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Comparison of the Beauvoir and Cínovec rare metal granite/greisen systems: Role of muscovitization on Li-Sn-W-Ta hydrothermal remobilization

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Abstract. We provide a comparative review of greisenization in the Beauvoir (France) and Cínovec (Czech Republic/Germany) deposits, which are two of the world's best studied examples of peraluminous Li-Sn-Ta-W-mineralized granitic systems. While the Cínovec granite cupola is two-to-eight times less enriched in rare metals than Beauvoir, a Li-Sn-W greisen deposit was formed in the former but not in the latter. At Beauvoir, alteration of igneous lepidolite produced Sn-rich and Li-W-Ta-depleted greisen muscovite. In contrast, igneous and greisen zinnwaldite at Cínovec have similar contents of Li, Sn, W and Ta. Late replacement of zinnwaldite by muscovite in the Cínovec greisen is marked by enrichment in Sn and depletion in Li, W and Ta, similar to greisen muscovite from Beauvoir. We conclude that muscovitization, although associated with secondary Sn enrichment, is not essential for the formation of mineralized greisens, which are primarily controlled by the emplacement depth of magmas and the intensity of pervasive alteration.

1 Introduction

Rare metal granites (RMG) represent the most fractionated members of granitic suites and are characterized by significant enrichment in rare lithophile elements such as Li, Be, Sn, W, Cs, Ta and Nb (Černý et al. 2005; Linnen and Cuney 2005). While the magmatic evolution and the magmatic-hydrothermal transition of RMG systems have been extensively studied (Linnen and Cuney 2005; Ballouard et al. 2016; Breiter et al. 2017; Harlaux et al. 2017; Kaeter et al. 2018; Michaud and Pichavant 2020), the factors controlling metal remobilization and the formation of mineralized alteration zones around granitic plutons are much less understood.

Among metasomatic processes that affect granitic cupolas, greisenization is commonly associated with Sn-W and RMG deposits (Černý et al. 2005). This feldspar-destructive alteration results from high-temperature interactions between granitic rocks and acidic fluids, locally forming Li-Sn-W deposits (Černý et al. 2005; Breiter et al. 2017). Although greisenization has been investigated from mineralogical, geochemical, experimental and modelling standpoints (Halter et al. 1996, 1998; Breiter et al. 2017; Launay et al. 2019, 2023), it is still unclear why some RMG systems develop mineralized greisen deposits while other do not.

In this paper, we provide a comparative review of greisenization at Beauvoir (France) and Cínovec (Czech Republic/Germany), which are two well-studied examples of RMG in Europe (Gourcerol et al. 2019). The greisens in these two localities show major differences in terms of volume of altered rocks and metal enrichment. Comparing the Beauvoir and

Cínovec deposits can provide, therefore, useful insights to better understand what controls the development of mineralized RMG-greisen systems.

2 Geological background

2.1 The Beauvoir RMG

The Beauvoir granite is located within the Echassières granitic complex in the NE part of the French Massif Central which belongs to the Moldanubian zone of the European Variscan belt. The Beauvoir granite was emplaced at ca. 315-310 Ma and is characterized by a strongly peraluminous S-type composition with a disseminated Sn-Li-Ta-Nb-Be mineralization (Cuney et al. 1992; Raimbault et al. 1995). The 900-m-long GPF-1 borehole drilled through the Beauvoir granite revealed a vertical zoning with three granitic units, which are from the upper to the lower (Cuney et al. 1992; Raimbault et al. 1995): (i) B1 unit (-100 to -450 m) corresponding to an albite-lepidolite-rich leucogranite containing globular quartz and rare anhedral perthitic K-feldspar; (ii) B2 unit (-450 to -750 m) consisting of a lepidolite-rich granular granite with idiomorphic quartz and low amounts of K-feldspar; and (iii) B3 unit (-750 to -880 m), which contains euhedral pink-colored K-feldspar and zinnwaldite. The abundance of accessory minerals (topaz, cassiterite, columbite-tantalite, microlite, and Li-Be phosphates) increases upward from the B3 to the B1 units, the latter being the most evolved (Cuney et al. 1992; Raimbault et al. 1995). The uppermost B1 unit exhibits greisen alteration consisting of a quartz-muscovite-topaz assemblage developed along fractures without significant mineralization (Monnier et al. 2020).

2.2 The Cínovec RMG

The Cínovec granite is located within the Krušné hory/Erzgebirge in the NW part of the Bohemian Massif which belongs to the Saxo-Thuringian zone of the European Variscan belt. The granite was emplaced at ca. 325-322 Ma into rhyolites of the Altenberg-Teplice caldera within a large volcanic-plutonic complex and is characterized by a moderately peraluminous A-type composition with enrichment in Li, Rb, Cs, Ta, Sn, W (Štemprok 2016; Breiter et al. 2017). Vertical zonation at Cínovec was documented by the 1600-m-long CS-1 borehole and consists of four major units, which are from top to bottom (Štemprok 2016; Breiter et al. 2017): (i) granite canopy (CnG; down to -260 m) composed of

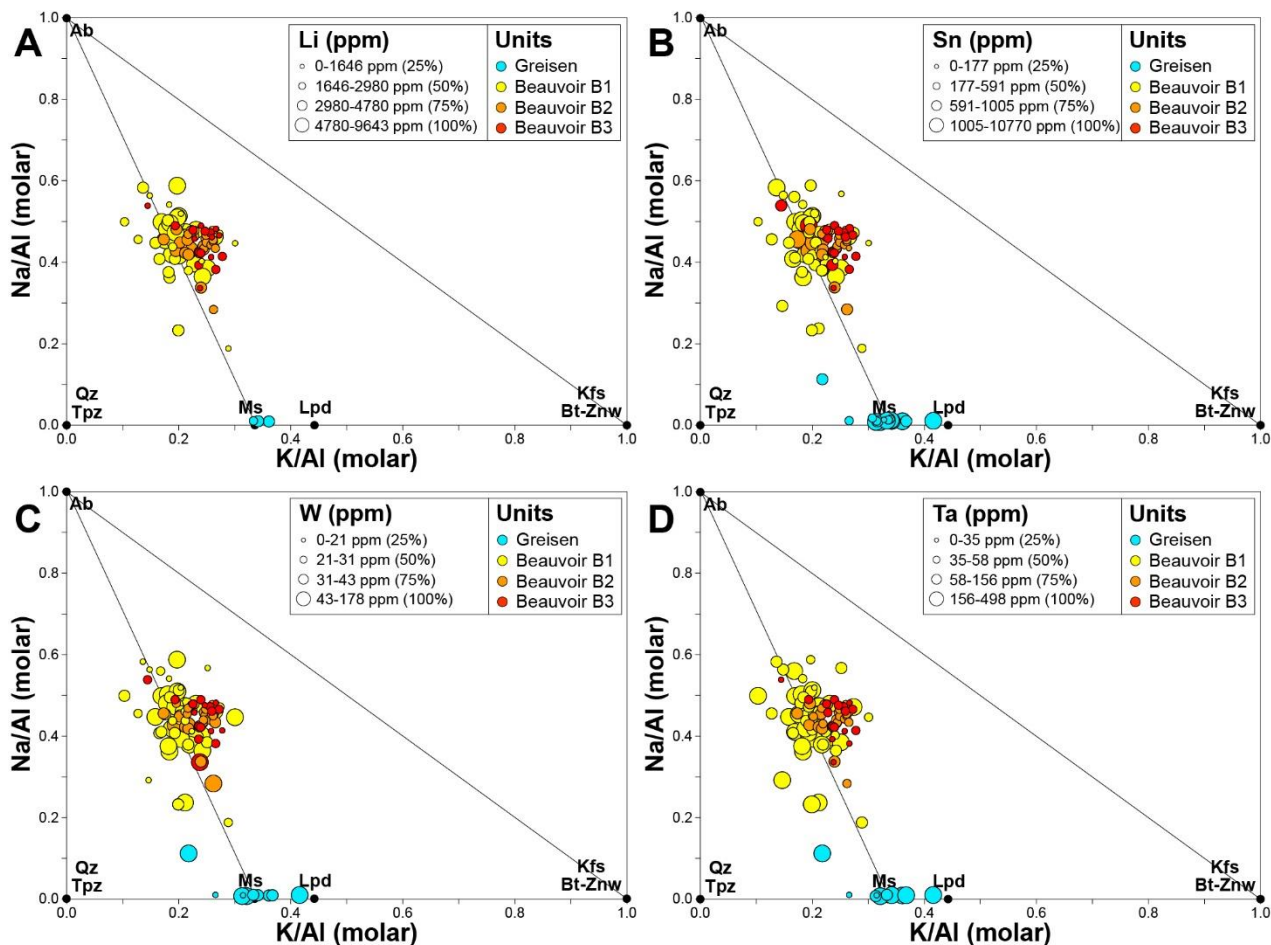


Figure 1. Bubbleplot diagrams of K/Al vs. Na/Al molar ratios for rock samples from Beauvoir illustrating the contents of Li, Sn, W, and Ta in granites and greisens. The bubble diameters correspond to quartile distribution (25%, 50%, 75%, 100%) of element concentrations. The node locations of common silicate minerals identified in these rocks are also plotted (Ab = albite, Bt = biotite, Kfs = K-feldspar, Lpd = lepidolite, Ms = muscovite, Qz = quartz, Tpz = topaz, Znw = zinnwaldite).

an equigranular fine-grained albite-zinnwaldite granite with subhedral albite, globular quartz, and rare K-feldspar; (ii) medium-grained porphyritic mica-free granite (MfG; -260 to -370 m), which contains subhedral quartz and anhedral K-feldspar and albite; (iii) fine- to medium-grained porphyritic albite-zinnwaldite granite (ZiG(m); -370 to -735 m) which shows evidence of commingling; and (iv) a lower suite of biotite granites (BtG; -735 to -1596 m) comprising fine-to-medium-grained porphyritic to coarse-grained equigranular facies with perthitic K-feldspar and subhedral plagioclase. Quartz-zinnwaldite greisens occur in the granite canopy, locally forming massive alteration zones. Disseminated mineralization in the greisen consists of irregularly distributed cassiterite, fluorite, topaz, columbite-tantalite, scheelite, wolframite and REE-F-carbonates (Breiter et al. 2017, 2019).

3 Results

3.1 Whole-rock compositions

Based on a compilation of whole-rock geochemical data from the Beauvoir and Cínovec RMG-greisen systems (Cuney et al. 1992; Raimbault et al. 1995; Dolejš and Štemprok 2001; Monecke et al. 2007;

Štemprok 2016; Breiter et al. 2017; Müller et al. 2018), we compared the enrichment in Li, Sn, W and Ta related to greisenization. Data were plotted in the K/Al vs. Na/Al molar ratio diagram, which is convenient to identify alteration trends and related mineralogical changes (Davies and Whitehead 2010). Compared to the uppermost Beauvoir granite (B1 unit: avg Li = 4575 ppm; Sn = 1077 ppm; Ta = 179 ppm; W = 41 ppm), the quartz-muscovite greisens have moderate enrichment in Sn (avg = 1944 ppm; +81%) but no specific enrichment in Li (avg = 3403 ppm; -26%), Ta (avg = 236 ppm; +32%) and W (avg = 45 ppm; +9%; Fig. 1). In contrast, quartz-zinnwaldite greisens at Cínovec are moderately to strongly enriched in Li (avg = 4314 ppm; +292%), Sn (avg = 1126 ppm; +744%), W (avg = 491 ppm; +1884%) and Ta (avg = 78 ppm; +97%) compared to the uppermost granite (CnG unit: avg Li = 1100 ppm; Sn = 133 ppm; W = 25 ppm; Ta = 40 ppm; Fig. 2).

3.2 Mica compositions

To further investigate the evolution of Li, Sn, W and Ta contents during greisenization of RMG systems, we also compared the trace element concentrations of igneous and greisen micas from Beauvoir and

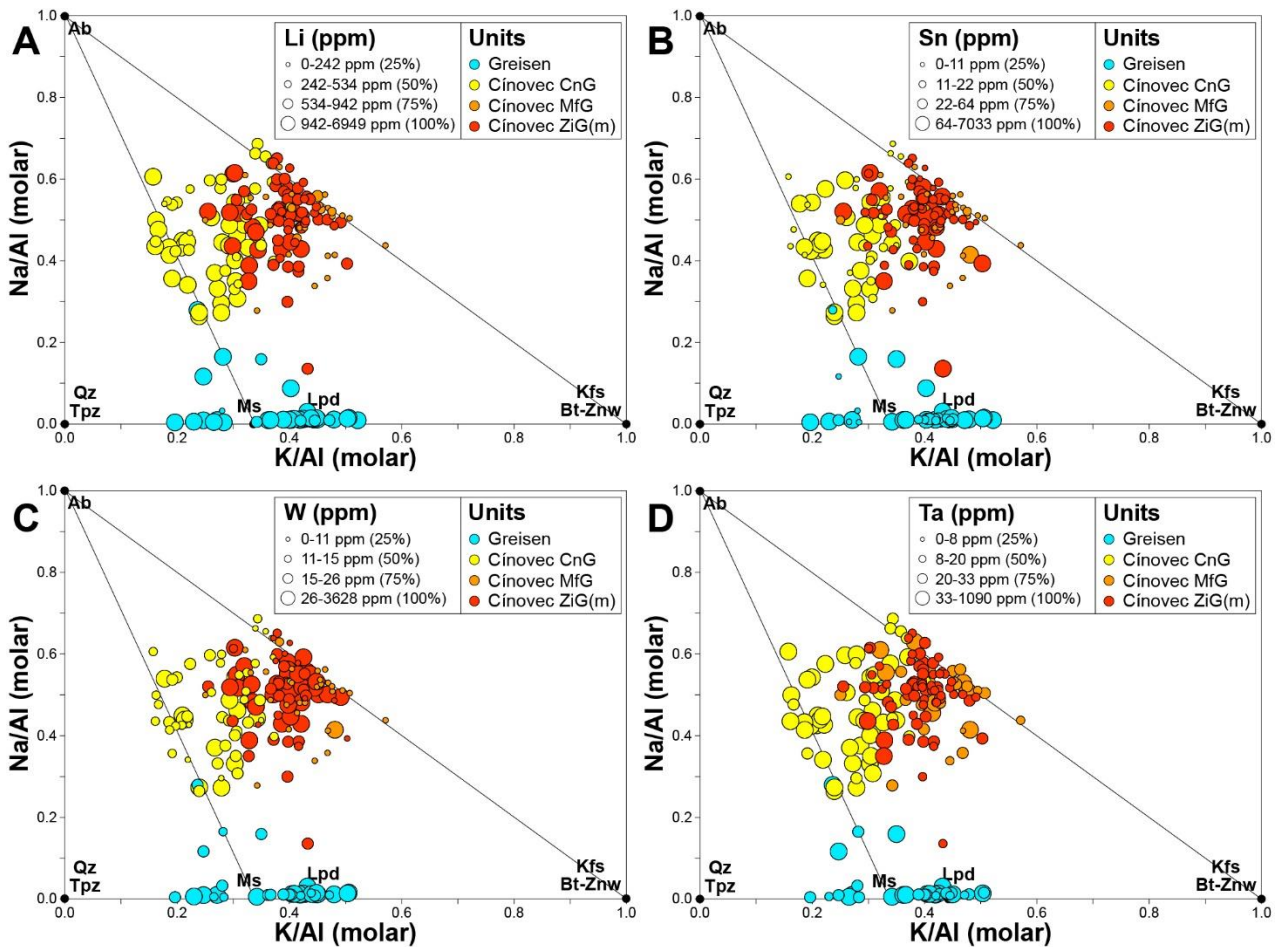


Figure 2. Bubbleplot diagrams of K/Al vs. Na/Al molar ratios for rock samples from Cínovec illustrating the contents of Li, Sn, W, and Ta in granites and greisens. The bubble diameters correspond to quartile distribution (25%, 50%, 75%, 100%) of element concentrations. The node locations of common silicate minerals identified in these rocks are also plotted (Ab = albite, Bt = biotite, Kfs = K-feldspar, Lpd = lepidolite, Ms = muscovite, Qz = quartz, Tpz = topaz, Znw = zinnwaldite).

Cínovec (Breiter et al. 2019; Monnier et al. 2022). At Beauvoir, greisen muscovite is strongly enriched in Sn (avg = 1173 ppm; +677%) but is significantly depleted in Li (avg = 648 ppm; -97%), W (avg = 2 ppm; -99%) and Ta (avg = 29 ppm; -52%) compared to igneous lepidolite from the B1 granite (avg Li = 25,127 ppm; Sn = 151 ppm; W = 246 ppm; Ta = 61 ppm; **Fig. 3A**). In contrast, greisen zinnwaldite from Cínovec has similar contents of Li (avg = 16,568 ppm), Sn (avg = 124 ppm), W (avg = 20 ppm) and Ta (avg = 19 ppm) compared to igneous zinnwaldite from the granite canopy (CnG unit: avg Li = 15,819 ppm; Sn = 122 ppm; W = 35 ppm; Ta = 40 ppm; **Fig. 3B**). However, late muscovite locally replacing zinnwaldite in the Cínovec greisen shows a marked enrichment in Sn (avg = 1287 ppm; +938%) and significant depletions in Li (avg = 3961 ppm; -76%), W (avg = 6 ppm; -70%) and Ta (avg = 17 ppm; -11%) relative to greisen zinnwaldite (**Fig. 3B**).

4 Discussion and conclusions

While the Cínovec RMG cupola is less enriched in rare metals than Beauvoir with two-to-eight times lower average contents of Li (1100 ppm vs. 4575 ppm), Sn (133 ppm vs. 1077 ppm), W (25 ppm vs. 41 ppm) and Ta (40 ppm vs. 179 ppm), it is associated

with a highly-mineralized Li-Sn-W greisen deposit. This difference of metal enrichment is recorded by the composition of micas, which are petrogenetic monitors of the evolution of RMG-greisen systems. At Beauvoir, alteration of Li-Sn-W-enriched igneous lepidolite produced Sn-rich and Li-W-Ta-depleted greisen muscovite, thus releasing Li, W and Ta in the hydrothermal fluid (Monnier et al. 2022). At Cínovec, there are no major changes of Li, Sn, W and Ta contents between igneous zinnwaldite and greisen zinnwaldite, the latter being interpreted to have fully re-equilibrated with the greisen-forming fluid (Breiter et al. 2019). Late alteration of zinnwaldite to muscovite in the Cínovec greisen is marked by a strong enrichment in Sn and depletion in Li, W and Ta, similar to greisen muscovite at Beauvoir. Therefore, muscovitization occurring in both RMG cupolas was not essential for the formation of mineralized greisens. Although it is associated with secondary Sn enrichment, muscovite alteration seems more an inhibitor of metal enrichment in greisens. The fact that massive mineralized greisens were formed at Cínovec but not at Beauvoir is likely related to different emplacement depths of magmas and volumes of fluids released. Greisenization and veining at

Cínovec were favored by hypabyssal emplacement (0.5-1.5 km) of the granitic magmas, thus causing widespread hydraulic fracturing and pervasive alteration of significant rock volumes (Štemprok 2016; Breiter et al. 2017). In contrast, the greater emplacement depth of the Beauvoir RMG (ca. 3-4 km) induced mostly fracture-related alteration, which may explain the lack of massive mineralized greisens (Cuney et al. 1992).

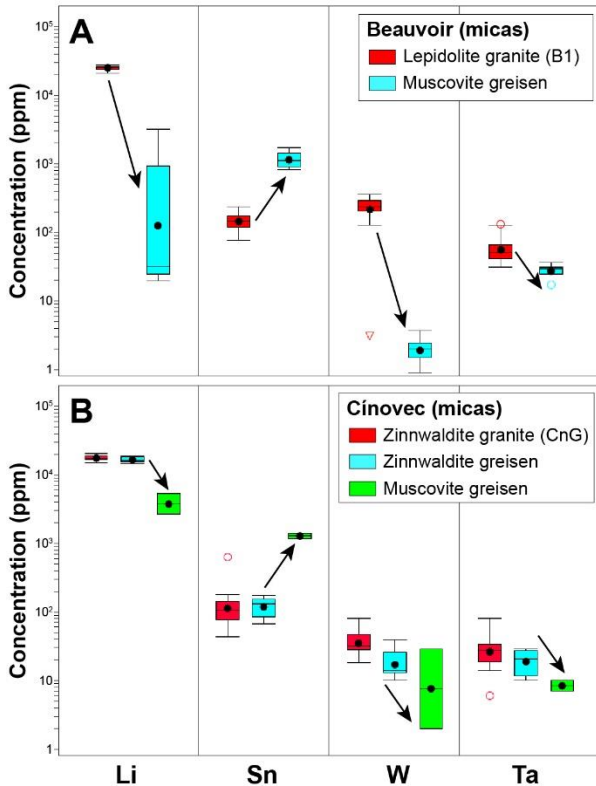


Figure 3. Box plots illustrating the evolution of Li, Sn, W and Ta contents in micas during greisenization of the granitic cupolas at Beauvoir (A) and Cínovec (B).

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