Foordite-thoreaulite, $Sn^{2+}Nb_2O_6$-$Sn^{2+}Ta_2O_6$: compositional variations and alteration products

PAVEL UHER[1], PETR ČERNÝ[2] & RON CHAPMAN[2]

[1]Department of Mineral Deposits, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia, puher@fns.uniba.sk
[2]Department of Geological Sciences, University of Manitoba, Winnipeg, MB., Canada, R3T 2N2

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 $Sn^{2+}Nb_2O_6$-$Sn^{2+}Ta_2O_6$ s.s.: at. Ta/(Ta+Nb)=0.23-0.92. $NbTa_{-1}$, $Pb^{2+}Sn^{2+}_{-1}$ and $Sb^{3+}Sn^{4+}Sn^{2+}_{-1}(Nb,Ta)^{5+}_{-1}$ are main substitutions. Pb and Sb occupy ≤21 at.% and ≤8 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 cassiterite and numerous Nb,Ta-oxide minerals.

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

INTRODUCTION

The rare mineral thoreaulite $Sn^{2+}Ta_2O_6$ was first described from the Manono granitic pegmatite, Congo (Buttgenbach, 1933). Foordite was described as a Nb-dominant analog (Černý et al., 1988). Until 1970`s, the formula of thoreaulite was written as $Sn^{4+}Ta_2O_7$ (e.g. Mumme, 1970). However, new structural and Mössbauer spectroscopy data revealed the dominant presence of Sn^{2+} and AB_2O_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, Maniéma, Urubu, Ungursay) 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.

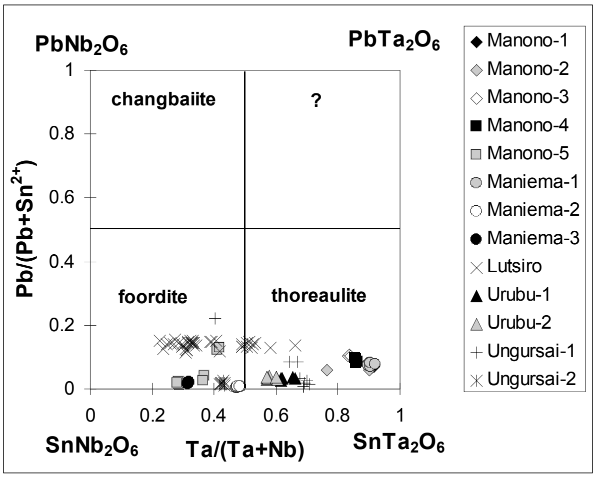

FIGURE 1. The foordite-thoreaulite-changbaiite-$PbTa_2O_6$ quadrilateral diagram (atomic proportions), showing considerably limited solid solution of the Pb-based components in foordite-thoreaulite.

Elevated contents of these elements were noted previously (up to 6 wt.% PbO and up to 1 wt.% Sb_2O_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_2O_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, changbaiite $PbNb_2O_6$ and a potential $PbTa_2O_6$ 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 changbaiite (Černý & Ercit, 1989).

Besides the simple homovalent $NbTa_{-1}$ and $Pb^{2+}Sn^{2+}_{-1}$ substitutions, the entry of trivalent Sb into the A-site requires a third, heterovalent $Sb^{3+}Sn^{4+}Sn^{2+}_{-1}(Nb,Ta)^{5+}_{-1}$ 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 fO_2 (Nekrasov et al., 1982, 1984) and at low μ(Fe,Mn,Na,Ca,F), where crystallization of cassiterite, columbite-tantalite or other common Nb-Ta phases is supressed (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-thoreaulite. It forms small irregular zones and veinlets, commonly with diffuse or patchy zoning and variable Ta/(Ta+Nb) ratio.

ALTERATION PRODUCTS OF FOORDITE-THOREAULITE

Influx of late pegmatitic to hydrothermal fluids under higher fO_2 causes breakdown of foordite-thoreaulite 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 - thoreaulite + ferrocolumbite-ferrotantalite + Ta-rich cassiterite. Valence calculation requires a presence of or Fe^{2+} or Sn^{2+} in cassiterite along with substitution: $Fe^{2+}(Nb,Ta)_2Sn^{4+}_{-3}$ (Manono, Maniema, Lutsiro and Ungursay pegmatites) or $Sn^{2+}(Nb,Ta)_2Sn^{4+}_{-3}$ (Manono and Urubu pegmatites). Local replacement of foordite-thoreaulite 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, “strontiomicrolite”), calciotantite, irtyshite, lithiotantite, cesplumtantite, fersmite and rankamaite are formed. Also, late simpsonite is present in the Manono and Maniema pegmatites.

ACKNOWLEDGEMENTS

This study was supported by a NSERC Research Grant and a Major Installation Grant to PČ, by a University of Manitoba Post-Doctoral Fellowship to PU and by Science and Technology Assistance Agency of the Slovak Republic under the contract No. APVV-0557-06.

REFERENCES CITED

Buttgenbach, H. (1933): Minéraux du Congo belge. Bull. Soc. Géologique Belgique, 56, 327-328.

Černý, P. & Ercit, T. S. (1989): Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. In: (Möller, P., Černý, P. & Saupé, F. (Eds.): Lanthanides, Tantalum and Niobium. Springer-Verlag, Berlin - Heidelberg, Germany, 27-79.

Černý, P., & Ercit, T. S. (2005) The classification of granitic pegmatites revisited. Canadian Mineralogist, 43, 2005-2026.

Černý, P., Fransolet, A.-M., Ercit, T. S. & Chapman, R. (1988): Foordite $SnNb_2O_6$, a new mineral species, and the foordite-thoreaulite series. Canadian Mineralogist, 26, 889-898.

Ercit, T. S. & Černý, P. (1988): The crystal structure of foordite. Canadian Mineralogist, 26, 899-903.

Graham, J. & Thornber, M. R. (1974): The crystal chemistry of complex niobium and tantalum oxides. I. Structural classification of MO_2 phases. American Mineralogist, 59, 1026-1039.

Khvostova, V. A., Lebedeva, S. I. & Maksimova, N. V. (1982): Tin-bearing tantalo-niobates and their typomorphic features. Rare minerals of tantalo-niobate group with lead. Izvestiya AN SSSR Seriya Geologiya, 9, 89-100 (in Russian).

Maksimova, N. V., Ilyukhin, V. V. & Belov, N. V. (1975): Crystal structure of thoreaulite $SnTa_2O_6$. Doklady Akademii Nauk SSSR, 223, 1115-1118 (in Russian).

Mumme, W. G. (1970): The crystal structure of thoreaulite, $SnTa_2O_7$, an example of tin in five-fold coordination. American Mineralogist, 55, 367-377.

Nekrasov, I. Y., Chistyakova, N. I. & Yevstigneyeva, T. L. (1984): On the relationships of thoreaulite, lithiotantite, rankamaite and cassiterite in rare-element pegmatites of Siberia. Mineralogicheskyi Zhurnal, 6, 42-55 (in Russian).

Nekrasov, I. Y., Nekrasova, R. A., Tsepin, A. I., Sipavina, L. V. & Remez, V. K. (1982): Thoreaulite from rare-element pegmatites of Siberia. Mineralogicheskyi Zhurnal, 4, 11-20 (in Russian).

Voloshin, A. V. & Pakhomovsky, Y. A. (1988): Mineralogy of tantalum and niobium in the rare-element pegmatites. Nauka Press, Leningrad, Russia (in Russian).

Voloshin, A. V., Pakhomovsky, Y. A., Stepanov, V. I. & Tyusheva, F. N. (1983): Lithiotantite $Li(Ta,Nb)_3O_8$ - a new mineral from granitic pegmatites of East Kazakhstan. Mineralogicheskyi Zhurnal, 5, 91-95 (in Russian).