Foordite-thoreaulite, Sn$^{2+}$Nb$_2$O$_6$-Sn$^{2+}$Ta$_2$O$_6$: compositional variations and alteration products

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ABSTRACT

Minerals of the foordite-thoreaulite series (FT) are scarce constituent of rare-element, Sn-Ta-Li-Cs-rich granitic pegmatites with low fO$_2$ environment. EMPA study of FT showed a broad range of continuous Sn$^{2+}$Nb$_2$O$_6$-Sn$^{2+}$Ta$_2$O$_6$ s.s.: at Ta/(Ta+Nb)=0.23-0.92, NbTa$_4$, Pb$^{2+}$Sn$^{2+}$, and Sn$^{2+}$Sn$^{4+}$Sn$^{2+}$, are main substitutions. Pb and Sb occupy ±21 at.% and ±5 at.% of the Sn$^{2+}$ site position, respectively. Sb shows positive correlation with Ta/(Ta+Nb). Influx of late fluids under higher fO$_2$ causes breakdown of FT and production of casiterite and numerous Nb, Ta-oxide minerals.

Keywords: Foordite, thoreaulite, Nb-Ta minerals, electron microprobe, granitic pegmatites.

INTRODUCTION

The rare mineral thoreaulite Sn$^{2+}$Ta$_2$O$_6$ was first described from the Manono granitic pegmatite, Congo (Buttenbach, 1933). Foordite was described as a Nb-dominant analog (Černý et al., 1988). Until 1970’s, the formula of thoreaulite was written as Sn$^{4+}$Ta$_3$O$_7$ (e.g. Mumme, 1970). However, new structural and Mössbauer spectroscopy data revealed the dominant presence of Sn$^{2+}$ and AB$_2$O$_6$ stoichiometry of foordite-thoreaulite (Graham & Thornber, 1974, Maksimova et al., 1975, Ercit & Černý, 1988). Linear correlations between composition (Ta, Pb and Sb contents) and unit-cell dimensions, density as well as mean refraction index of foordite-thoreaulite were also demonstrated (Černý et al., 1988). Moreover, foordite-thoreaulite mineral assemblages and their secondary phases were described (e.g. Khvostova et al., 1982, Voloshin et al., 1983, Nekrasov et al., 1984, Voloshin & Pakhomovsky, 1988, Černý et al., 1988).

Despite of the above-mentioned data, the foordite-thoreaulite series have been so far insufficiently examined. The aim of our study is contribute to the understanding of the foordite-thoreaulite minerals and their breakdown products from most localities known to date by detailed electron-microprobe study.

COMPOSITION OF FOORDITE-THOREAULITE

Foordite - thoreaulite minerals have been found only in Proterozoic to Palaeozoic rare-element granitic pegmatites (Manono, Maniême, Urubu, Ungursal) or alluvial clastic sediments (Lutsiro). All primary occurrences belong to complex, Li-Cs-Ta-rich (LCT family) pegmatites of spodumene or petalite subtype (after classification of Černý & Ercit, 2005), enriched in Sn and with low fO$_2$ environment.

The electron-microprobe study of foordite-thoreaulite series reveal a wide and almost continuous compositional variability of Ta/(Ta+Nb) at. from 0.23 to 0.92, perceptibly broader than reported to date (0.30 to 0.91; Černý et al., 1988, Voloshin & Pakhomovsky, 1988). Pb and Sb are the most widespread A-site substituents in foordite-thoreaulite.

Elevated contents of these elements were noted previously (up to 6 wt.% PbO and up to 1 wt.% Sb$_2$O$_3$; Voloshin et al., 1983, Voloshin & Pakhomovsky, 1988, Černý et al., 1988), but our results reveal higher values: up to 9.8 wt.% PbO and 2.1 wt.% Sb$_2$O$_3$ (21 at.% Pb and 8 at.% Sb of the A-site). A Pb/(Pb+Sn$^{2+}$) vs. Ta/(Ta+Nb) quadrilateral diagram shows a compositional relationship between the foordite-thoreaulite series, changbaite PbNb$_2$O$_6$ and a potential PbTa$_2$O$_6$ phase (Fig. 1). This wide compositional gap between the Sn- and Pb-end-members can be explained by the differences between the monoclinic layered structure of foordite-thoreaulite and the trigonal framework structure of changbaite (Černý & Ercit, 1989).

Besides the simple homovalent NbTa$_4$ and Pb$^{2+}$Sn$^{2+}$ substitutions, the entry of trivalent Sb into the A-site requires a third, heterovalent Sb$^{3+}$Sn$^{2+}$, (Nb,Ta)$_3$ substitution. This mechanism, qualitatively suggested by Černý et al. (1988), is now clearly documented by linear negative trends between these elements, as well as by the presence of tetravalent tin in the B-site position (0 to 6 at.% Sn$^{4+}$ of the total Sn), calculated by charge-balancing.

Primary large crystals of the foordite-thoreaulite are compositionally very homogeneous. Due to the presence of dominant Sn$^{2+}$, foordite-thoreaulite minerals...
are considered to precipitate under appropriate low $f_{O_2}$ (Nekrasov et al., 1982, 1984) and at low $\mu$(Fe,Mn,Na,Ca,F), where crystallization of cassiterite, columbite-tantalite or other common Nb-Ta phases is suppressed (Černý et al., 1988). These conditions locally persisted to later stages, beyond the crystallization of the coarse primary phases, and produced a younger generation of foordite-thoearalite. It forms small irregular zones and veinlets, commonly with diffuse or patchy zoning and variable Ta/(Ta+Nb) ratio.

**ALTERATION PRODUCTS OF FOORDITE-THOEARALITE**

Influx of late pegmatitic to hydrothermal fluids under higher $f_{O_2}$ causes breakdown of foordite-thoearalite and production of cassiterite and numerous Nb-Ta-oxide minerals. Our study revealed a broad variability of secondary phases. At Lutsiro pegmatite, foordite is replaced by mosaic fine-grained aggregate of secondary foordite - thoearalite + ferrocolumbite-ferrotantalite + Ta-rich cassiterite. Valence calculation requires a presence of or Fe$^{2+}$ or Sn$^{4+}$ in cassiterite along with substitution: Fe$^{2+}$(Nb,Ta)$_2$Sn$^{4+}$, (Manono, Maniema, Lutsiro and Ungursay pegmatites) or Sn$^{2+}$(Nb,Ta)$_2$Sn$^{4+}$ (Manono and Urubu pegmatites). Local replacement of foordite-thoearalite by alkali-bearing (Li, Na, K, Cs, Ca) Nb-Ta phases is widespread; irregular veinlets and zones of pyrochlore-group minerals (pyrochlore, microlite, plumbopyrochlore, plumbomicrolite, stannomicrolite, “strotniomicrolite”), calciotantalite, irtyshite, liithiottantite, cesplumotantite, fersmite and rankamaite are formed. Also, late simpsonite is present in the Manono and Maniema pegmatites.

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