

(Y,REE)-(Ti,Nb,Ta)-oxide minerals from NYF pegmatites of the Třebíč Massif, Moldanubicum, Czech Republic; U/Th, Y/REE and Ta/Nb fractionation trends

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The aeschynite-group minerals (AGM) are typical accessory phases in NYF pegmatites of the Třebíč Durbachite Massif. It forms a large (~540 km²), probably sheet-like body emplaced in medium- to high-grade metamorphic rocks. Durbachites (quartz melasyenite to melagranite, U-Pb age 343±6 Ma.) are metaluminous (ASI = 0.85-0.93), ultrapotassic (5.2-6.5 wt.% K₂O), highly magnesian (3-10.4 wt.% MgO), and enriched in Cr, Rb, Cs, U and Th. They are interpreted as a product of mixing of enriched mantle magma and crustal melt.

The NYF pegmatites from the Třebíč Massif are represented by rather primitive allanite subtype pegmatites, abundant euxenite subtype pegmatites, and the most evolved zinnwaldite-masutomilite-elbaite pegmatite from Kracovice (Novák et. all 1999). Pegmatites of the euxenite subtype form dikes and lenses, up to ~ 1 m thick, and commonly have transitional contacts. The zoned internal structure comprises from contact inwards: medium- to coarse-grained granitic unit (Kfs+Qtz+oligoclase+Bt); graphic unit (Kfs+Qtz); blocky Kfs (pale green amazonite) and locally small quartz core; aplitic units are present at some localities. Albite units are developed at more evolved pegmatites. The following accessory minerals were found: AGM, allanite-(Ce), ilmenite, pseudorutile, titanite, beryl, Nb-rutile, pyrochlore group minerals, zircon, monazite-(Ce), and tourmaline (Al-poor schorl-dravite to Al-rich schorl) indicating higher degree of fractionation. Euxenite subtype pegmatites are generally F and P poor, and only locally B enriched.

Aeschynite-group minerals (AGM)

We studied AGM at six localities, which slightly differ in degree of fractionation. They usually form only one morphological and paragenetic type within a single pegmatite body except the locality Vladislav, where AGM are common in blocky K-feldspar, and rare in graphic unit and blocky quartz. AGM are fairly homogenous in the BSE image disregarding alteration and replacement by secondary pyrochlore-group minerals (similar in composition). X-ray study of AGM samples heated to 700 °C yielded mostly aeschynite-type phase (three samples), a euxenite-type phase plus pyrochlore were found in one sample (Čech et. all 1999). Seven hydrothermally recrystallized samples heated to ~700-800°C gave exclusively an aeschynite-type structure (± pyrochlore). The EMP analyses provided quite high totals of oxides (96.5-99.5) and A:B ratio close to 2. Two compositionally distinct types of AGM (type X and type Y) were recognized. Because they differ significantly in the occupation of A and B sites (Fig.1), we discussed them individually.

A site: *Type X* is compositionally highly variable and includes aeschynite-(Y), Ca-rich aeschynite-(Y), Ca-rich niobaeschynite-(Ce) and Y,REE-rich viegezzite. The A site is occupied by highly variable amounts of Y (0.054-0.546 apfu), Ca (0.039 - 0.507 apfu), \sum REE (0.197 - 0.489 apfu). The U and Th contents are lower and less variable; site vacancy is low, up to 0.08 apfu. The minor cations include Fe, Mn, Zr, Sc and Sn < 0.05 apfu. *Type Y* (U,Th,Ti-rich aeschynite) is occupied chiefly by U (0.218 - 0.261 apfu) and Th (0.102-0.147 apfu). Calcium (0.149 - 0.263 apfu), Y (0.108 to 0.152 apfu), and \sum REE (0.177 to 0.191 apfu) are lower relative to the *X type*. The minor cations include Fe > Mn, Zr and Sn < 0.065 apfu.

B site: The compositions of the *type X* fall into the large field. Titanium (1.060-1.188 apfu) predominates over moderate to high Nb (0.653-0.814 apfu) and commonly low Ta (up to 0.136 apfu). Three samples from tourmaline-bearing pegmatites are Ta-enriched (0.193-0.779 apfu). *Type Y* is evidently Ti-enriched relative to other AGM (Ti = 1.248 - 1.642 apfu); moderate to low Nb (0.240 - 0.610 apfu) and low Ta (0.072 - 0.124 apfu) are typical.

Substitution mechanisms

The substitutions were derived from the theoretical aeschynite composition (Y,REE)TiNbO₆. Minor participation of the substitutions Ca(U,Th)(Y,REE)₂ and (U,Th)Ti(Y,REE)₁(Nb,Ta)₁ is typical in the *type X*. In Ca-rich AGM significant substitution CaNb(Y,REE)₁Ti₁ tends to the CaNb₂O₆ composition (Y,REE-rich viegezzite). The *type Y* (U,Th,Ti-rich aeschynite) is characterized by the significant substitution (U,Th)Ti(Y,REE)₁(Nb,Ta)₁ relative to *type X*. This substitution tends to the composition R⁴⁺Ti₂O₆, where R⁴⁺ = (U > Th), which corresponds to monoclinic brannerite C 2/m.

Geochemical fractionation and behavior of REE

The degree of geochemical fractionation of NYF granitic pegmatites and of Y,REE,Nb,Ta,Ti-oxide minerals may be generally specified using the ratios $U/(U+Th)$, $Y/(Y+REE)$, $Ta/(Ta+Nb)$, $(Nb+Ta)/(Ti+Nb+Ta)$. We compared the above values normalized according to the first one. We found concomitant increasing of $U/(U+Th)$ and $Y/(Y+REE)$ values; however, the ratios $Ta/(Ta+Nb)$ and $(Nb+Ta)/(Ti+Nb+Ta)$ behave more irregularly and generally in the opposite way. Consequently, the $Ta/(Ta+Nb)$ fractionation commonly well developed in LCT pegmatites and also in some NYF pegmatites (Ercit 2004) does not work in the studied NYF pegmatites of the TM. The highest Ta contents were found in AGM (niobaeschynite-(Ce) and tantalaeschynite-(Ce)) from tourmaline-bearing pegmatites from Klučov and Pozďátka. The samples of AGM from different textural-paragenetic units at the pegmatite Vladislav exhibit almost identical chemical composition; consequently, no fractionation of AGM was recorded within the single pegmatite.

We found three distinct types of normalized REE patterns in AGM: LREE-enriched, HREE-enriched and transitional. Very low variation was recorded within single grains and within a single locality (Vladislav). The Dy/Y ratio in REE-oxide minerals indicating activity of F (Gramaccioli & Pezzotta 2000) confirmed its very low activity at four localities (4.1-6.7), but increasing at Chlumeck (8.6-11.4) and chiefly at tourmaline-bearing pegmatite in Klučov (5.1-44.2), where Ta-enriched AGM occur.

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