topaz than the massive greisen. The main ore minerals within the veins are cassiterite (up to 2 cm in size) and wolframite (up to 10 cm in size) which occur in co-genetic nests either at interstices and cavities of vein quartz or as selvages at the vein contacts. Scheelite (up to 1 cm) is a minor ore phase which precipitated mostly on quartz and zinnwaldite in cavities as a late phase. In the apical parts the veins consists occasionally of dense aggregates of stalked, yellow topaz known as pyknite. The flat veins were the major target of the historical mining.

(III) The flat veins (type II) are cross-cut and displaced by sub-vertical, up to 50 cm wide quartz-zinnwaldite dykes historically called Morgengänge and in the following steep veins. The vertical displacement of the flat veins by the steep veins can be several meters. The steep veins exhibit the same style of mineralization as the flat veins. However, the ore grade is principally lower than those of the flat veins. Greisen selvages (<3 cm) are only occasionally developed.

Štemprok (1960) distinguished in addition K-feldspar (adularia) metasomatism with textures resembling pegmatites, and minor sulphide mineralization with arsenopyrite, galena, sphalerite, tennantite, chalcopyrite, bismuth, bismuthinite, wittichenite, pyrite and opal superimposing the major ore types. Deposition of the sulphides was accompanied by

sericitization and kaolinization. Supergene alteration affected the sulphide mineralization in the upper part of the cupola resulting in the formation of malachite, philipsbornite, mimetite, olivenite and some rare supergene oxide minerals.

In general, the deposit was formed by repeated influx of magma-derived ore-bearing solutions into the albite granite cupola. During the first stage the fluids penetrated and replaced the albite granite forming massive greisens whereas at the second stage the fluids precipitated mainly flat veins and steep veins of the cupola. The flat and steep veins are also considered as greisen-type mineralization. The fractures were formed apparently by the contraction due crystallization and degassing of the granite in its upper part. The solutions moved to the place of ore deposition from lower levels of the intrusion as testified by the finding of greisens in the deep parts of the granite body (about 1200 m; Seltnann et al., 1998). There was an effective interplay of repeated tectonic movements, fluid migration and precipitation which led to the formation of the deposit and the manifestations of post-magmatic alterations down to the deepest known parts of the intrusion (about 1600 m; Seltnann et al., 1998).

The samples investigated in this study were collected in the Tiefer Bünaustolln adit of the Vereinigt Zwitterfeld mine (Figure 3). The adit exposes the northern German part of the deposit at the 750-m level. The Tiefer Bünaustolln was developed at about 1550 under the name Tiefer Zinnwalder Erbstollen to exploit the Sn-W mineralization hosted by the Zinnwald albite granite. However, tin mining goes back at least until 1378 when the name Zinnwald (Tin Forest) was recorded for the first time. Since that time primary tin ores have been mined with various intensities in the Zinnwald-Cínovec district. The most active period of mining was during the World War I and II. After World War II mining in the Tiefer Bünaustolln was abandoned and continued in the Czech part of the district only. The last mine in the Czech village of Cínovec was closed down in 1990. The amount of extracted tin from the Cínovec-Zinnwald district was about 40,000 t (Štemprok et al., 1995). Between 1990 and 1992 the adit Tiefer Bünaustolln was secured and upgraded for tourism. Recent Li, Sn and W resource estimations for the German and Czech parts of the deposit are provided in Table 1.

3. Samples and methods

3.1. Sampling

The samples were collected in the Tiefer Bünaustolln adit of the Vereinigt Zwitterfeld zu Zinnwald visitor mine in 2015. The adit cuts through the northern part of the Zinnwald/Cínovec Sn-W-Li deposit at the 750-m level (Figure 3). The adit was chosen as sampling site for the following reasons: (1) the adit allowed sampling of a c. 600 m long, horizontal, NE-SW-striking profile through the northern part of the deposit; (2) the samples provide a complementary data set to the vertical sampling profile (drill hole CS-1) through the Zinnwald pluton at the Czech side of the deposit studied by Breiter et al. (2017); and (3) there are no surface outcrops of the mineralization and albite granite. The samples include quartz of the Teplice rhyolite phase TR3 (youngest stage), Zinnwald albite granite and its stockscheider, massive quartz-zinnwaldite greisen, vein quartz, and a 3-cm large euhedral quartz crystal from a cavity within a flat vein (Flöz 11; Supplementary Material Table SM1).

All samples were prepared as polished thick (c. 300 μm) sections glued on standard glass slides 2.8×4.8 cm for LA-ICP-MS analysis and SEM-CL. The bulk compositions of rocks exposed in the Tiefer Bünaustolln (Teplice rhyolite, Zinnwald albite granite and massive greisen) were determined at ACME laboratories in Vancouver, Canada (ACME Labs, 2017).

3.2. Scanning electron microscope cathodoluminescence

The quartz grains were studied with SEM-CL to visualize intra-granular growth zoning and alteration structures and to choose areas for LA-ICP-MS analysis. SEM-CL imaging reveals micro-scale (1 μm to 1 mm wide) growth zoning, alteration structures and different quartz generations which cannot be distinguished by other methods. Grey-scale contrasts visualized by SEM-CL are caused by the heterogeneous distribution of lattice defects (e.g., oxygen and silicon vacancies, broken bonds) and lattice-bound trace elements (e.g., Götze et al., 2001). Although the physical background of the quartz CL is not fully understood, the structures revealed by CL give information about crystallisation, deformation and fluid-mediated overprint.

The used CL detector was a Centaurus BS backscattered electron type attached to a LEO 1450VP analytical SEM at the Geological Survey of Norway in Trondheim. The applied acceleration voltage and current at the sample surface were 20 kV and 2 nA, respectively. The SEM-CL images were collected from one scan of 43 s photo speed and a processing resolution of $1,024 \times$

768 pixels and 256 grey levels. The brightness and contrast of the collected CL images were improved with the PhotoShop software.

3.3. Laser ablation inductively coupled plasma mass spectrometry

Concentrations of Li, Be, B, Mn, Ge, Ga, Rb, Sr, Na, Al, P, K, Ca, Ti, Fe, Sb, Zn, and U were determined by LA-ICP-MS. The quartz samples were prepared as surface-polished, 300- μm -thick sections mounted on standard glass slides. The analyses were undertaken on a double-focusing sector field inductively coupled plasma mass spectrometer, HR-SF-ICP-MS, model ELEMENT XR from Thermo Scientific at the Geological Survey of Norway in Trondheim, Norway. The instrument is linked to a New Wave UP193FX ESI Excimer laser probe. The 193-nm laser had a repetition rate of 15 Hz, a spot size of 75 μm , and energy fluence about 5 to 6 J/cm^2 on the sample surface. A continuous raster ablation on an area of approximately $150 \times 300 \mu\text{m}$ was applied. The approximate depth of ablation was between 10 and 50 μm . A Hitachi CCD video camera, type KP-D20BU, attached to the laser system, was used to observe the laser ablation process and to avoid microscopic mineral and fluid inclusions. The carrier gas for transport of the ablated material to the ICP-MS was He mixed with Ar. The isotope ^{29}Si was used as the internal standard applying the stoichiometric concentration of Si in SiO_2 . External multistandard calibration was performed using the reference materials NIST SRM 610, 612, 614, and 1830. In addition, the applied reference materials include the BAM No. 1 amorphous SiO_2 glass from the Federal Institute for Material Research and Testing in Germany and the Qz-Tu synthetic pure quartz monocrystal provided by Andreas Kronz from the Geowissenschaftliches Zentrum Göttingen (GZG), Germany. Certified, recommended, and proposed values for these reference materials were taken from Jochum et al. (2011) and from the certificates of analysis where available. For the calculation of P concentrations, the procedure of Müller et al. (2008) was applied. Each measurement comprised 15 scans of each isotope, with the measurement time varying from 0.15 s/scan for K in medium mass resolution mode to 0.024 s/scan of, for example, Li in low mass resolution mode. An Ar blank was run before each reference material and sample measurement to determine the background signal. The background was subtracted from the instrumental response of the reference material/sample before normalization against the internal standard in order to avoid effects of instrumental drift. This was carried out to avoid memory

effects between samples. A weighted least squares regression model, including several measurements of the six reference materials, was used to define the calibration curve for each element. Ten sequential measurements on the BAM No.1 SiO₂ quartz glass were used to estimate the limits of detection (LOD) which were based on triple standard deviation (3σ) of the 10 measurements.

4. Results

4.1. Whole rock chemistry

Bulk analyses of rocks exposed in the adit Tiefer Bünaustolln (Teplice rhyolite, Zinnwald albite granite and massive greisen) are provided in Table 2. These rocks comprise the Teplice rhyolite phase TR3 (host rock of the Zinnwald granite pluton), albite granite and massive quartz-zinnwaldite greisen (strongly greisenized albite granite). In Figure 5 main and trace element data are plotted together with published data from Cocherie et al. (1991), Seltmann et al. (1998), and Breiter et al. (2012).

The mildly peraluminous, high-K calc-alkaline Teplice rhyolite phase TR3, being the host rock of the Zinnwald granite cupola and the Sn-W-Li mineralization, has the most primitive composition compared to the other rocks exposed in the Tiefer Bünaustolln with relatively high Ti, Mg, K and P and low Al, Mn, Li and F concentrations. In the context of the evolution of the Altenberg-Teplice caldera the Teplice rhyolite TR3, being the last effusive stage of the Teplice formation prior to the caldera collapse, represents chemically a moderately evolved rhyolitic sequence (Breiter, 1997; Breiter et al., 2001; Müller et al., 2005). The magmatic suite of the Zinnwald pluton including the greisens is enriched in F, Li, Cs, Rb, Th, K, Nb, Ta, Y, Yb, Sn, W, and depleted in Ti, Mg, Ba, Sr and Zr. Distinct similarities in the trace element and REE patterns (Figures 5C and D) imply a common source of the Teplice rhyolite and the Zinnwald granite melts as suggested already by Müller et al. (2005). The differentiation degree progresses almost consistently from the Teplice rhyolith, protolithionite granite, albite granite, albite microgranite towards the massive quartz-zinnwaldite greisen reflected by increasing Li, Mn, F, Rb, Nb, Ta, Sn, W and decreasing Ti, Sr, Zr, Ba, LREE. The Li₂O content of the greisen is higher (mean $0.63 \pm$

0.45 wt.%; $n = 3$) than that of the Zinnwald albite granites (0.29 ± 0.35 wt.%; $n = 12$; Cocherie et al., 1991; Seltnann et al., 1998; Breiter et al., 2012 and this study). The albite granite has higher average Ta (mean 43.7 ± 19.8 ppm; $n = 12$) and W (119.1 ± 378.7 ppm; $n = 12$) than the greisen (30.1 ± 12.9 ppm Ta; 21.8 ± 16.6 ppm W; $n = 3$). High average W of albite granite is caused by a concentration spike of sample CS-1 162.3 m (2511 ppm W) analyzed by Cocherie et al. (1991). The Zinnwald albite granite samples 2.6A, 2.7 and 4.8A were affected by greisenization as indicated by low Na_2O and high LOI (Table 2). Geochemically, the protolithionite granite and albite granite have a strong A-type signature with $10^4 \cdot \text{Ga}/\text{Al} > 5$ (by mass).

4.2. Microstructures of quartz visualized by SEM-CL

Teplce rhyolite (host rock)

The Teplce rhyolite (phase TR3) is the host rock of the Zinnwald granite cupola and contains magmatic quartz phenocrysts (1–5 mm) with complex concentric growth zoning previously described by Müller et al. (2005) and Breiter et al. (2012; Figure 6A). The boundaries of the growth zones are subrounded. In the investigated sample the growth zone boundaries are blurred compared to sharp boundaries observed by Müller et al. (2005) and Breiter et al. (2012). This is presumably caused by increased Ti diffusive migration (Ti defects are mainly responsible for the observed zoning in igneous quartz; e.g. Müller et al. 2000) due the contact metamorphism by the albite granite. The primary zoning is intensively overprinted by secondary, nearly non-luminescent (black in SEM-CL) quartz forming a dense network of healed microfractures.

Zinnwald albite granite

Quartz from the Zinnwald albite granite forms drop-like crystals up to 5 mm in size with amoeboid grain boundaries. The crystals exhibit weakly contrasted, oscillatory growth zoning which continues into the amoeboid crystal margin (Figure 6B). The boundaries of the oscillatory growth zones are straight, with sharp edges. The luminescence intensity is generally higher in the crystal cores and decreases towards the crystal margin. The outermost growth zones exhibit very weak CL and growth zoning can be hardly recognized. The crystals contain commonly concentrically arranged inclusions of euhedral albite (“snow-ball” texture; Beus, 1962; Müller and Seltnann, 1999).

Stockscheider (endocontact pegmatite)

The pegmatitic quartz of the stockscheider has fernlike, dendritic crystal shape. The crystals, which are up to 8 cm long, form comb-like textures perpendicular to the contact with the Teplice rhyolite (Figures 6C, D). The stockscheider quartz has dull CL and does not show primary growth zoning but exhibits a dense network of microfractures healed with nearly non-luminescent, secondary quartz.

Massive greisens within the Zinnwald albite granite

The dull-luminescent, massive greisen quartz shows oscillatory growth zoning of low contrast (Figures 7A and B) similar to those of the snowball-textured quartz but with lower CL intensity. The CL reveals that the massive greisen quartz consists of clusters of individual, more or less isomorphic, “drop-like” quartz grains 1 to 10 mm in size. The grains commonly display relics of former rock-forming minerals of feldspars or snow-ball textured quartz in the crystal cores, indicating that these relics served as nuclei for the greisen quartz. Secondary structures (healed microfractures) are common but much less abundant than in other quartz varieties.

Hydrothermal flat and steep veins

Quartz of the hydrothermal veins is megacrystic with crystals up to 30 cm in length. The dull luminescent vein quartz shows fine oscillatory growth zoning with low contrast (Figure 7C). In general the crystals grew perpendicular to the vein contacts. Occasionally, small (1-5 mm) isomorphic, “drop-like” crystals occur in the central part of the veins (Figure 7D). These crystals form clusters and nucleated at sericite and feldspar/kaolinite. Open cavities in the flat veins contain commonly euhedral, up to 20 cm long whitish to smoky crystals. The 5-cm long smoky crystal investigated in this study is free of oscillatory zoning but shows sector zoning (Figure 7E). Secondary structures, represented by microfractures healed with nearly non-luminescent or bright luminescent quartz, are less common as in the magmatic and massive greisen quartz.

4.2 Quartz chemistry

Chemical variability among rock types

The complete list of trace element concentrations (Li, Be, B, Mn, Ge, Rb, Sr, Al, Ti, and Fe) in quartz of the investigated samples is given in the Supplementary Material Table SM2. Average contents are listed in Table 3. Concentrations of Na, K, Ca, P, Ga, Sb, Zn, and U are generally below the limits of detection (7, 13, 16, 3, 0.05, 0.02, 1.5, and 0.01 ppm, respectively) and are, thus, not provided. In Figure 8 concentrations of Al, Ti, Li and Ge are plotted. These elements commonly occur in elevated concentrations in quartz and their variation reflect, in general sense, the P-T-X conditions of the melt and fluids from which the crystals growth.

Aluminium concentrations vary between 10 and 561 ppm. Its average content increases from TR3 (oldest rock; 158 ppm) to the stockscheider (456 ppm) but drops in the greisen quartz down to 189 ppm and further down to 95 and 91 ppm in the flat and steep veins (youngest rocks; Table 3). The Ti concentrations range from <0.5 to 15.1 ppm. The average values decrease more or less continuously from the Teplice rhyolite (14.5 ppm), Zinnwald albite granite (4.1 ppm), stockscheider (5.6 ppm), greisen (5.0 ppm) to the veins (3.2 and 2.1 ppm, respectively). The continuous decrease reflects decreasing crystallization temperatures and pressures during magmatic-hydrothermal evolution. It should be noted that Müller et al. (2005) and Breiter et al. (2012) detected up to 123 ppm, respectively, 105 ppm Ti in bright luminescent growth zones of the quartz phenocrysts in TR3. Compared to the average abundances in the quartz of flat veins, the Ti concentration of sample 1.11 (Flöz 7) is exceptionally high (11.4 ppm; n = 3). In order to confirm the concentration spike the locality was resampled (samples 1.11x, 1.11y). One sample was taken exactly at the same site (1.11x) and the other sample (1.11y) 50 cm away. Sample 1.11x has similar high Ti concentration of 11.4 ppm (n = 3), whereas sample 1.11y has a lower content of 8.0 ppm, which is nevertheless significantly higher than the other vein samples. .

In the Al versus Ti plot (Figure 8A) quartz of oldest magmatic rock (Teplice rhyolite) has highest Ti concentrations which decrease in the protolithionite granite and albite granite accompanied by increasing Al concentrations. The stockscheider quartz has highest Al concentrations representing the most evolved and youngest magmatic facies. This trend follows the established quartz composition trend of the Altenberg-Teplice caldera (Müller et al., 2005; Breiter et al., 2012, 2017). The greisens and veins plot mostly outside the magmatic trend towards lower Al and Ti. However there is an overlap which does not allow a clear distinction between magmatic and hydrothermal quartz (Figures 8A and B).

The Li content in quartz of the albite granite, greisens, and veins is generally low (<10 ppm) except some concentration spikes >20 ppm Li (albite granite sample 2.6A, vein samples 1.3, 3.1A-C, 3.4). Quartz phenocrysts in the Teplice rhyolite and stockscheider quartz have highest average Li of 25.4 ± 2.3 ppm and 22.9 ± 7.8 ppm, respectively, compared to the other rock types. In the Al versus Li plot the samples show weak positive linear correlations with different slopes for different rock types (Figure 8C). The correlations are due to substitution $\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^+$, where Al replaces Si in the tetrahedral site and Li^+ enters interstitial lattice position (e.g. Dennen, 1966). Data which plot along the 1:1 Al:Li molar ratio line indicate that almost all Al^{3+} defects are charge-compensated by Li^+ ; alternative charge compensator are H^+ , Na^+ , or K^+ . Magmatic quartz of the Teplice rhyolite and hydrothermal quartz of the veins plot closest to the 1:1 line. Germanium concentrations vary from 0.05 to 2.49 ppm, which corresponds to the range described from other magmatic systems (e.g. Jacamon and Larsen, 2009). Quartz of the albite granite, stockscheider and flat veins has highest average Ge (1.5-1.6 ppm; Table 3). In the Al versus Ge plot both elements show rock-specific correlations with different slopes of the regression lines (Figure 8D). The slopes increase from magmatic towards hydrothermal indicating that hydrothermal quartz increasingly incorporates more Ge in lieu of Al. In this way magmatic quartz might be distinguished from hydrothermal quartz in Ge-rich systems. Fe concentrations above the detection limit (>1.0 ppm) are observed only in TR3 (mean 4.6 ppm) and stockscheider (mean 7.5 ppm). Manganese concentrations are typically higher in igneous quartz than in hydrothermal quartz (Table 3). Beryllium concentrations are in the range of <0.03 to 1.78 ppm, being highest in the stockscheider quartz (0.81 ± 0.07 ppm). Boron concentrations are relative consistent (around 1 ppm), except the stockscheider quartz with 2.1 ppm. Average Rb concentrations vary between 0.03 to 6.60 ppm, being highest in the stockscheider quartz (6.60 ± 2.47 ppm). Strontium concentrations are generally <0.1 ppm except stockscheider quartz (mean 0.3 ppm) and quartz of the steep veins (mean 0.2 ppm). Considering the average contents, stockscheider quartz (very high in Be, B, Mn, Rb, Sr, Al, and Fe) displays major differences relative to the ensemble of the other samples (Table 3).

Spatial variation of quartz chemistry in flat veins was investigated along a 600-m long section through the northern part of the Zinnwald/Cínovec Sn-W-Li deposit at the 750 m adit level. It should be considered that the lateral sampling profile crosscut several different flat veins which dip 15 to 40° NE. There is no systematic change in the Al, Ti, Ge, and B concentrations in

quartz from the contact to the interior of the deposit (Standard deviations are higher than the variation of the average values; Figure 9).

The graphs in Figure 10 illustrate the variability of Al, Ti, Ge, and Li in three quartz samples taken from the top, centre, and bottom of a flat, 60-cm thick vein (Flöz 11). The variation of these elements within one quartz sample (3.1A-C) is in the same range as the variability of all three samples (“entire” vein) suggesting that there is no significant chemical gradient across the vein.

A 2-cm long, euhedral quartz crystal from a cavity in a flat vein (Flöz 11) was measured across the crystal to check the intra-granular variation of trace elements (Figure 7E). The crystal was chosen because it shows primary growth zoning revealed by SEM-CL. Li decreases from the core to the rim of the crystal, whereas Al increases slightly. All other trace elements do not show systematic variations between core and rim of the crystal.

Discussion

Causes of the chemical diversity of quartz in the Zinnwald/Cínovec Sn-W-Li deposit

Rusk (2012) showed that concentrations of Al and Ti vary systematically among epithermal deposits, orogenic Au deposits and porphyry-type deposit and can be used to fingerprint the type of ore deposit based on the trace element composition. Figure 11A shows the logarithmic Ti and Al plot with compiled data of c. 30 porphyry-type, orogenic Au, and epithermal deposits (colour-shaded fields) according to Rusk (2012) compared with data from the Zinnwald/Cínovec Sn-W-Li deposit. Data from Zinnwald/Cínovec overlap with orogenic Au and porphyry-type deposits. Porphyry-type and granite-related rare metal deposits are both transitional magmatic-hydrothermal systems (orogenic Au deposits not) and the composition of quartz in these systems appears to be similar. The Zinnwald/Cínovec quartz exhibits, however, significant differences with those in the porphyry-type, and we now discuss the possible reasons for these.”

First, the lower Ti in Zinnwald/Cínovec quartz, compared to the porphyry-type quartz, indicates lower crystallization temperature and/or pressure and/or lower Ti activity a_{TiO_2} of the melt or fluid (Wark and Watson, 2006; Huang and Audétat, 2012). Previous calculations

of the crystallisation temperature and pressure of the Zinnwald albite granite by Thomas, (1994) and Thomas et al. (2005) based on melt and fluid inclusion microthermometry revealed 627 to 664 °C and 1.1 kbar, respectively. Estimations of the quartz crystallization temperatures of the flat veins utilizing fluid inclusion microthermobarometry indicate formation temperatures of the main Sn-W mineralization between ~400 to 510°C (Ďurišová et al., 1979; Sushchevskaya et al., 1996; Graupner et al., 2005; Albrecht, 2017) and pressures of 0.4 to 1.1 kbar (Sushchevskaya et al., 1996; Webster et al., 2004; Albrecht, 2017). These estimates are based on fluid inclusion studies in both cassiterite and quartz (Ďurišová et al., 1979; Sushchevskaya et al., 1996; Webster et al., 2004; Graupner et al., 2005) and on the TitaniQ geothermobarometry (Albrecht, 2017). Because the formation of massive greisen postdates the granite crystallization and predates the vein formation, the crystallization temperatures of the massive greisen quartz were probably in the range of 510 to 627°C, considering the published temperature estimates given above.

Albrecht (2017) calculated $a\text{TiO}_2$ of 0.11 for the Zinnwald albite granite melt based on melt inclusion data provided by Thomas et al. (2005). However, $a\text{TiO}_2$ of the greisen- and vein-forming fluids is likely to be ≤ 0.11 because Ti preferentially partitions into the melt during fluid-melt separation (Lester et al., 2013). The calculated crystallization temperatures of quartz applying the TitaniQ thermobarometer by Huang and Audétat (2012) are $575 \pm 48^\circ\text{C}$ for the albite granite, $612 \pm 5^\circ\text{C}$ for the stockscheider, $610 \pm 23^\circ\text{C}$ for the massive greisen, $536 \pm 77^\circ\text{C}$ for the flat veins, and $516 \pm 58^\circ\text{C}$ for the steep veins. Temperatures of the greisen and veins are minimum crystallization temperatures due the uncertainty of the $a\text{TiO}_2$ in the hydrothermal fluid. Nevertheless, the temperatures determined with TitaniQ thermobarometer are in good agreement with temperatures calculated by microthermometry of fluid inclusions.

Compared to other deposit types and other hydrothermal mineralization (e.g., Landtwing and Pettke, 2005; Jourdan et al., 2009), the second main difference exhibited by the Zinnwald/Cinovec system is the generally low Al content in quartz and its little variation, in particular of the flat and steep veins (Figure 11A). The controls on Al concentrations in quartz are still under debate (e.g. Rusk, 2012). Breiter and Müller (2009) stated that there is no correlation between the Al in igneous quartz and the Al content and peraluminosity of the parental melt, which is supported by our data. Greisens have a higher alumina saturation index ($\text{ASI} = \text{molar Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) = 2.6\text{-}4.2$) than the albite granite ($\text{ASI} = 1.0\text{-}3.5$) but both rocks contain quartz with similar Al. Rusk et al. (2008) and Müller et al. (2010b) suggested

that the variations of Al concentration (5 ppm to ~5000 ppm) in hydrothermal quartz related to porphyry deposits may result from fluctuations of the fluid pH during the quartz crystallisation. In general, the high Al concentration in quartz may reflect the ratio of the total Al^{3+} and Si^{4+} activities in the hydrothermal fluid, which is strongly dependent on fluid temperature and pH (Pokrovskii and Helgeson, 1995; Salvi et al., 1998; Götze, 2016). The minimum of the total Al/Si ratio in hydrothermal solutions shifts to lower pH at higher temperatures up to ~200°C (Götze, 2016) suggesting that elevated pH favours Al^{3+} uptake of quartz in low-temperature ($\leq 200^\circ\text{C}$) environments (Perny et al., 1992; Götze, 2016). Anyway, we interpret the little variation and general low Al concentrations of the investigated quartz as crystallization of the Zinnwald/Cínovec deposit at more stable conditions and presumably relative stable pH compared to porphyry systems.

The decreasing Ti content and increasing Al content (i.e., the increase in the Al/Ti-ratio) in igneous quartz (Teplič rhyolite, protolithionite granite, albite granite, stockscheider) shown in Figure 8A is one of the hallmarks of progressive magma differentiation (Müller et al., 2002, 2010a; Breiter and Müller, 2009). Individual magmatic rock types of the Zinnwald/Cínovec Sn-W-Li deposit (Teplič rhyolite, albite granite, stockscheider) follow this Al-Ti trend, whereas the majority of the hydrothermal (magmatic-derived) quartz data (massive greisens, flat and steep veins) plot outside this trend towards lower Al and Ti. The dataset published by Breiter et al. (2017) shows a similar pattern. There is an overlap of data for massive greisen and veins with the albite granite data. The overlap is caused by the occurrence of both magmatic and hydrothermal quartz generations in the albite granite and massive greisens as revealed by the CL observations. The outermost growth zones of the snow-ball textured quartz in the albite granite corresponds in CL and trace element content to the greisen quartz. In the massive greisen relics of snow-ball textured quartz represent the remains of magmatic quartz.

In particular the data set of massive greisens and albite granite shows the strongest overlap (Figure 8B). The overlap is caused by the fact that the albite granite exposed in the Bünaustolln is slightly greisenized to different degrees and thus contains both magmatic quartz (snowball-textured quartz) and greisen quartz. On the other hand, massive greisen contains relics of magmatic quartz which were not completely replaced. Massive greisen is overprinted by albite granite which contains both remains of magmatic quartz overgrown and/or replaced by greisen quartz. Both quartz populations (snowball-textured quartz and greisen quartz) can be hardly distinguished in SEM-

CL due to similar CL properties. Similar observations have been made by Breiter et al. (2017). Puzzling are the exceptional high Ti concentrations (10 to 13 ppm) of vein quartz sample 1.11 (Flöz 7). This anomaly is very limited in dimension (about 0.5 m in lateral extension of the 35-cm thick vein. High crystal growth rate, which favors high uptake of trace elements at temperatures $>400^{\circ}\text{C}$ (e.g., Martin and Armington, 1983), can be excluded, because in that case other trace elements should exhibit similar anomalies. The stockscheider quartz being enriched in all measured trace elements (except Ti) is interpreted as an example of high trace element incorporation due to disequilibrium growth during high growth rate in a strongly undercooled melt at the albite granite contact. The high growth rate is documented by the dendritic crystal habit of the stockscheider quartz (Figure 6C, D). The high Ti in sample 1.11 is maybe an inherited signature of the magmatic precursors.

Lithium concentrations in quartz of the Zinnwald/Cínovec deposit are low compared to other Li-rich magmatic systems as for example, the Tres Arroyos granite–pegmatite system in Spain (Garate-Olave et al., 2017) or the Li pegmatites of Borborema, Brazil (Beurlen et al., 2011). Quartz of the Tres Arroyos granite suite contains 35 to 71 ppm Li and related pegmatites up to 134 ppm Li. The Borborema pegmatites contain quartz with up to 150 ppm Li. The low Li concentrations in quartz of albite granite, greisens, and veins is surprising because these rocks are enriched in Li_2O (Figure 5B) with zinnwaldite as the major carrier containing up to 4 wt.% Li_2O (Johan et al., 2012). Zinnwaldite might serve as a Li moderator. However, as shown for the Tres Arroyos and Borborema pegmatites Li micas do not act necessarily as buffers of the Li content in quartz (Beurlen et al., 2011; Garate-Olave et al., 2017). We interpret that the low Li content to be the result of the limited Al content in the quartz lattice. Lithium serves as charge compensator for substitutional Al^{3+} defects ($\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^{+}$), where Al replaces Si in the tetrahedral site and Li^{+} enter in interstitial lattice position (e.g., Dennen, 1966). Results of our and previous studies imply that the Li:Al atomic ratio in quartz does not exceed 1. Similar observations had been made by Jordan et al. (2009), Müller and Koch-Müller (2009), Breiter and Müller (2009), Beurlen et al. (2011) and Garate-Olave et al. (2017). Thus, the Li uptake by quartz is limited by the amount of Al^{3+} which substitutes Si^{4+} .

Germanium is compatible in quartz and substitutes for Si^{4+} . Because of the compatibility the amount of lattice-bound Ge is primarily controlled by the amount of available Ge in the melt or fluid. The Zinnwald/Cínovec system is strongly enriched in Ge (2.8-3.1 ppm in the albite

granite whole rock; Breiter et al., 2012) whereas the average concentration of Ge in the upper crust is 1.4 ppm (Rudnick and Gao, 2004). The enrichment is reflected in the quartz chemistry with high average Ge concentrations in quartz ranging from 0.9 ppm (steep veins) to 1.6 ppm (Stockscheider and greisens). The decreasing average Ge in hydrothermal quartz (greisen to steep veins) is according to Pokrovski and Schott (1998) explained by the decreasing Ge solubility in the hydrothermal fluid with decreasing temperature. One of the most significant outcomes of this study is the revealed increase of the Ge/Al ratio from magmatic to hydrothermal quartz (except stockscheider) despite that the Ge concentrations in quartz decrease with decreasing formation temperature (Table 3). In other words, Ge becomes more preferably incorporated as Al in quartz at hydrothermal conditions. Using the Ge/Al ratio magmatic and hydrothermal quartz of the Zinnwald/Cínovec Sn-W-Li deposit can be clearly distinguished from each other even if both hydrothermal and magmatic quartz populations occur in the massive greisens as well as in the albite granite) as discussed above (Figure 8D). The magmatic and hydrothermal quartz generations in both rocks are distinguishable by their Ge/Al weight ratio: magmatic quartz has a Ge/Al ratio of <0.008 whereas hydrothermal quartz a ratio of >0.008 .

Economic implications

The Zinnwald/Cínovec Sn-W-Li deposit is currently a target of Li exploration both on German and Czech territory. Given that the deposit may be mined in future for Li with Sn and W, quartz separates might be used as a by-product to minimize the waste volume and to increase the profitability. The vein quartz has lowest total trace element contents, which range from 20 to 250 ppm (mean 128 ± 56 ppm). These concentrations classify the hydrothermal quartz as chemical “intermediate quality” according to Harben (2002) and Müller et al. (2012). Other advantages of exploiting the vein quartz are the large crystal size (>1 cm), the low content of mineral inclusions within the crystals, and distinct whitish to bright greyish colouration allowing colour sorting. Disadvantage is low volume of the vein quartz, 1 to 3 % of the granite cupola which is restricted to the uppermost 100 meters of the deposit. The albite granite and greisen quartz has highly variable total trace element contents that range from 67 to 440 ppm (mean 233 ± 127 ppm). These attributes assign the quartz to transitional intermediate to medium quality according to Harben (2002). Due to the high content of mineral inclusions in albite granite and greisen quartz

(e.g. Figure 6B) it is expected that only medium quality quartz product will be achieved applying several processing steps (e.g. Larsen and Kleiv 2015, 2016).

Conclusions

The results of the study and the implications for the genesis and the economy of the Zinnwald/Cínovec Sn-W-Li deposit are summarized as follows:

- The magmatic and hydrothermal quartz populations related to the late Variscan Zinnwald/Cínovec Sn-W-Li greisen-type deposit are characterized by general low contents and low variation range of Al and Ti compared to porphyry-type deposits. The low variation indicates relative consistent crystallization conditions (temperature, pressure and fluid chemistry) during ore precipitation.
- Within the deposit magmatic and hydrothermal quartz populations are distinguished by their Al, Ti, Li and Ge concentrations and ratios. Magmatic quartz has higher Al and Ti concentrations compared to hydrothermal quartz. The Ge/Al ratio in quartz increases systematically from high to low temperatures of quartz crystallization (664 to ~400°C = temperature range including published data and our estimates) even though Ge decreases with decreasing formation temperature. Titanium decreases as well with decreasing temperatures. The albite granite and massive quartz-zinnwaldite greisen contain both magmatic and hydrothermal quartz populations which are distinguishable by the Ge/Al and Li/Al ratios. It should be tested if other mineralized systems show similar trace element trends.
- Fast crystal growth rates as indicated by dendritic crystal habits of the stockscheider quartz, which crystallized at the contact of the Zinnwald granite cupola, result in exceptional high trace element concentrations and, thus, disequilibrium growth.

- The chemistry of quartz in hydrothermal flat and steep veins related to the Sn-W mineralization does not show systematic variation along a 600 m long, lateral profile crosscutting the northern part of the deposit. Thus, crystallization conditions were supposedly relatively consistent during precipitation of quartz and associated ore minerals (wolframite, cassiterite).
- The maximum concentration of Li in the quartz lattice is limited by the amount of Al necessary for charge compensation despite that the parental melts or fluids were highly enriched in Li. The maximum of the atomic Al:Li in hydrothermal and magmatic quartz is 1.
- The calculated crystallization temperatures of quartz of the Sn-W mineralization applying the TitaniQ thermobarometer by Huang and Audétat (2012) are $536 \pm 77^{\circ}\text{C}$ for the flat veins and $516 \pm 58^{\circ}\text{C}$ for the steep veins, somewhat higher than published estimations of the formation temperatures (~ 400 to 510°C) based on fluid inclusion microthermobarometry.
- The study provides the first estimates of the formation temperature of the stockscheider quartz $612 \pm 5^{\circ}\text{C}$ and massive greisen $610 \pm 23^{\circ}\text{C}$. The latter represents the formation temperature of the main Li(-mica) mineralization.
- In economic terms, the hydrothermal vein quartz with an average total trace element content of 128 ± 56 ppm has intermediary chemical quality and can serve as a by-product if colour sorting and other processing steps are applied. Rock-forming quartz of the Zinnwald albite granite and massive greisen with an average total trace element content of 233 ± 127 ppm has medium quality and in addition contains many mineral inclusions which may complicate the processing.

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Tables

Table 1. Lithium, Sn and W resource estimations for the German and Czech part of the Zinnwald/Cínovec deposit.

Table 2. Whole rock analyses of rocks from the Tiefer Bünaustolln adit.
Greisen – massive quartz-zinnwaldite greisen, TR3 – Teplice rhyolite phase 3, ZiG – Zinnwald albite granite. Fe_2O_3 is given as the total of ferrous and ferric oxide value.

Table 3. Average compositions of quartz in various rock types determined by LA-ICP-MS.
LOD – limit of detection, n – number of analyses, STD – Standard deviation, ZiG – Zinnwald albite granite.

Supplementary Material

Table SM1. List and location of individual samples.

Coordinates are given as UTM Zone U33 and as Gauß-Krüger values. TR3 – Teplice rhyolite phase 3; ZiG – Zinnwald albite granite. The altitude is given in meters above sea level.

Table SM2. Trace element concentrations in quartz from different rock types exposed in the Tiefer Bünaustolln adit.

TR3 – Teplice rhyolite phase 3; ZiG – Zinnwald albite granite; LOD – Limit of detection.

Figure captions

Figure 1. Simplified geological map showing the igneous units of the eastern Erzgebirge volcano-plutonic complex with the Altenberg-Teplice caldera (framed by the Altenberg-Frauenstein microgranite) as the major magmatic structure. Modified from Hoth et al. (1995) and Mlčoch (1994). The black square in the Zinnwald-Georgenfeld-Cínovec area indicates the location of the map shown in Figure 2.

Figure 2. A - Geological map of the Zinnwald-Georgenfeld-Cínovec area. Modified from Baumann et al. (2000). X-Y marks the location of the cross section shown in (B). B – E-W cross section through the northern German part of the Zinnwald granite cupola.

Figure 3. Map of the Tiefer Bünaustolln with sampling sites. Sample 5.0 which was taken at the 767-m level is not indicated in the map. Coordinates are given as Gauß-Krüger values.

Figure 4. A – Massive quartz-zinnwaldite (qtz-zwd) greisen (dark violet) hosted by the Zinnwald albite granite (ZiG). B – Typical flat, 25-cm thick quartz-zinnwaldite vein (Flöz) hosted by massive quartz-zinnwaldite greisen. C – Flat vein (Flöz 12; sample 4.6) with visible wolframite (wf) and cassiterite (cst). The thickness of the flat vein in the center of the image is about 60 cm. D – Zinnwaldite-rich flat vein (yellow arrows) in massive hematitized quartz-zinnwaldite greisen. Zinnwaldite in the vein forms comb textures along the vein contacts. The vein contains several cavities where quartz crystal faces are coated with hematite (redbrown areas). Below the vein there is a leucocratic pegmatite vein (white arrows) pre-dating the formation of the hydrothermal vein. E – 20-cm wide quartz vein (Albert Morgengang) with massive wolframite mineralization (wf) along the vein contacts. With permission of the Museum of the Vereinigt Zwitterfeld zu Zinnwald visitor mine, Zinnwald-Georgenfeld. F – Stockscheider with megacrystic K-feldspar (kfs) and pegmatite quartz (pqz) crosscut by a 3-cm wide, flat quartz vein (fqz). The stockscheider is greisenized on both sides of the vein. Height of specimen 16 cm.

Figure 5. A - SiO₂ versus alumina saturation index plot of rocks exposed in the Tiefe Bünaustolln adit. Large symbols are data of this study and small symbols represent published

data from Cocherie et al. (1991), Seltmann et al. (1998), and Breiter et al. (2012). B - SiO₂ versus Li₂O plot. C – Upper continental crust(UCC)-normalized diagram of selected incompatible elements. UCC values are from Rudnick and Gao (2004). D – Chondrite-normalized rare earth element patterns applying the chondrite values of Anders and Grevesse (1989).

Figure 6. SEM-CL images of quartz. A – Quartz phenocryst in the Teplice rhyolite (sample 1.3B) with concentric growth zoning overprinted by a dense network of healed vein-like structures (black). B - Quartz phenoblast (snowball-textured quartz) in the Zinnwald albite granite with numerous inclusions of platy albite (pinkish shaded) (sample 2.6A). The phenoblast shows weakly contrasting growth zoning. C – Quartz of the stockscheider pegmatite with dendritic habitus surrounded by K-feldspar (Kfs) and zinnwaldite. The stockscheider quartz is of branched, dendritic structure devoid of growth zoning. D – Sketch highlighting the dendritic, almost spruce-like habit and growth direction of the stockscheider quartz shown in (C).

Figure 7. SEM-CL images of quartz. A – Quartz crystal aggregate in massive quartz-zinnwaldite greisen showing fine, weakly contrasted growth zoning (sample 2.4A). B – Quartz with oscillatory growth zoning in massive quartz-zinnwaldite greisen. The type of zoning resembles those of the phenoblasts in the Zinnwald albite granite and, therefore, this type of crystal cores represent overgrown, relic (greisenized) phenoblasts (sample 2.4A). C – Coarse-grained, hydrothermal vein quartz (Flöz 7) with oscillatory growth zoning (sample 1.11). D – Cluster of the small vein quartz crystals (Flöz 7) with sericite/albite/kaolinite (white) inclusions in the crystal cores and interstices (sample 1.11). E – Tip of a euhedral smoky quartz crystal from a cavity in a flat vein (Flöz 11) with displayed laser ablation spots and concentrations of Al, Ti, Li, and Ge. Sample 5.0.

Figure 8. Trace element chemistry of quartz. TR3 – Teplice rhyolite phase 3, BtG – Zinnwald protolithionite granite, ZiG – Zinnwald albite granite, apfu – atoms per formula unit.

Figure 9. Trace element variability of quartz of flat veins along a 600 m long profile through the northern part of the Zinnwald/Cínovec Sn-W-Li deposit at the 750-m level (Tiefer Bünaustolln). The dots represent average values of three LA-ICP-MS analyses.

Figure 10. Variability of trace element concentrations in hydrothermal quartz across one flat vein (Flöz 7). A – Photograph of the sampling site with sampling locations. B – Al versus Ti plot. C – Al versus Li plot. D – Al versus Ge plot. The grey shaded areas correspond to all analyses of quartz of flat veins.

Figure 11. A – Logarithmic Ti versus Al plot of quartz of the Zinnwald/Cínovec Sn-W-Li deposits compared with data from Rusk (2012) including c. 30 porphyry-type (Cu-Mo-Au) deposits, orogenic Au deposits, and epithermal deposits. For symbol explanation see Figure 8A. B – Logarithmic Al/Ti versus Ge/Ti plot. For explanations of symbols and shaded areas see Figure 8A.

 

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10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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Table 1. Lithium, Sn and W resource estimations for the German and Czech part of the Zinnwald/Cínovec deposit.

	Ore tonnage (Mt)	Li grade (ppm)	Sn grade (ppm)	W grade (ppm)	Reference
German part of the deposit	50 (measured+indicated+inferred resources)	3200	400	80	SolarWorld Solicium GmbH (2014)
Czech part of the deposit	220 (inferred resources)	2600	500	200	Wardell Armstrong International (2015)

Table 2. Representative whole rock analyses of rock exposed in the Tiefer Bünaustolln. The Zinnwald albite granite samples 2.6A, 2.7 and 4.8A were affected by greisenization as indicated by low Na₂O and high LOI.

Rock	TR3	ZiG	ZiG	ZiG	ZiG	Greisen	Greisen	Greisen
Sample	1.3B	2.6A	2.7	3.4A	4.8A	1.4A	2.4A	4.6A
Major elements (wt.%)								
SiO ₂	76.21	74.69	74.8	73.65	72.45	74.34	79.63	73.22
TiO ₂	0.16	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Al ₂ O ₃	12.19	13.77	15.1	14.81	15.98	15.42	11.07	15.56
Fe ₂ O ₃ ^{tot}	1.60	0.90	0.79	0.99	1.08	0.90	2.79	3.55
MnO	0.01	0.09	0.08	0.10	0.13	0.10	0.26	0.41
MgO	0.20	0.12	0.11	0.08	0.08	0.09	<0.01	<0.01
CaO	0.37	0.66	0.1	0.37	0.85	0.34	0.54	0.32
Li ₂ O	<0.02	0.19	0.26	0.22	0.39	0.15	0.71	1.03
Na ₂ O	0.75	1.33	0.09	3.15	1.60	0.05	0.04	0.04
K ₂ O	5.91	4.45	5.05	4.48	4.16	4.87	2.35	2.82
P ₂ O ₅	0.04	<0.01	0.01	<0.01	0.01	0.01	<0.01	0.01
F	0.16	0.69	0.30	0.45	>1.00	0.38	>1.00	>1.00
O=F	0.07	0.29	0.13	0.19	>0.42	0.16	>0.42	0.42
LOI	2.30	3.20	3.50	1.80	3.00	3.40	2.10	2.30
Sum	99.99	100.40	100.33	100.31	101.16	100.23	100.94	100.70
ASI	1.4676	1.6779	2.6043	1.3833	1.8406	2.5813	3.0817	4.2041
Trace elements (ppm)								
As	4.7	1.7	2.7	18.5	19.1	30.7	76.9	16.9
B	37	30	37	20	5	42	14	<3
Ba	351	296	318	101	173	211	42	172
Be	4	6	3	9	8	6	11	16
Bi	1.3	7.8	15.4	1.6	3.7	18.3	9	7.5
Co	1.8	0.8	1.2	0.8	<0.2	0.6	0.5	0.4
Cs	19.6	40.4	41	34.6	43.1	40.2	74.8	106.4

Cu	41.7	144.6	29.6	25.1	1.3	20.3	3.9	2.5
Ga	19.5	39.3	42.7	43.3	43.1	45.8	29.8	33.8
Hf	6.1	5.8	6.6	5.8	6.4	8.5	6.1	7.5
Mo	0.9	2.1	0.1	0.1	43.2	0.9	0.6	0.3
Nb	15.8	99.1	95.4	102.2	64.3	79.8	37.3	56.6
Pb	17.4	8.4	15.9	10.2	4.5	27.1	15.5	2.6
Rb	530	2214	2102	1992	2108	2020	2257	3163
Sc	3	8	8	6	6	7	13	20
Sn	42	145	135	156	360	186	133	4665
Sr	26.3	7.9	9.3	15.5	18.4	14.9	29.2	10.1
Ta	1.6	38.5	40.7	37.5	27.1	34.9	13.7	32.7
Th	43.6	14.8	20	17.7	18.6	21.9	40.2	27.9
U	9.2	8.7	11.1	11.4	5.9	10.4	4.2	7.1
W	36.9	16.3	19.2	16.7	12.5	28.5	77.4	18.7
Zn	32	57	44	64	70	49	131	276
Zr	175	40.2	41.9	37.4	43.1	51.2	45	44.4
Y	49.5	20.1	21.2	18.1	16.3	15.3	14.9	11.4
La	55.8	10.8	14.2	12.9	13.4	18.2	12.6	11.1
Ce	112	29.4	40.6	33	39.5	48.2	34.4	34.5
Pr	12.55	3.59	4.58	3.94	4.44	5.22	3.91	3.76
Nd	42.8	10.1	11.5	10.3	12	12.8	10.3	10
Sm	9.18	2.92	3.42	2.67	3.16	3.19	2.83	2.34
Eu	0.37	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Gd	8.62	2.59	2.84	2.23	2.33	2.32	1.89	1.6
Tb	1.44	0.75	0.78	0.62	0.67	0.64	0.54	0.48
Dy	8.82	5.44	5.82	4.52	4.88	4.59	4.05	3.47
Ho	1.81	1.13	1.21	1.02	1.03	1	0.86	0.72
Er	5.42	4.26	4.74	4	3.76	3.67	3.49	2.93
Tm	0.8	0.94	1.04	0.87	0.86	0.83	0.76	0.67

Yb	5.04	8.39	8.76	7.65	7.39	7.37	6.81	5.9
Lu	0.75	1.3	1.35	1.19	1.19	1.15	1.07	0.9

Greisen – massive quartz-zinnwaldite greisen, TR3 – Teplice rhyolite phase 3, ZiG – Zinnwald albite granite.

Table 3. Average trace element concentration in quartz determined by LA-ICP-MS.

LOD	n	Li		Be		B		Mn		Ge		Rb		Sr		Al		Ti		Fe	
		0.1 mean	STD	0.03 mean	STD	0.2 mean	STD	0.1 mean	STD	0.1 mean	STD	0.01 mean	STD	0.01 mean	STD	6.1 mean	STD	0.5 mean	STD	1.0 mean	STD
TR3	3	25.4	2.3	<0.03		1.5	0.5	0.5	0.2	0.9	0.1	0.16	0.03	0.07	0.01	157.8	44.0	14.5	0.6	4.6	0.2
ZiG	12	9.6	7.8	0.34	0.28	1.0	0.4	0.4	0.4	1.5	0.5	0.35	0.57	0.07	0.05	207.4	132.6	4.1	1.7	<1.0	
Stockscheider	3	22.9	7.8	0.81	0.07	2.1	0.6	1.0	0.6	1.6	0.2	6.60	2.47	0.32	0.43	456.5	96.2	5.6	0.3	7.5	4.2
Greisen Flöze (with sample 1.11)	9	7.4	4.6	0.30	0.12	1.1	0.5	0.3	0.1	1.6	0.3	0.49	0.44	0.07	0.03	189.1	111.1	5.0	2.2	<1.0	
Flöze (without sample 1.11)	54	9.8	11.0	0.27	0.25	1.3	0.6	0.2	0.2	1.1	0.7	0.27	0.36	0.08	0.09	95.2	47.2	3.2	3.5	<1.0	
Morgengänge	45	11.1	11.5	0.25	0.27	1.4	0.6	0.2	0.2	1.0	0.6	0.25	0.38	0.08	0.09	91.4	48.8	1.8	1.2	<1.0	
	12	5.3	2.3	0.17	0.10	0.9	0.2	0.1	0.1	1.4	0.4	0.16	0.09	0.15	0.31	78.6	30.7	2.1	1.6	<1.0	

LOD – limit of detection, n – number of analyses, STD – Standard deviation, ZiG – Zinnwald albite granite.

Supplementary Material Table SM1 to

Müller, A., Herklotz, G., Giegling H.:

Chemistry of quartz related to the Zinnwald/Cínovec Sn-W-Li greisen-type deposit, Eastern Erzgebirge, Germany

Table SM1. Sample list. Coordinates are given as Gauß-Krüger values. The altitude is given in meters above sea level.

Sample nr	Rock type	Thickness of Flöz/ Morgengang (cm)	Dip direction/dip angle of Flöz and Morgengang (°)	R (Gauß-Krüger)	H (Gauß-Krüger)	Altitude
1.1	minor Flöz above Flöz 1 (Flöz -2) in TR3	6 to 8	60/25	5413115	5623439	752
1.3	minor Flöz above Flöz 1 (Flöz -1) in TR3	10 to 15	38/30	5413069	5623371	752
1.3A	stockscheider (endocontact pegmatite hosted by ZiG	-	83/26	5413062	5623354	750
1.3B	TR3	-	-	5413072	5623368	751
1.4	minor Flöz above Flöz 1 (Flöz 0) hosted by ZiG	8 to 12	0/25	5413048	5623339	752
1.4A	Massive greisenized ZiG	-	-	5413043	5623330	752
1.6	Flöz 2 hosted by ZiG	20 to 30	108/16 (?)	5413057	5623283	752
1.11	Flöz 7 hosted by massive greisenized ZiG	20 to 40	horizontal	5413023	5623169	752
1.12	Daniel Morgengang hosted by massive greisenized ZiG	6 to 8	142/83	5413024	5623136	752
2.2	Flöz 8 hosted by ZiG	25	51/32	5413060	5623112	752
2.4	Greiszecher Morgengang hosted by ZiG	6 to 8	312/86	5413092	5623059	753
2.4A	Massive quartz-zinnwaldite greisen	-	-	5413092	5623058	752
2.5	Flöz 7 hosted by ZiG	20	64/40	5413097	5623027	753
2.6A	ZiG	-	-	5413120	5622975	753
2.7	ZiG	-	-	5413105	5622955	763
3.1A	Flöz 7 hosted by ZiG	60	50/39	5413090	5622925	770
3.1B	Flöz 7 hosted by ZiG	60	50/39	5413090	5622925	770
3.1C	Flöz 7 hosted by ZiG	60	50/39	5413090	5622925	770
3.4	Flöz 8 hosted by ZiG	50	359/20	5413029	5623017	758
3.4A	ZiG	-	-	5413029	5623014	758

Sample nr	Rock type	Thickness of Flöz/ Morgengang (cm)	Dip direction/dip angle of Flöz and Morgengang (°)	R (Gauß-Krüger)	H (Gauß-Krüger)	Altitude
3.7	Flöz 9 hosted by massive greisenized ZiG	30	50/24	5412993	5623065	754
4.1	Daniel Morgengang hosted by massive greisenized ZiG	10 to 15	128/83	5412964	5623079	753
4.2	Flöz 11 hosted by massive greisenized ZiG	15 to 20	18/19	5412942	5623046	753
4.6	Flöz 12 hosted by massive greisenized ZiG	50 to 150	-	5412897	5622926	750
4.6A	Massive quartz-zinnwaldite greisen	-	-	5412902	5622933	747
4.8	Neuschacht Morgengang hosted by greisenized ZiG	6 to 10	133/89	5412847	5622896	752
4.8A	ZiG	-	-	5412862	5622899	753
5.0	Quartz crystal from cavity in Flöz 11	-	-	5413078	5622951	767

Flöz – historical name for flat hydrothermal veins; Morgengang – historical name for vertical hydrothermal veins; TR3 – Teplice rhyolite phase 3; ZiG – Zinnwald albite granite.

Supplementary Material Table SM2 to

Müller, A., Herklotz, G., Giegling H.:

Chemistry of quartz related to the Zinnwald/Cínovec Sn-W-Li greisen-type deposit, Eastern Erzgebirge, Germany

Table SM2. Trace element concentrations in quartz from different rock types exposed in the adit Tiefer Bünaustolln transecting the northern part of the Late-Variscan Zinnwald/Cínovec Sn-W-Li greisen-type deposit in the Eastern Erzgebirge/Krušné Hory (German/Czech Republic).

Concentrations were determined by LA-ICP-MS and are given in ppm.

		Element	Li	Be	B	Mn	Ge	Rb	Sr	Al	Ti	Fe	Ga
		Measured isotope	Li ⁷	Be ⁹	B ¹¹	Mn ⁵⁵	Ge ⁷⁴	Rb ⁸⁵	Sr ⁸⁸	Al ²⁷	Ti ⁴⁷	Fe ⁵⁶	Ga ⁶⁹
		LOD	0.1	0.03	0.2	0.1	0.1	0.01	0.01	6.1	0.5	1.0	0.01
sample nr.	rock type	analysis nr.											
1.3B	TR3	1.3B-A	27.9	<0.03	2.0	0.6	0.9	0.18	0.07	134.6	14.4	4.8	0.13
		1.3B-B	24.9	0.07	1.0	0.3	1.0	0.12	0.08	130.3	14.0	4.8	<0.01
		1.3B-C	23.5	<0.03	1.5	0.7	0.8	0.18	0.06	208.5	15.1	4.3	<0.01
2.6A	ZiG	2.6A-A	10.8	0.27	1.4	0.2	1.9	0.40	0.05	147.8	6.6	<1.0	0.05
		2.6A-B	17.5	0.57	1.0	0.6	2.3	0.48	0.10	304.9	3.9	<1.0	0.10
		2.6A-C	27.2	1.02	2.0	1.4	1.7	2.09	0.05	387.2	3.1	1.4	0.07
2.7	ZiG	2.7-A	1.7	0.07	1.0	0.2	1.0	0.04	0.07	59.5	6.4	<1.0	<0.01
		2.7-B	6.4	0.22	0.7	0.2	0.7	0.13	0.06	130.0	1.9	<1.0	0.09
		2.7-C	3.7	0.20	0.7	0.2	0.7	0.13	0.22	107.5	0.8	<1.0	0.05
3.4A	ZiG	3.4A-A	4.6	0.28	0.9	0.3	1.9	0.17	0.06	309.8	4.8	1.1	0.10
		3.4A-B	6.9	0.16	1.3	0.2	1.1	0.05	0.05	116.8	4.8	<1.0	0.00
		3.4A-C	14.4	0.44	0.9	0.2	1.6	0.28	0.06	410.1	5.5	2.0	0.10
4.8A	ZiG	4.8A-A	2.0	0.13	0.8	0.1	2.2	0.04	0.05	82.8	3.8	<1.0	0.00
		4.8A-B	15.9	0.63	0.9	0.3	1.8	0.29	0.04	347.6	3.6	1.3	0.04
		4.8A-C	3.9	0.13	0.8	0.3	1.5	0.09	0.05	84.2	4.4	<1.0	0.07
1.3A	Stockscheider	1.3A-A	13.8	0.73	1.3	0.4	1.4	4.56	0.08	437.2	5.8	6.8	0.10

		1.3A-B	27.3	0.88	2.4	1.1	1.6	5.89	0.82	371.4	5.6	3.8	0.10
		1.3A-C	27.5	0.82	2.5	1.6	1.7	9.34	0.07	560.9	5.3	12.0	0.17
1.1	Flöz -2	1.1-A	1.8	0.25	1.5	0.4	0.0	0.79	0.06	45.5	2.0	<1.0	0.03
		1.1-B	4.7	0.35	2.9	0.2	0.1	2.13	0.04	33.0	2.4	<1.0	<0.01
		1.1-C	2.0	0.06	1.3	0.3	0.1	0.62	0.35	29.2	2.7	<1.0	0.02
1.3	Flöz -1	1.3-A	14.0	0.00	0.5	0.1	0.8	0.01	0.07	69.3	0.6	<1.0	<0.01
		1.3-B	33.1	0.05	0.7	0.1	0.9	<0.01	0.04	103.2	0.9	<1.0	<0.01
		1.3-C	3.3	0.07	1.1	0.1	0.1	0.02	0.04	35.8	4.0	<1.0	0.08
1.4	Flöz 0	1.4-A	1.7	0.22	2.2	0.2	0.1	0.43	0.07	45.1	2.5	1.7	0.08
		1.4-B	2.6	0.31	2.1	0.1	0.1	0.47	0.12	45.1	2.1	<1.0	<0.01
		1.4-C	3.2	1.78	3.7	0.7	0.1	0.95	0.31	141.1	5.9	<1.0	0.14
1.6	Flöz 2	1.6-A	3.6	0.17	2.2	0.2	0.6	0.19	0.12	63.6	1.5	<1.0	0.06
		1.6-B	3.4	0.07	1.4	0.0	0.3	0.03	0.06	76.6	5.2	<1.0	0.07
		1.6-C	2.1	0.27	0.9	0.3	1.5	0.06	0.05	58.9	1.5	<1.0	<0.01
1.11	Flöz 7	1.11-A	2.1	0.37	0.4	0.0	2.0	0.16	0.05	82.3	10.2	<1.0	<0.01
		1.11-B	2.5	0.36	1.2	0.2	2.2	0.20	0.08	112.6	13.1	<1.0	<0.01
		1.11-C	9.7	0.28	1.4	0.4	2.2	0.29	0.08	78.7	10.9	<1.0	0.07
1.11x	Flöz 7 (resampled)	1-11-C-A	2.0	0.26	0.5	0.4	1.8	0.52	0.04	116.3	11.6	<1.0	<0.01
		1-11-C-B	1.8	0.38	0.9	0.4	2.0	0.49	0.05	130.7	12.4	<1.0	0.16
		1-11-C-C	3.1	0.26	0.7	0.3	2.0	0.15	0.03	94.2	10.1	<1.0	<0.01
1.11y	Flöz 7 (resampled)	1-11-D-A	2.7	0.57	0.9	0.4	2.1	0.40	0.08	151.4	8.0	<1.0	<0.01
		1-11-D-B	3.3	0.26	1.3	0.9	2.5	0.84	0.22	179.4	9.4	1.0	<0.01
		1-11-D-C	0.3	0.23	1.3	0.3	1.9	0.51	0.02	80.7	6.6	<1.0	<0.01
2.5	Flöz 7	2.5-A	0.6	0.04	0.8	0.2	0.9	0.04	0.06	10.2	1.2	<1.0	<0.01
		2.5-B	1.4	<0.03	1.4	0.1	0.2	0.14	0.04	37.0	2.1	<1.0	0.03
		2.5-C	1.4	0.06	1.3	0.2	1.9	0.05	0.08	8.2	1.5	<1.0	0.03
3.1A	Flöz 7	3.1A-A	20.7	0.42	1.9	0.7	1.1	0.76	0.07	150.5	4.0	<1.0	0.13
		3.1A-B	27.9	0.54	1.6	0.4	1.7	0.51	0.06	187.7	0.8	<1.0	0.05
		3.1A-C	9.3	0.21	0.8	0.2	0.8	0.18	0.02	93.0	2.9	<1.0	0.05

3.1B	Flöz 7	3.1B-A	36.1	0.36	1.8	0.0	1.3	0.02	0.05	136.4	0.9	<1.0	0.08
		3.1B-B	34.9	0.16	2.0	0.0	1.7	0.01	0.05	165.9	1.6	<1.0	0.11
		3.1B-C	24.1	0.11	1.7	0.2	1.0	0.27	0.07	148.7	1.6	<1.0	0.06
3.1C	Flöz 7	3.1C-A	35.6	0.42	1.8	0.2	1.4	0.22	0.06	112.5	2.9	<1.0	0.06
		3.1C-B	0.7	0.14	0.7	0.2	0.8	0.05	0.04	41.5	2.7	<1.0	<0.01
		3.1C-C	1.6	0.24	1.0	0.2	0.9	0.11	0.04	88.1	2.7	<1.0	0.06
2.2	Flöz 8	2.2-A	9.3	0.41	1.9	0.1	1.7	0.11	0.09	119.3	0.8	<1.0	0.06
		2.2-B	0.4	0.13	1.3	0.1	1.7	0.03	0.05	107.6	<0.5	<1.0	0.06
		2.2-C	7.5	0.25	1.4	0.4	1.9	0.13	0.54	154.0	1.1	<1.0	0.09
3.4	Flöz 8	3.4-A	36.1	0.32	2.2	0.1	2.4	0.01	0.05	172.3	2.8	<1.0	0.12
		3.4-B	32.2	0.28	2.2	0.1	2.2	0.18	0.05	132.7	2.7	<1.0	0.05
		3.4-C	23.5	0.43	1.9	0.1	2.0	0.05	0.03	186.2	2.2	<1.0	0.08
3.7	Flöz 9	3.7-A	1.0	0.43	1.4	0.3	0.6	0.07	0.08	63.2	0.9	<1.0	0.07
		3.7-B	9.8	0.13	1.0	0.1	0.7	0.25	0.07	74.5	1.4	<1.0	0.08
		3.7-C	4.0	0.11	1.0	0.1	0.7	0.02	0.06	28.1	0.7	<1.0	<0.01
4.2	Flöz 11	4.2-A	4.2	0.19	1.0	0.1	0.8	0.04	0.06	55.9	1.0	<1.0	<0.01
		4.2-B	5.3	0.13	0.7	0.2	0.9	0.05	0.05	52.5	0.4	<1.0	<0.01
		4.2-C	4.7	0.13	0.7	0.1	1.1	0.04	0.07	30.9	1.2	<1.0	<0.01
5.0	Flöz 11 crystal	5-A	8.6	0.29	1.2	0.1	1.3	0.04	0.06	136.1	0.6	<1.0	0.13
		5-B	10.4	0.29	1.1	0.3	0.4	0.20	0.04	110.5	2.0	<1.0	0.06
		5-C	10.9	0.20	1.1	0.2	0.5	0.14	0.05	104.7	0.8	<1.0	0.10
		5-D	16.3	0.15	1.2	0.3	0.7	0.05	0.07	104.3	<0.5	<1.0	0.12
		5-E	16.8	0.07	1.1	0.3	0.6	0.03	0.07	101.4	1.8	<1.0	0.08
		5-F	12.6	0.12	1.1	0.2	0.6	0.26	0.05	102.9	1.5	<1.0	0.17
4.6	Flöz 12	4.6-A	5.8	0.22	0.8	0.3	1.0	0.33	0.09	90.9	1.6	<1.0	<0.01
		4.6-B	4.0	0.48	1.1	0.6	1.4	0.87	0.09	139.2	0.9	<1.0	0.10
		4.6-C	6.9	0.41	1.1	0.3	1.3	0.08	0.06	121.0	1.2	<1.0	0.05
1.12	Daniel Morgengang	1.12-A	5.3	0.00	0.6	<0.1	0.9	0.11	1.15	51.3	0.7	<1.0	<0.01

		1.12-B	1.7	0.13	0.9	<0.1	1.5	0.11	0.04	84.4	2.8	<1.0	<0.01
		1.12-C	9.2	0.30	1.3	0.1	1.9	0.22	0.07	137.3	1.5	<1.0	0.05
4.1	Daniel Morgengang	4.1-A	4.8	0.18	0.8	0.2	1.8	0.24	0.05	123.8	4.1	1.9	0.08
		4.1-B	7.4	0.25	1.1	0.2	1.5	0.18	0.04	70.8	4.4	<1.0	0.05
		4.1-C	5.4	0.27	1.0	0.1	1.5	0.36	0.07	95.8	4.4	<1.0	0.07
2.4	Felix Morgengang	2.4-A	6.6	0.07	1.0	0.2	1.0	0.17	0.06	68.3	0.8	<1.0	0.05
		2.4-B	7.2	0.26	1.1	0.2	1.0	0.20	0.05	74.2	0.9	<1.0	0.11
		2.4-C	2.5	0.15	0.8	0.1	1.0	0.03	0.05	30.2	0.7	<1.0	0.04
4.8	Neuschächter Morgengang	4.8-A	6.7	0.26	0.9	0.2	1.7	0.17	0.05	81.9	2.6	<1.0	<0.01
		4.8-B	5.3	0.02	0.6	0.3	1.5	0.07	0.12	81.2	1.7	<1.0	0.06
		4.8-C	2.0	0.10	0.5	0.2	1.0	0.08	0.05	43.4	<0.5	<1.0	0.08
2.4A	massive greisen	2.4A-A	8.2	0.46	1.0	0.4	1.7	0.33	0.03	310.0	6.3	2.3	0.06
		2.4A-B	1.6	0.29	1.0	0.2	1.8	0.15	0.06	188.9	4.5	<1.0	0.09
		2.4A-C	4.3	0.49	1.0	0.4	1.6	0.24	0.04	310.1	5.6	1.4	0.05
1.4A	massive greisen	1.4A-A	14.3	0.31	1.8	0.4	1.8	0.83	0.06	95.6	6.9	1.2	0.12
		1.4A-B	8.4	0.32	1.5	0.3	2.1	0.29	0.08	330.4	6.3	2.2	0.04
		1.4A-C	7.8	0.20	1.6	0.4	1.6	0.31	0.14	90.7	6.0	<1.0	<0.01
4.6A	massive greisen	4.6A-A	1.3	0.10	0.5	0.1	1.3	0.06	0.06	45.3	<0.5	<1.0	<0.01
		4.6A-B	7.6	0.30	0.9	0.5	1.2	1.44	0.10	233.2	3.3	1.3	0.10
		4.6A-C	13.3	0.28	0.6	0.3	1.6	0.76	0.06	97.4	5.9	<1.0	0.04

Flöz – historical name for flat hydrothermal veins; Morgengang – historical name for vertical hydrothermal veins; TR3 – Teplice rhyolite phase 3; ZiG – Zinnwald albite granite; LOD – Limit of detection.