Geology, Geophysics & Environment 2016, vol. 42 (1): 61–62

Composition of Nb-Ta-Ti-Sn-W oxide minerals: indicators of magmatic to hydrothermal evolution of the Cínovec granite intrusion and Sn-W deposit (Czech Republic)

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The Cínovec (Zinnwald) Sn-W ore deposit is genetically linked to intrusion of late Variscan, highly fractionated granite which expresses the latest evolutionary stage of a volcano-plutonic system of the Teplice caldera. Whole intrusion is relatively highly fractionated and from bottom (~1500 m) to top part of cupola-shaped deposit is obviously following succession from biotite (annite) granodiorite-granite-zinnwaldite granite, with the partly greisenized uppermost part at 300–500 m depth (Štemprok 1965, 1971). In 1961–63 the Czechoslovakian Geological Survey (CGS) drilled a 1596 m deep borehole in the Sn-W-mineralized Cínovec granite cupola (Štemprok 1965, Štemprok & Šulcek 1969). All studied rock types include W- and Sn-bearing minerals (wolframite series, scheelite and cassiterite) and disseminated accessory Nb-Ta-Ti-W-Sn minerals (Štemprok & Šulcek 1969, Štemprok 1989, Johan and Johan 1994) which were obtained from the collection of CGS in Prague and studied by BSE and electron microprobe. They crystallized in following succession: rutile + columbite + cassiterite (biotite granodiorite) → rutile + columbite + W-rich ixiolite + cassiterite + scheelite in zinnwaldite granite. Textural relationships of these Nb-Ta-Ti-Sn-W minerals indicate predominantly their magmatic origin and part of them (e.g., cassiterite and columbite) show minor post-magmatic alteration phenomena like distinctly inhomogeneous mixtures of secondary pyrochlore-group minerals ("oxykenopyrochlore" and oxycalciopyrochlore). Nb/Ta and Fe/Mn fractionation trends led to characteristic Mn and Ta enrichment from bottom (biotite granite) to uppermost zinnwaldite granite, especially in columbite-group minerals. While Nb/Ta fractionation is limitedly applied, effective Fe/Mn fractionation led to significant Mn – enrichment of late-magmatic phases [columbite-(Mn) and W-rich ixiolite].

Post-magmatic to hydrothermal metasomatic fluids caused partial greisenization of the granites and this stage is represented by latest columbite + scheelite + cassiterite + wolframite assemblage. The last two minerals were objects of extensive mining in the past. Although the hydrothermal system was enriched in F and Li (presence of topaz and zinnwaldite), there are only relatively limited Nb/Ta and Fe/Mn fractionations in post-magmatic columbite. Similarly to primary fractionation, both Nb/Ta and Fe/Mn ones take place and overlap characteristic primary Mn-enrichment. Effective Mn-redistribution is predominantly controlled by crystallization of Mn-dominant wolframite like hübnerite in the hydrothermal stage. Scandium is typical rare element in primary (magmatic) and secondary (hydrothermal) mineral assemblage. While primary Sc-fractionation continues the ongoing Sc-enrichment mostly in columbite to uppermost parts of intrusion, the hydrothermal Sc-redistribution is controlled by

http://dx.doi.org/10.7494/geol.2016.42.1.61 ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

crystallization of main ore mineral – wolframite, which consumed a major part of scandium.

Main substitution mechanisms in rutile-cassiterite-wolframite-columbite assemblage include following heterovalent substitutions: (i) $Ti_3(Fe,Mn)^{2+}_{-1}(Nb,Ta)_{-2}$, (ii) $Ti_2Fe^{3+}_{-1}(Nb,Ta)_{-1}$, (iii) $(Nb,Ta)_4Fe^{2+}_{-1}W_{-3}$. Moreover, a part of minor cations can enter via: (iv) $(Fe,Mn)^{2+}_1W_1(Fe,Sc)^{3+}_{-1}(Nb,Ta)_{-1}$ into wolframite lattice, (v) $W_1(Ti,Sn)_1(Nb,Ta)_{-2}$, (vi) $(Sc,Fe)^{3+}_3(Fe,Mn)^{2+}_{-2}(Nb,Ta)_{-1}$, and (vii) $W_2Sc^{3+}_1(Nb,Ta)_{-3}$ into columbite lattice. Calculated Fe^{3+} can be introduced into rutile lattice predominantly via mechanism (ii), while via (iv) into wolframite lattice and together with Sc^{3+} via (vi) into columbite lattice. The last mechanism results in charge imbalance of *A* and *B* positions of columbite lattice entering R^{3+} cations to. The distinctly varying calculated Fe^{3+} values can refer to changing fO_2 during columbite, rutile, W-rich ixiolite and wolframite crystallization.

Therefore, the textural and crystallo-chemical features of studied Nb-Ta-Ti-Sn-W oxide minerals in the Cínovec granite cupola reflect a complex geochemical development of this granite system and ore mineralization from primary magmatic stage, through late-magmatic to subsolidus conditions, and ending in distinct hydrothermally – metasomatic overprint of pre-existing phases.

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