# Reactive fluid flow and integrated fluxes recorded by tin-bearing greisens, Krušné hory (Erzgebirge) Mts., central Europe

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Abstract. We use transport theory to evaluate integrated fluid fluxes responsible for the formation of tin-bearing greisens in the Western Krušné hory (Erzgebirge) granite pluton in central Europe. The pluton consists of multiple intrusive units of low- to high-Li-F-P biotite, two-mica, and topaz-zinnwaldite granites. Greisens form subvertical dyke swarms that have formed by constant-volume replacement (mica-quartz greisens, topaz-quartz greisens, monomineralic quartz greisens), followed by hydrofracturing (quartz veins). We use alteration reaction progress to assess the magnitude of chemical disequilibrium for infiltrating aqueous fluid and the timeintegrated fluid flux necessary to reproduce the observed modal variations. The integrated fluid fluxes are  $10^{2-3}$  m<sup>3</sup> fluid per m<sup>2</sup> rock. Assuming the flow rate of  $10^{-10}$  m s<sup>-1</sup>, formation of a typical greisen vein requires  $10^{5-7}$  m<sup>3</sup> fluid phase. For 5 wt.% H<sub>2</sub>O dissolved H<sub>2</sub>O in granitic melt, the fluid would have exsolved from 3.10<sup>5</sup>-2.10<sup>8</sup> m<sup>3</sup> magma, that is, a reservoir with size of 80-700 m in each direction, which is comparable to the host intrusion.

**Keywords.** greisen, alteration, hydrothermal flow, fluid flux

### 1 Introduction

Advances in our understanding of thermodynamics of fluid-mineral interactions at elevated temperatures and pressures now permit calculation of time-integrated fluid fluxes and total fluid volumes to be estimated from petrological record in alteration or mineralization zones. By estimating mineral reaction progress from modal variations in zonal alteration sequence, we can balance respective fluid-mineral reactions and convert their progress into integrated fluid fluxes if the driving pressure and temperature gradients are known or can be reasonably well estimated. We illustrate application of this method to interpretation of mica-quartz and topazquartz greisen veins with cassiterite mineralization hosted by granites of the Krušné hory (Erzgebirge) batholith emplaced in the Saxothuringian zone of the Variscan orogen (360-310 Ma) in central Europe.

## 2 Geological setting

The Western Krušné hory (Erzgebirge) pluton is a discontinuous exposure, 70 by 30 km large, of biotite, two-mica and topaz-zinnwaldite granites (324-312 Ma). Traditionally, this suite of low- to high-Li-F-P granites is subdivided into an older, less evolved, intrusive complex (OIC) and a younger, highly evolved, intrusive complex (YIC) that is accompanied by extensive tin  $\pm$  tungsten mineralization of the greisen type (Breiter et al. 1999).

Our study was conducted in the Horní Blatná

composite body, which forms a continuous outcrop 7 by 6 km large, accompanied by two stocks of extremely evolved, perphosphorous topaz-zinnwaldite granites (Fig. 1). The intrusive sequence consists of multiple intrusive units, which differ in their whole-rock and modal composition as well as in textural appearance. This granitic body is interpreted to represent an apical, moderately to highly evolved residual granitic melts emplaced beneath the roof of the batholith.



**Figure 1.** Geological map of the Horní Blatná composite body in the Western Krušné hory pluton.

The intrusive rocks correspond to the biotite or twomica granites, locally with tourmaline, the topaz-lithian annite granites with tourmaline, and the topazzinnwaldite granites. The less evolved varieties are characterized by porphyritic texture with a fine-grained groundmass, the moderately evolved types are mediumto coarse-grained with microgranite bodies, and the extremely evolved granites are generally fine-grained and devoid of phenocrysts, although K-feldspar megacrysts forming solidification fronts (stockscheider) are locally present. All granites are chemically evolved (75-77 wt. % SiO<sub>2</sub>; 12.5-15.0 wt. % Al<sub>2</sub>O<sub>3</sub>), moderately to strongly peraluminous (alumina saturation index, ASI = 1.1-1.2), with high concentrations of phosphorous (0.18-0.97 wt. % P<sub>2</sub>O<sub>5</sub>), lithium (0.05-0.28 wt. % Li<sub>2</sub>O), and fluorine (0.20-1.45 wt. % F). Strong depletion in mafic constituents (2.7-0.8 wt. % MgO + FeO<sub>tot</sub>; mg# =0.49-0.04; 0.22-0.40 wt. % TiO<sub>2</sub>) provides further evidence for protracted magmatic fractionation. The major- and trace-element concentrations characterize the granites as continental collisional magmas derived from predominantly sedimentary precursors (Förster et al. 1999).

#### 3 Hydrothermal alteration

Granites of the Horní Blatná composite body show increasing evidence for postmagmatic hydrothermal alteration: (i) pervasive tourmalinization and formation of tourmaline ± quartz-rich cavities in granites, (ii) focused tourmalinization in the surrounding phyllites leading to the formation of massive tourmalinites and tourmaline fracture fillings, with rare cassiterite mineralization, and (iii) widespread incipient greisenization, which becomes increasingly focused into vertical permeable zones leading to the formation of spatially zoned mica-quartz, topaz-quartz and monomineralic quartz greisens, with abundant cassiterite mineralization (Fig. 2). Greisens form subvertical veins and swarms up to 1.5 m thick, 400 m long, and 800 m deep that cross cut all compositional and textural granite types (Stemprok and Dolejš 2010).



**Figure 2.** Greisen veins penetrating fine- to medium-grained granites. The continuity of primary magmatic textures as well as the distribution and preservation of quartz phenocrysts indicates that greisens have formed by granite replacement under constant volume.

#### 4 Mineral chemistry

Chemical composition was analyzed using the TESCAN Vega scanning electron microscope with the EDS detector X-Max 50 (Institute of Petrology and Structural geology, Charles University in Prague). Measurements were carried out with an accelerating voltage of 15 kV,

beam current of 1.5 nA and the acquisition time of 100 s.

The granites are typical subsolvus granites with coexisting Na-rich plagioclase and K-feldspar. Their major element composition was recalculated to formula units on 8 oxygen equivalent basis. The K-feldspars are homogeneous or variably exsolved and exhibit perthite lamellae or albite rims and overgrowths. K-feldspar phenocrysts and matrix grains are frequently very pure ( $Or_{98}Ab_{02}$ ) but some extend to Na-rich varieties ( $Or_{69}Ab_{30}An_{01}$ ) until the alkali feldspar solvus has been reached. Plagioclase composition forms a linear trend originating at  $Or_{03}Ab_{87}An_{10}$  and evolving towards pure albite ( $Or_{01}Ab_{99}$ ). Rare plagioclase xenocrysts from incompletely assimilated metasediments contain up to 35 mol. % anorthite (Fig. 3).



**Figure 3.** Chemical composition of feldspars in granites and greisens (present as relics). Abbreviations: Ab – albite, Or – orthoclase, An – anorthite. The solid curves are solvus isotherms at T = 300, 400, 500 and 600 °C, respectively, and P = 1 kbar.

Granites and greisens contain two micas (lithian annite and muscovite) or a single dark mica (zinnwaldite). Lithium in micas was calculated using the correlation relationships by Tischendorf et al. (2004):  $Li_2O = 0.289 \text{ Si}O_2 - 9.658 \text{ and } Li_2O = 0.3935 \text{ F}^{1.326}$  (in wt. %) for dark and white micas, respectively. The weight percentage concentrations were recalculated to formula units using 11 oxygen equivalents while assuming all iron to be present in the Fe<sup>2+</sup> state. The composition of both micas varies strongly and correlates with the degree of magma geochemical evolution (Fig. 4). The dark micas are lithian annites through zinnwaldites and trilithionites, with mg# = 0.46-0.03, 3.69-0.13 wt. % TiO<sub>2</sub> and 0.5-7.8 wt. % F. Correspondingly, the lithium concentrations reach up to 4.70 wt. % Li<sub>2</sub>O. The white micas are lithian muscovites (up to 0.48 wt. % F, 4.87 wt. % Li<sub>2</sub>O and 0.40 wt. % Na<sub>2</sub>O), which evolved during greisenization to low-Li-F muscovites with declining proportions of the zinnwaldite and aluminoceladonite end-members.

Tourmalines in granites, greisens and tourmalinites hosted in phyllites are optically zoned, ranging from brown or greenish brown to blue varieties. The blue varieties appear to represent late hydrothermal growth zones or replacements. The tourmaline formula units were recalculated using the sum of tetrahedral and octahedral cations in the T, Z and Y sites to be 15 while allowing for octahedral vacancies associated with every three Ti atoms. All tourmalines are assumed to be Li-free and contain only ferrous iron. Tourmalines in granites are close to schorl end-member (Fig. 5), but those from tourmalinites show greater variability (2.26-2.70 wt. % Na<sub>2</sub>O; up to 0.70 wt. % CaO; mg# = 0.02-0.41). The deficiency in sodium is reflected in the partially vacant X site (up to 0.5 vpfu). The compositional trend of tourmalines corresponds to evolution from pure schorl to a mixture of foitite and oxy-dravite, corresponding to local derivation of Mg, Fe and Al from phyllites.



**Figure 4.** Chemical composition of micas in granites and greisens. Abbreviations: acel – aluminoceladonite, ann – annite, eas – eastonite, ms – muscovite, sid – siderophyllite, pli – polylithionite, tri – trilithionite, zwd – zinnwaldite.

#### 5 Alteration reactions and fluid transport

Greisen formation involves: (i) hydrolysis characterized by breakdown of plagioclase and K-feldspar, and formation of white mica with quartz, (ii) replacement of white mica by topaz and additional quartz, and (iii) silicification leading to the formation of monomineralic quartz greisens. At this stage, transition from volumeconserved replacement to open-space (fracture) filling occurs. Individual stages of greisen formation are summarized by the following reactions:

3 ab + 2.17 kf + 3.45 HCl = 1.72 mu + 10.34 qz + 3 NaCl + 0.45 KCl

$$2 \text{ mu} + 2 \text{ HCl} = 3 \text{ tp} + 3 \text{ qz} + 2 \text{ KCl}$$

$$SiO_2(aq) = SiO_2(qz)$$

We propose a reactive-transport model to simulate the progress of alteration reactions and to estimate the fluid fluxes necessary for the formation of the spatial zoning. In this model we evaluate the disequilibrium fluid infiltration and the pressure-temperature gradient simultaneously. Using a series of initial conditions, from 650 °C and 1 kbar (magmatic fluid phase exsolving at the solidus) to 400 °C and 500 bar (conditions of greisen formation), the formation of muscovite-quartz greisens requires a time-integrated flux of ~10<sup>2</sup> to 10<sup>5</sup> m<sup>3</sup> fluid per m<sup>2</sup> rock, whereas the formation of topaz-quartz greisens is predicted to occur at ~10<sup>2</sup> to ~10<sup>6</sup> m<sup>3</sup> fluid per m<sup>2</sup> rock (Fig. 6).



**Figure 5.** Chemical composition of tourmalines in granites, greisens and tourmalinites. Abbreviations: schl – schorl, drav – dravite, foi – foitite. The prefix "oxy" indicates oxy-varieties of respective end-members.

The fluxes can be further specified by constraining permissible modal variations and volume changes. For the volume-conserved replacement to occur, the integrated fluid flux could not have exceeded  $\sim 10^3$  m<sup>3</sup> fluid per m<sup>2</sup> rock. In addition, the incoming fluids must have been in disequilibrium with the host rocks (originating at T = 480 °C or higher) in order to produce

the topaz-bearing alteration assemblages. For a conservative estimate of the time-integrated fluid flux on the order of  $10^2$  to  $10^3$  m<sup>3</sup> fluid per m<sup>2</sup> rock, the plausible flux rate is ~  $10^{-10}$  to  $10^{-8}$  m s<sup>-1</sup>. Thus the formation of a single greisen vein with a typical volume of  $10^3$  to  $5 \cdot 10^4$  m<sup>3</sup> would require  $10^5$ - $3 \cdot 10^7$  m<sup>3</sup> aqueous fluid. By using mass balance and an assumed 5 wt. % H<sub>2</sub>O dissolved in a granitic magma, such amount of fluid phase would have exsolved from  $5 \cdot 10^5$  to  $3 \cdot 10^8$  m<sup>3</sup> magma, or an intrusion measuring approx. 80 to 700 m in each dimension (Fig. 7). These estimates are comparable with dimensions of intrusive units of the Horní Blatná composite intrusion.



**Figure 6.** Integrated fluid flux vs. initial fluid temperature, responsible for the chemical disequilibrium at the inflow into the greisen formation site. The larger is the magnitude of initial disequilbrium, the lower fluid flux is necessary to reproduce the mineral assemblages of mica-quartz and topaz-quartz greisens.



**Figure 7.** Relationship between the vein volume and the required magma volume necessary to produce the interpreted fluid fluxes (assuming 5 wt. %  $H_2O$  dissolved in a granitic magma).

### 6 Conclusions

The Western Krušné hory (Erzgebirge) batholith comprises a sequence of low- to high-Li-F-P biotite, two-mica and topaz-zinnwaldite granites that host tintungsten mineralization of greisen type. Greisens form vertical vein swarms, which formed by hydrolytic replacement of the host granites but late-stage hydrofracturing lead to the formation of monomineralic quartz greisens. We propose a reactive-transport model, based on local equilibrium, embodied in the transport theory, to estimate time-integrated fluid flux necessary for the formation of observed spatial alteration zoning. By considering chemical disequilibrium of infiltrating fluid we estimate the time-integrated fluid fluxes approx.  $10^2$ - $10^3$  m<sup>3</sup> m<sup>-2</sup> in order to maintain constant-volume replacement with no net mass addition. This estimate is two to three orders of magnitude smaller than fluid fluxes published for focused fluid flow in brittle fractures or ductile shear zones. Furthermore, the calculated fluid fluxes are several orders of magnitude smaller than in local equilibrium models. However, the results indicate that no involvement of external (e.g., meteoric) fluids is necessary.

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