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Y,REE,Nb,Ta,Ti-oxide (AB₂O₆) minerals from REL–REE euxenite-subtype pegmatites of the Třebíč Pluton, Czech Republic; substitutions and fractionation trends

Radek Škoda a,b,*, Milan Novák a

^a Institute of Geological Sciences, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic
^b Czech Geological Survey, Czech Republic

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Abstract

Aeschynite-group minerals (AGM) and euxenite-group minerals (EGM) occur in REL-REE euxenite-subtype pegmatites from the Třebíč Pluton, Czech Republic. They form strongly metamictized, light brown to black, equigranular to needle-like, subhedral to anhedral grains enclosed in blocky K-feldspar and less commonly in albite, and blocky quartz, and in the graphic unit (quartz and K-feldspar). Both AGM and EGM are homogeneous to slightly heterogeneous in BSE images. They are not commonly associated with the other primary Y,REE,Ti,Nb-bearing minerals, i.e. allanite-(Ce), monazite-(Ce), titanite, and ilmenite, which occur within the same textural-paragenetic unit. Aeschynite-(Y), aeschynite-(Ce), aeschynite-(Nd), nioboaeschynite-(Ce), tantalaeschynite-(Ce), vigezzite and polycrase-(Y) were identified using EMP and canonical discrimination analysis [Ercit, T.S., 2005a. Identification and alteration trends of granitic-pegmatite-hosted (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals: a statistical approach. Can. Mineral. 43, 4 1291–1303.]. The exchange vector ^ACa ^B(Nb,Ta) ^A(Y,REE)₋₁ ^BTi₋₁ or its combination with the exchange vector ${}^{A}\text{Ca}_{2}$ ${}^{B}\text{(Nb,Ta)}_{3}$ ${}^{A}\text{(U,Th)}_{-1}$ ${}^{A}\text{(Y,REE)}_{-1}$ ${}^{B}\text{Ti}_{-3}$ have been elucidated for the AGM. The exchange vector ${}^{A}\text{Ca}$ REE)_2 is predominant in the EGM. The AGM are enriched in HREE, whereas LREE are concentrated in the EGM. Weak to noneexistent geochemical fractionations, as expressed by the U/(U+Th), Y/(Y+REE), Ta/(Ta+Nb) and (Nb+Ta)/(Ti+Nb+Ta) ratios, were noted for single grains from both the AGM and EGM, as well as in grains of polycrase-(Y) from four different texturalparagenetic units located in the Vladislav pegmatite. Simultaneous increase of U/(U+Th) and Y/(Y+REE) in the AGM during fractionation is typical. The Ta/(Ta+Nb) fractionation is usually weak and contradicts the Y/(Y+REE) and U/(U+Th) fractionation trends. This unusual behavior of Nb and Ta may be controlled by associated Ti-rich minerals (titanite, ilmenite, rutile), the composition of parental melt and/or by elevated F activity. The AGM and EGM from pegmatites of the Třebíč Pluton are quite similar in composition to those from REL-REE euxenite-subtype pegmatites in the Trout Creek Pass, Chaffee County, Colorado, USA, which are generally Ca,U,Th-depleted, show lower Ta/(Ta+Nb), and lower variation in HREE/LREE. © 2006 Elsevier B.V. All rights reserved.

Keywords: Aeschynite-group minerals; Euxenite-group minerals; Electron microprobe; Canonical discrimination analysis; Substitutions; Fractionation; REL-REE pegmatites; Třebíč Pluton; Czech Republic

E-mail addresses: rskoda@sci.muni.cz (R. Škoda), mnovak@sci.muni.cz (M. Novák).

^{*} Corresponding author.

1. Introduction

Aeschynite-group minerals (AGM) and euxenitegroup minerals (EGM) are typical accessory phases in REL-REE (rare-element-rare earth) pegmatites of euxenite subtype (Černý and Ercit, 2005). They have the general formula AB2O6, where the eight-fold coordinated A-site is occupied primarily by Y, REE, Ca, U, and Th, and the six-fold coordinated B-site is characterized by Ti, Nb, and Ta. The occupancies of the A- and B-site in the AGM and EGM are similar, but the LREE are preferentially incorporated into the AGM, whereas Y and HREE are incorporated into the EGM (Ercit, 2005a). Both the AGM and EGM are orthorhombic with the (Pbmn) and (Pcan) space groups, respectively. Due to a metamict state, crystal structure studies were performed on annealed samples or on synthetic analogues (Aleksandrov, 1962; Komkov and Belopolsky, 1966; Ewing and Ehlmann, 1975; Bonazzi et al., 2002; Tomašič et al., 2004). Bonazzi and Menchetti (1999) refined the crystal structure of the natural non-metamict aeschynite-(Y). They suggested a new structural formula $A_{1-x}B_2C_xO_6$ with the C-site occupancy < 0.04 apfu, coupled with a corresponding vacancy in the A-site. A X-ray powder study of high temperature recrystallized samples or canonical discrimination analyses were used to distinguish between metamict AGM and EGM (Ewing, 1976; Ercit, 2005a). A review of currently valid mineral species is given in Table 1.

Granitic pegmatites and their Y,REE,Nb,Ta,Ti-oxide minerals have been studied at several localities and pegmatite districts (e.g., Simmons et al., 1987; Albertini

Table 1 Review of currently valid aeschynite-group and euxenite-group minerals (Mandarino and Back, 2004)

	Ideal formula	Symmetry
Aeschynite-group minerals		
Aeschynite-(Y)	$Y(Ti, Nb)_2O_6$	Pbnm
Aeschynite-(Ce)	Ce(Ti, Nb) ₂ O ₆	Pbnm
Aeschynite-(Nd)	Nd(Ti, Nb) ₂ O ₆	Pbnm
Nioboeschynite-(Ce)	Ce(Nb, Ti) ₂ O ₆	Pbnm
Tantalaeschynite-(Y)	Ca, Y(Ta, Nb, Ti) ₂ O ₆	Pbnm
Vigezzite	CaNb ₂ O ₆	Pbnm
Rynersonite	CaTa ₂ O ₆	Pbnm
Euxenite-group minerals		
Euxenite-(Y)	$Y(Nb, Ti)_2O_6$	Pcan
Tanteuxenite-(Y)	Y(Ta, Ti, Nb) ₂ O ₆	Pcan
Polycrase-(Y)	$Y(Ti, Nb)_2O_6$	Pcan
Uranopolycrase	UTi ₂ O ₆	Pcan
Yttrocrasite	$(U, Th)(TiFe^{3+})_2(O, OH)_6$	n.d.
Fersmite	CaNb ₂ O ₆	Pcan

and Andersen, 1989; Hanson et al., 1992; Ercit, 1994; Lumpkin, 1998; Hanson et al., 1998; Kjellman et al., 1999; Aurisicchio et al., 2001; Bonazzi et al., 2002; Ercit, 2005a,b). Nevertheless, knowledge concerning the fractionation trends in these minerals is quite limited (Ercit, 2005b). The REL-REE euxenite-subtype pegmatites from the Třebíč Pluton investigated in this study contains both AGM and EGM. Potential substitution mechanisms and the usefulness of canonical discrimination analysis for recognition of minerals from both groups are discussed (cf., Ewing, 1976; Ercit, 2005a). Fractionation trends in the AGM and EGM within a single grain, a single pegmatite body, and within the overall pegmatite district are studied as well as the factors, which may control Y/(Y+REE), U/(U+Th), and Ta/(Ta+Nb) fractionation.

2. Geological setting

The Třebíč Pluton is the parental granite-syenite of the euxenite-subtype pegmatites, investigated in this study. It belongs to the ultrapotassic plutonic rocks $(MgO > 3 \text{ wt.}\%, K_2O/Na_2O > 2; Foley et al., 1987)$ of the durbachite series. Durbachitic rocks form two large synexhumation tabular bodies — the Třebíč Pluton and the Milevsko Pluton in the Moldanubicum (Žák et al., 2005). They are interpreted as a product of mixing between an enriched mantle magma and a crustal melt (Holub et al., 1997a; Janoušek et al., 2000). They were classified by Finger et al. (1997) as high-K, I-type granitoids. Similar rocks are known from the Black Forrest, Germany and from the Vosges, France (Holub et al., 1997a). The bulk composition of the Třebíč Pluton is characterized by a metaluminous signature (ASI= 0.85-0.93), high contents of K_2O (5.2–6.5 wt.%), MgO (3.3–10.4 wt.%), P₂O₅ (0.47–0.98 wt.%), Rb (330– 410 ppm), Ba (1100-2470 ppm), U (6.7-26.2 ppm), Th (28.2-47.7 ppm), Cr (270-650 ppm), K/Rb=133-171, and Nb/Ta=8.3-17.3. Radiometric dating (Pb-Pb zircon) indicates a Lower Carboniferous age of 343±6 Ma (Holub et al., 1997b).

The Třebíč Pluton forms a large (~540 km²), tabular body, emplaced in medium- to high-grade metamorphic rocks (cordierite migmatites, biotite-sillimanite gneisses) in the eastern part of the Moldanubicum (Fig. 1). It is consists of several tectonic segments, which represent somewhat different erosion levels (Fig. 2). Porphyric, amphibole–biotite melasyenite to quartz melasyenite and melagranite is locally foliated to various degrees mainly near contacts with host rocks. The granite–syenite is composed of subhedral orthoclase crystals, up to 3 cm in size. These are enclosed in a

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