Complex W,Nb,U,Ti,Fe-oxide minerals from the granitic pegmatite No. 3, Dolní Bory - Hatě, Czech Republic

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ABSTRACT

Complex W,Nb,U,Ti,Fe-oxide minerals were found in andalusite-diaspore aggregate from a simply zoned, barren pegmatite at Dolní Bory. Primary phases include ferberite, niobian ferberite I, wolframoixiolite and U,Fe,Nb,W-phase; secondary subsolidus breakdown products are niobian ferberite II, tungstenian ferrocolumbite, rutile and $ScPO_4$ phase. Substitutions in primary phases and conditions of formation of complex W,Nb,U,Ti,Fe-oxide minerals are discussed.

Keywords: *ferberite, wolframoixiolite, subsolidus breakdown, granitic pegmatite, Dolní Bory.*

INTRODUCTION

Niobium-tantalum oxide minerals with substantial amounts of W have been sporadically reported from granitic pegmatites. On the basis of their chemical composition, they were termed niobian wolframite, tungstenian columbite, tungstenian ixiolite, *wolframoixiolite or W-ixiolite*, and *wolframowodginite*; however, in many cases their structural type was not determined because of the microscopic particle size. Tungsten-rich Nb,Ta-oxide minerals are known from distinct types and subtypes of granitic pegmatites ranging from geochemically primitive pegmatites to highly evolved, Li-rich, complex pegmatites. Most examined pegmatites, that contain W-rich Nb,Ta-oxide minerals, belong to the LCT family, although elevated W contents were found also in Nb,Ta,Ti-oxide minerals from NYF pegmatites (Aurisicchio et al. 2001, Škoda et al. 2006).

THE PARENT PEGMATITE

The zoned and steeply dipping pegmatite dike No. 3 from Dolní Bory-Hatě, about 5 m thick and several tens meters long, cuts granulitic rock of the Bory Granulite Massif, Moldanubicum. Its internal structure shows, from the contact inwards: a thin border granitic unit (K-feldspar+quartz+ oligoclase+biotite±muscovite); a subordinate wall zone of graphic unit (K-feldspar+quartz±muscovite); and a core built up of large blocky K-feldspar and quartz. Rare intermediate albite unit is commonly located between the graphic zone (or blocky K-feldspar) and blocky quartz. It contains minor to accessory schorl, muscovite, andalusite, sekaninaite and fluorapatite (Staněk 1997).

Complex W,Nb,U,Ti,Fe-oxide minerals occur exclusively in the coarse-grained andalusite-diaspore nodule, about 1 m in diameter, enclosed in massive quartz (Novák and Šrein 1989). The nodule consists of dominant euhedral to subhedral, columnar to conic crystals of andalusite, up to 5 cm long. Thin lamellae of grayish diaspore, about 1 mm thick and up to 2 cm across, occur exclusively in a central part of the nodule. Textural relations of andalusite and diaspore observed in thin sections and BSE images show no replacement features between these minerals. Undeformed andalusite suggests that diaspore crystallized earlier. Local sequential accumulations and vein-like aggregates of pyrophyllite, kaolinite and muscovite-illite are common. All late minerals replaced andalusite, but left diaspore almost intact. Other minerals in the nodule include: schorl, foitite, monazite-(Ce), xenotime-(Y), zircon, ilmenite, rutile, augelite, pyrite and secondary autunite. Novák and Taylor (2005) suggested T < 400 °C for P = 2 kbar for the formation of the assemblage andalusite+diaspore.

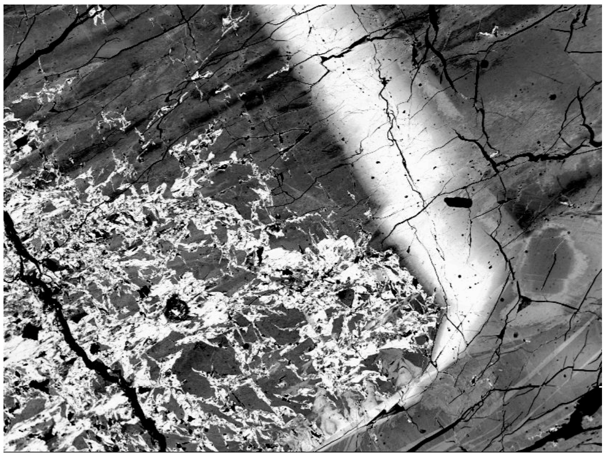

FIGURE 1. BSE image of a fragment of a primary crystal, oscillatory zoned from ferberite (white) to heterogeneous *wolframoixiolite* (dark gray) and niobian ferberite I (pale gray). The network of fine bright grains consists of secondary niobian ferberite II. The length of the figure is ~ 0.5 mm.

COMPLEX W,Nb,U,Ti,Fe-OXIDE MINERALS

Primary black, tabular, subhedral to euhedral crystals, up to 2 cm in size, vary dominantly from ferberite to *wolframoixiolite* in composition. Complex zoning is characteristic: primary, coarse but narrow oscillatory zones consist of subordinate ferberite and dominant *wolframoixiolite* (Fig. 1). The latter commonly exhibits very fine oscillatory to patchy internal zones of niobian ferberite (Fig. 1, 2). Very rare elongated tiny blebs of a U,Fe,Nb,W-phase also are present in the *wolframoixiolite*. Textural relations and chemical composition define aggregates of secondary phases: a fine-grained mixture of niobian ferberite II > ferrocolumbite >> rutile > $ScPO_4$ phase (Fig. 2). The last two minerals are always closely associated. Very rare scheelite and ilmenite were also identified.

FIGURE 2. BSE image (detail of Fig. 1) of secondary aggregate of niobian ferberite II (pale) and columbite (gray) in heterogeneous *wolframoixiolite* with fine oscillatory zones of niobian ferberite I (pale). The scale bar is 0.1 mm.

CHEMICAL COMPOSITION

The chemical compositions of primary W,Nb,U,Ti,Fe-oxide minerals - ferberite (74-65 wt. % WO_3), niobian ferberite I (61-44 wt.% WO_3), *wolframoxiolite* (42-19 wt.% WO_3) and U,Fe,Nb,W-phase (27-23 wt.% WO_3) - are characterized by large variation in W/(W+Nb+Ta) and calculated $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ but low and almost constant $Mn/(Mn+Fe^{2+}_{tot})$ and Ta/(Ta+Nb). Subordinate to minor contents of P, U, Ti, Zr, Si, Sc, Al and Ca are particularly typical of *wolframoxiolite* and of the U,Fe,Nb,W-phase. Their concentrations vary from low to negligible in ferberite to very high in *wolframoxiolite* up to: P_2O_5 0.30, UO_2 2.71, TiO_2 4.81, ZrO_2 2.84, SiO_2 0.93, Sc_2O_3 4.36, Al_2O_3 0.87, CaO 1.02 and in U,Fe,Nb,W-phase up to: P_2O_5 0.27, UO_2 19.82, TiO_2 4.15, ZrO_2 2.56, SiO_2 0.81, Sc_2O_3 4.03, Al_2O_3 1.37, CaO 0.74 (all in wt.%). The U,Fe,Nb,W-phase exhibits increased U and W but decreased contents of Nb. Secondary niobian ferberite II shows composition very similar to niobian ferberite I, tungstenian columbite has high content of Ti and Fe^{2+}/Fe^{3+} ratio. Rutile is highly heterogeneous with high concentrations of Fe, Nb and/or W.

SUBSTITUTION MECHANISMS

The substitution schemes were derived only for primary phases – from ferberite to *wolframoixiolite*, assuming absence of vacancies in the crystal structure and disordered nature of the individual phases. The dominant substitution is:

(1) $(R^{3+}R^{5+})\,(R^{2+}W)_{-1}$,

where $R^{2+} = Fe^{2+}$,Mn,Ca; $R^{3+} = Fe^{3+}$,Sc,Al; R^{4+} = Ti,Zr,Si,U; R^{5+} = Nb,Ta,P; however, the chemical composition of *wolframoixiolite* commonly close to the formula $(R^{2+}{}_3R^{3+}{}_{2.5}R^{4+}R^{5+}{}_{2.5}W_3)_{\Sigma12}O_{24}$ implies evident participation of R^{4+} cations (chiefly Ti) in the substitution by the exchange vector:

(2) $(R^{4+})_2\,(R^{2+}W)_{-1}$.

Consequently, the combination of (1) and (2) vectors expressed via the combined exchange vector:

(3) $(R^{3+}{}_3R^{4+}R^{5+}{}_3)_2\,(R^{2+}W)_{-7}$,

seems to be the best expression of the actual mechanism of substitution from ferberite to *wolframoixiolite*. The homovalent substitutions expressed by the exchange vectors: $Fe^{2+}Mn_{-1}$, $TaNb_{-1}$ and $ScFe^{3+}{}_{-1}$ are rather negligible.

CONCLUSIONS

Complex W,Nb,U,Ti,Fe-oxide minerals from Dolní Bory represent unique example of very heterogeneous complex aggregate of several primary and secondary phases. Highly variable $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ in minerals show that $f(O_2)$ played a significant role in formation of W,Nb,U,Ti,Fe-oxide minerals disregarding crystal-structural factors (see e.g., Johan and Johan 1994). Almost constant Ta/(Ta+Nb) in primary and secondary phases suggests low mobility of Nb and Ta during breakdown process as was found in other Nb,Ta-oxide minerals (Novák and Černý 1998). Close relationship of W,Nb,U,Ti,Fe-oxide minerals to andalusite-diaspore aggregate indicates temperatures below 400 °C for primary phases and even lower temperatures for the breakdown products are plausible.

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