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**FERROTAPIOLITE AS A PSEUDOMORPH OF STIBIOTANTALITE
FROM THE LAŠTOVIČKY LEPIDOLITE PEGMATITE, CZECH REPUBLIC;
AN EXAMPLE OF HYDROTHERMAL ALTERATION AT CONSTANT Ta/(Ta + Nb)**

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ABSTRACT

Dark brown porous ferrotapiolite is a dominant product of alteration in pseudomorphs after primary stibiotantalite from the lepidolite pegmatite at Laštovičky, western Moravia, Czech Republic. Two compositionally distinct varieties of ferrotapiolite were recognized, a volumetrically dominant Fe³⁺-rich phase and a very rare Sb-rich phase. Niobium-rich ferrotapiolite, with up to 17.51 wt.% Nb₂O₅ (0.61 *apfu*), is highly heterogeneous, with Ta/(Ta + Nb) of 0.69 to 0.84 and Mn/(Mn + Fe) of 0.01 to 0.05; Fe₂O₃calc. ≤ 3.09 wt.% (0.18 Fe³⁺ *apfu*, ~0.16 to 0.22 Fe³⁺ *apfu* from Mössbauer spectroscopy) in the ferrian variety, and Sb₂O₃ ≤ 9.87 wt.% (0.34 Sb³⁺ *apfu*) in antimonoo variety. The unit-cell dimensions of ferrian ferrotapiolite (4.746 < *a* < 4.757 Å, 9.198 < *c* < 9.244 Å) calculated from X-ray powder-diffraction data indicate highly variable degrees of structural order. The substitution NbTa₋₁ is dominant; the minor substitution Fe³⁺₃Fe²⁺₋₂R⁵⁺₋₁ typical of the ferrian ferrotapiolite strongly suggests the incorporation of Fe³⁺ at both the *A* and the *B* sites in ferrotapiolite, indicative of solid solution toward Fe³⁺TaO₄. The substitution Sb³⁺₃Fe²⁺₋₂R⁵⁺₋₁ in the antimonoo variety tends to an end-member composition of SbTaO₄, corresponding to stibiotantalite; however, it very likely reflects microscopic relics of primary stibiotantalite in ferrotapiolite hidden below the surface of polished samples. Stibiotantalite is replaced by ferrotapiolite along irregularly distributed fractures according to the hypothetical reaction 2Sb(Ta,Nb)O₄ + Fe(OH)₂ + 2H₂O = Fe(Ta,Nb)₂O₆ + 2Sb(OH)₃. Such a significant Fe-enrichment (stibiotantalite *versus* newly formed ferrotapiolite), documented by abundant secondary ferrotapiolite at Laštovičky, is exceptional among products of secondary replacement after primary (Nb,Ta)-oxide minerals in granitic pegmatites. High Fe₂O₃ in ferrotapiolite indicates high but variable *f*(O₂) during alteration. Values of Ta/(Ta + Nb) in primary stibiotantalite and secondary ferrotapiolite are virtually equal; they suggest very low mobility of both Nb and Ta. Absence of hydrothermal (fluid) fractionation of Nb from Ta in granitic pegmatites and low mobility of Ta and Nb documented here and in other studies support the importance of magmatic processes as a dominant factor in crustal fractionation of Ta from Nb.

Keywords: ferrotapiolite, stibiotantalite, hydrothermal alteration, Nb and Ta fractionation, lepidolite-bearing granitic pegmatite, Laštovičky, Czech Republic.

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SOMMAIRE

Une ferrotapiolite brun foncé et poreuse est le produit prédominant de l'altération par pseudomorphose de la stibiotantalite primaire d'une pegmatite à lépidolite de Laštovičky, en Moravie occidentale, République Tchèque. Deux variétés de ferrotapiolite sont distinguées, une riche en Fe^{3+} et largement prédominante, et l'autre riche en Sb. La ferrotapiolite riche en Fe^{3+} et en Nb, avec jusqu'à 17.51% de Nb_2O_5 (en poids; 0.61 *apfu*), est fortement hétérogène, avec $\text{Ta}/(\text{Ta} + \text{Nb})$ entre 0.69 et 0.84, et $\text{Mn}/(\text{Mn} + \text{Fe})$ entre 0.01 et 0.05; la teneur en Fe_2O_3 calculée atteint 3.09% (poids; 0.18 Fe^{3+} *apfu*, entre ~0.16 et 0.22 Fe^{3+} *apfu* selon la spectroscopie de Mössbauer). La variété riche en antimoine peut atteindre 9.87% (poids; 0.34 Sb^{3+} *apfu*). Les paramètres réticulaires de la ferrotapiolite riche en Fe^{3+} ($4.746 < a < 4.757$ Å, $9.198 < c < 9.244$ Å), calculés à partir des données en diffraction X (méthode des poudres) indique un degré d'ordre très variable. La substitution NbTa_{-1} est dominante; la substitution $\text{Fe}^{3+}_3\text{Fe}^{2+}_2\text{R}^{5+}_{-1}$ est moins importante, et semble indiquer la présence de Fe^{3+} aux deux sites de la structure, A et B, et donc une solution solide vers le pôle $\text{Fe}^{3+}\text{TaO}_4$. La substitution $\text{Sb}^{3+}_3\text{Fe}^{2+}_2\text{R}^{5+}_{-1}$ dans la seconde variété pourrait exprimer une solution solide vers le pôle SbTaO_4 , c'est-à-dire la stibiotantalite; toutefois, il est probable que le déplacement en composition est dû à la présence de reliques microscopiques de stibiotantalite primaire dans la ferrotapiolite, cachées sous la surface des échantillons polis. La stibiotantalite est remplacée par la ferrotapiolite le long de fractures distribuées de façon irrégulière selon la réaction hypothétique $2\text{Sb}(\text{Ta},\text{Nb})\text{O}_4 + \text{Fe}(\text{OH})_2 + 2\text{H}_2\text{O} = \text{Fe}(\text{Ta},\text{Nb})_2\text{O}_6 + 2\text{Sb}(\text{OH})_3$. Un tel enrichissement important en fer (stibiotantalite transformée en ferrotapiolite), documenté par la présence d'une abondance de ferrotapiolite secondaire à Laštovičky, est exceptionnelle parmi les produits du remplacement des oxydes primaires de (Nb,Ta) dans les pegmatites granitiques. Les teneurs élevées en Fe_2O_3 de la ferrotapiolite indiquent des niveaux élevés mais variables de $f(\text{O}_2)$ au cours de l'altération. Les valeurs de $\text{Ta}/(\text{Ta} + \text{Nb})$ dans la stibiotantalite primaire et la ferrotapiolite secondaire sont presque égales, ce qui fait penser que le Nb et le Ta ont une mobilité très faible. L'absence de fractionnement hydrothermal de Nb par rapport au Ta dans les pegmatites granitiques et la faible mobilité de Ta et Nb, établie ici et dans d'autres travaux, soulignent l'importance des processus magmatiques dans le fractionnement du Ta par rapport au Nb dans la croûte.

(Traduit par la Rédaction)

Mots-clés: ferrotapiolite, stibiotantalite, altération hydrothermale, fractionnement du Ta par rapport au Nb, pegmatite granitique à lépidolite, Laštovičky, République Tchèque.

INTRODUCTION

Products of hydrothermal alteration of stibiotantalite include a wide spectrum of minerals such as microlite and its antimonoan, uranoan and stannian varieties, stibiomicrolite, manganotantalite, cessstibantite, wodginite, natrotantite, alumotantite, sosedkoite, rynersonite, and fersmite (*e.g.*, Černý & Harris 1973, Foord & Mrose 1978, von Knorring & Sahama 1979, Voloshin *et al.* 1981, Voloshin & Pakhomovskiy 1983, 1988, Černý & Ercit 1985, Ercit 1986, Ercit *et al.* 1993, Baldwin 1989, Novák & Černý 1998a, Novák & Šrein 1999, Černý *et al.* 2004). Secondary ferrotapiolite after stibiotantalite is only known from the lepidolite pegmatite at Laštovičky (Staněk 1973, Novák & Černý 1998a). In addition, ferrotapiolite was described as a product of hydrothermal replacement of simpsonite from the localities Leshaiya, Kola Peninsula, Russia (Voloshin *et al.* 1981, Voloshin & Pakhomovskiy 1983), Tanco, Bernic Lake, Manitoba, Canada, and Alto do Giz, Minas Gerais, Brazil (Ercit 1986, Ercit *et al.* 1986), and as a replacement product of holtite (Voloshin & Pakhomovskiy 1988). Secondary ferrotapiolite recrystallized from remnants of an earlier generation of tapiolite was studied by von Knorring & Fadipe (1981) from the Bulema pegmatite, Uganda. Textural relations in the mineral assemblage involving ferrotapiolite, manganotapiolite, cassiterite, microlite and native antimony from the Tiainen pegmatite, Eräjärvi, Finland

(Lahti *et al.* 1983) also indicate a secondary origin of the tapiolite-series minerals.

Ferrotapiolite is a dominant product of alteration in pseudomorphs of stibiotantalite from the lepidolite pegmatite at Laštovičky, western Moravia, Czech Republic. Here we describe chemical composition, structural state and compositional relationship of ferrotapiolite to the parent stibiotantalite. This mineral assemblage seems to be confined to the system $\text{Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5\text{-Sb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-FeO}$. Zoned primary stibiotantalite enclosed in quartz and lepidolite is evidently suitable for the study of cation-exchange reactions between stibiotantalite and fluid to give ferrotapiolite (see Putnis 2002), mobility of the individual elements in the above system, and particularly the potential fractionation of Nb from Ta during the process of hydrothermal alteration (*e.g.*, Green 1995, Linnen & Keppler 1997).

OCCURRENCE AND PARAGENESIS

The Laštovičky pegmatite is situated in the northernmost part of the Bory pegmatite district, western Moravia (Fig. 1). The district comprises numerous symmetrically zoned pegmatite dikes with abundant schorl, biotite, muscovite, andalusite and sekaninaite. There are also several evolved phosphate-bearing pegmatites with primary (Fe,Mn)-phosphates (triplite, zwieselite, triphylite) and the most evolved lepidolite-subtype pegmatites, Laštovičky, Dobrá Voda and Dolní Bory,

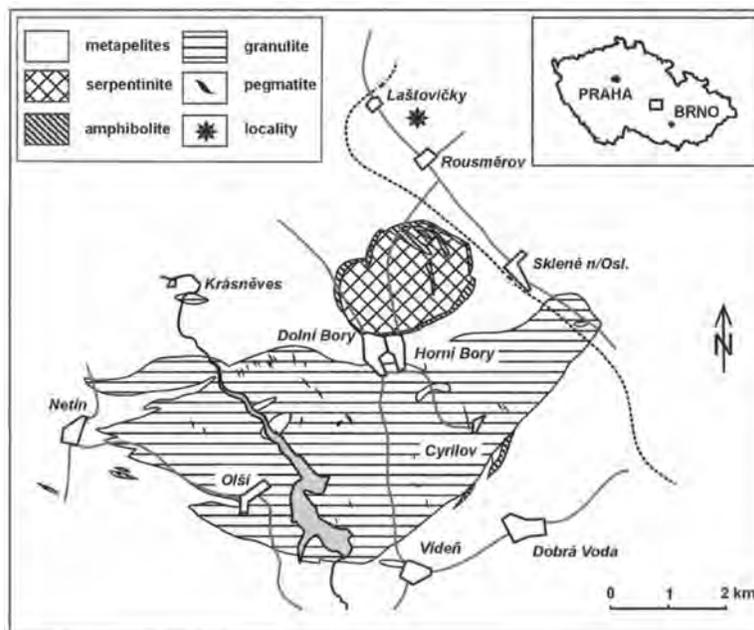


FIG. 1. Schematic geological map of the Bory pegmatite district, as modified from Duda (1986); the location of the Laštovičky pegmatite is indicated.

dike No. 21 (see Novák *et al.* 1992). The internal structure and mineralogy of the Laštovičky pegmatite were described by Staněk (1973), Novák & Černý (1998a), and Selway *et al.* (1999). The symmetrically zoned pegmatite dike, up to 1 m across, cross-cuts a biotite–sillimanite gneiss. It consists, from the contacts inward, of (i) a granitic zone (Kfs + Qtz + Pl + Ms + Bt), (ii) a graphic zone (Kfs + Qtz) evolving to (iii) blocky K-feldspar, (iv) an albite unit (Ab + Qtz + Ms–Lpd + Srl–Elb), and (v) a lepidolite unit (Lpd + Qtz + Ab + Elb) with rare pockets, situated in the center of the dike.

Niobium–tantalum oxide minerals are represented by columbite-group minerals, stibiotantalite, ferrotapiolite and very rare stibiomicrolite (Staněk 1973, Novák & Černý 1998a). Rare platy crystals (< 2 mm) of ferrocolumbite–manganocolumbite with $Ta/(Ta + Nb)_{at}$ in the range 0.12 to 0.15 and $Mn/(Mn + Fe)_{at}$ in the range 0.48 to 0.63 are closely associated with muscovite–quartz aggregates and green elbaite located in the outer part of the albite-dominant unit. A large crystal of manganocolumbite (~ 2 cm) from an albite–quartz aggregate associated with lepidolite in the inner part of albite unit was described by Staněk (1973).

METHODS

Ferrotapiolite and stibiotantalite were analyzed on a Cameca Camebax SX–50 instrument in wavelength-dis-

persion (WDS) mode at the Department of Geological Sciences, University of Manitoba, Winnipeg: a beam diameter of 1–2 μm , an accelerating potential of 15 kV, a sample current of 20 mA and a counting time of 20 s were used for Ca, Nb, and Ta; 40 mA and 50 s were used for Ba, Fe, Mn, Pb, Sb, Bi, Sn, Ti, U, Si, and W. The following standards were used: manganotantalite ($TaM\alpha$), $MnNb_2O_6$ ($MnK\alpha$, $NbL\alpha$), $FeNb_2O_6$ ($FeK\alpha$), $CaNb_2O_6$ ($CaK\alpha$), SnO_2 ($SnL\alpha$), quartz ($SiK\alpha$), rutile ($TiK\alpha$), $BiTaO_4$ ($BiM\alpha$), mimetite ($PbM\alpha$), stibiotantalite ($SbL\alpha$), UO_2 ($UM\alpha$), $Ba_2NaNb_5O_{15}$ ($BaL\alpha$) and metallic W ($WM\alpha$). The data were reduced using the PAP routine of Pouchou & Pichoir (1984, 1985). Some of the chemical analyses were performed on a JEOL JXA–50 electron microprobe at the Geological Institute of Academy of Sciences, Prague, operating in a WDS mode, at an accelerating potential of 20 kV and a specimen current of 1.5 to 3.0 nA. The following standards were used: ferberite ($WM\alpha$), metallic Ta ($TaM\alpha$), $LiNbO_3$ ($NbL\alpha$), cassiterite ($SnL\alpha$), TiO_2 ($TiK\alpha$), ZrO_2 ($ZrL\alpha$), SiO_2 ($SiK\alpha$), metallic Sc ($ScK\alpha$), metallic Sb ($SbL\alpha$), Fe_2O_3 ($FeK\alpha$), Mn_3O_4 ($MnK\alpha$), apatite ($CaK\alpha$), pyroxene ($CaK\alpha$). The data were reduced using ZAF corrections. Normalization on three cations and six atoms of oxygen per formula unit was used for calculation of Fe^{3+} in ferrotapiolite.

^{57}Fe Mössbauer spectroscopy was carried out at the Institute of Physics of Materials, Academy of Sciences, Brno, Czech Republic. Mössbauer spectra of tapiolite were collected at room temperature (RT MS) in transmission geometry using ^{57}Co in a Rh source with a 1024-register multichannel analyzer. The spectrum was processed using a standard package of computer programs by a least-squares procedure assuming Lorentzian line shapes constrained to equal linewidths. Results (isomer shift δ and quadrupole splitting σ) were calibrated with an α -Fe foil. Ferrotapiolite is a strong gamma-ray absorber because of its high Ta content. Thus it was not possible to work with an ideal thickness of sample to obtain high-quality spectra, because the amount of available material was limited and its texture is porous (with potential relics of stibiotantalite).

X-ray powder-diffraction data were obtained on a computer-controlled X-ray diffractometer Stadi-P (Stoe & Cie GmbH) in transmission mode, with $\text{CoK}\alpha_1$ radiation [with a Ge (111) monochromator], externally calibrated with Si (NBS 640b) and position-sensitive detector at the Institute of Geological Sciences, Masaryk University, Brno. The diffraction patterns were evaluated and unit-cell dimensions were refined using the Stoe WinXPow software package. The porosity of the ferrotapiolite was measured from BSE images of the polished surface; the software SigmaScan Pro was used for image analysis.

RESULTS

Description of stibiotantalite and ferrotapiolite

Bright yellow stibiotantalite forms irregular grains and loose fragments of crystals, up to 8 mm in size, all

showing a good cleavage. It is commonly found in debris inside the pockets. Stibiotantalite is associated with quartz, pink elbaite to rossmanite, and pale violet trilithionite, but its paragenetic position among the pocket minerals is not clear (Staněk 1973). It contains very rare, tiny inclusions of native antimony ($\leq 2 \mu\text{m}$). Subhedral grains of stibiotantalite ($\leq 3 \text{mm}$) also are enclosed in massive quartz and in coarse flakes of lepidolite located close to the pockets.

Stibiotantalite is replaced along irregularly developed fractures by dark brown, porous ferrotapiolite (Fig. 2). The measured porosity varies from 28 vol.% in fresh portions to ~50% in relatively weathered portions of ferrotapiolite, where pores were commonly filled by late hydrothermal clay minerals (possibly montmorillonite and cookeite; Fig. 2). The ferrotapiolite may volumetrically predominate over primary stibiotantalite, but no ferrotapiolite or other (Nb,Ta)-oxide minerals were observed outside the replaced stibiotantalite grains. The observed sequence of replacement is: stibiotantalite (with small inclusions of native antimony) \rightarrow very rare stibiomicrolite (with small inclusions of cesstibantite) \rightarrow ferrotapiolite. The sequence is similar to that observed in the Dobrá Voda pegmatite, located in the Bory pegmatite district (Novák & Černý 1998a, Novák & Staněk 1999).

On the basis of chemical composition, we recognized two compositionally distinct varieties of ferrotapiolite at Laštovičky: a volumetrically dominant ferrian variety and a very rare Sb-rich variety. The latter variety forms small, irregular areas ($\leq 50 \mu\text{m}$), brighter in the BSE image than the ferrian variety. The measured porosity and a large part of chemical compositions presented here pertain to the volumetrically dominant ferrian variety; Mössbauer spectra and X-ray-diffraction

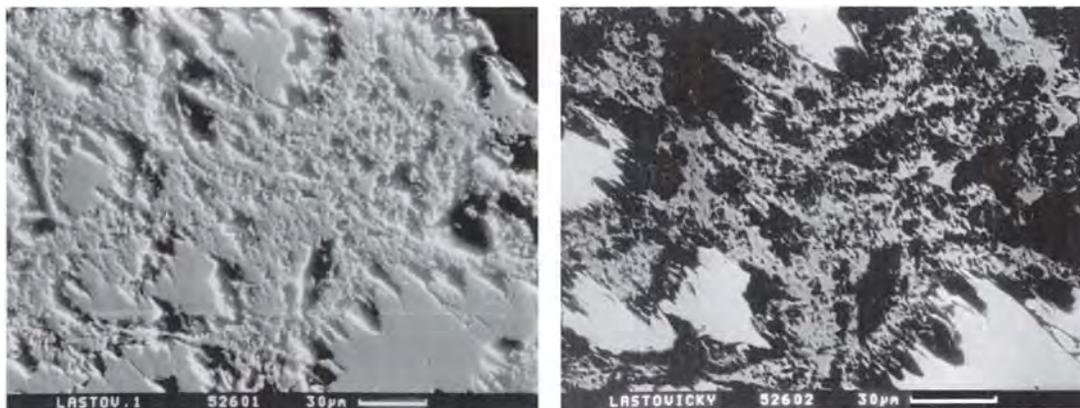


Fig. 2. SEM (a) and BSE (b) images of primary stibiotantalite (bright in BSE) and secondary Fe^{3+} -rich ferrotapiolite (grey in BSE). Note the high porosity of the ferrotapiolite; pores (black in BSE) are commonly filled by clay minerals.

data had to be unavoidably collected on mixtures with variable proportions of the two varieties; however, the ferrian variety very likely predominated in all samples.

Chemical composition, Mössbauer spectroscopy and X-ray powder diffraction

Primary stibiotantalite exhibits significant zoning in terms of Ta/(Ta + Nb), which ranges from 0.67 to 0.92 from core to rim (Table 1). Minor elements include Sn (≤ 0.67 wt.% SnO₂) and W (≤ 0.55 wt.% WO₃). Other elements such as Ti, Bi, U, Pb, Fe and Mn were mostly detected in minor quantities close to or below their detection limits.

Ferrotapiolite is highly heterogeneous in Ta/(Ta + Nb), from 0.69 to 0.84, and it has a very high Nb content, up to 0.61 *apfu* (Table 1). Most of the Ta/(Ta + Nb) values are tightly clustered, but a single composition with 0.61 *apfu* Nb surpassed the highest Nb content recorded to date in the minerals of the tapiolite series (as reviewed by Wise & Černý 1996). Values of Mn/(Mn + Fe) are very low, from 0.01 to 0.05. Concentrations of minor elements in both compositional types of ferrotapiolite include W (≤ 1.61 wt.% WO₃), Mn (≤ 0.76 % MnO), Ti (≤ 0.28 % TiO₂), Ca (≤ 0.13 % CaO), Fe (≤ 3.09 % Fe₂O₃_{calc}; 0.18 *apfu* Fe³⁺) in the ferrian variety, and particularly Sb (≤ 9.87 % Sb₂O₃; 0.34 *apfu* Sb³⁺) in the antimonoan variety.

In order to verify our calculation of Fe³⁺ content from stoichiometry, we performed measurements on Mössbauer spectra. The representative room-temperature spectra of ferrian ferrotapiolite (Fig. 3) are characterized by two absorption maxima showing a predominance of Fe²⁺; complex absorption overlaps occur near the Fe³⁺ quadrupole envelopes. All samples thus were fitted to three quadrupole doublets with ⁵⁷Fe hyperfine parameters characteristic of high-spin Fe²⁺ in octahedral coordination. Hyperfine parameters are: $\delta = 1.10(1)$, $1.06(1)$ and $1.14(2)$ mm/s and $\sigma = 3.02(1)$, $2.52(1)$ and $1.85(2)$ mm/s, respectively. Hyperfine parameters are similar to those presented by Kinast *et al.* (2002). At least three additional doublets of Fe³⁺ in octahedral coordination could be fitted, but their hyperfine parameters vary, depending on the specific fit model (more fit models are possible owing to complex overlaps within the range 0 to 1.5 mm/s of the spectra and low Mössbauer response of our samples). Hyperfine parameters of Fe³⁺ for the best-fit model are: $\delta = 0.20$, 0.40 and 0.50 mm/s and $\sigma = 0.43$, 0.62 and 1.04 , respectively (the latter doublet seems to represent charge balance between Fe²⁺ and Fe³⁺). For ferrian ferrotapiolite, the proportion of Fe³⁺ varies from 16 to 22% of the total Fe, depending on fit model used for solution of any given spectrum. Thus the calculated and Mössbauer-determined contents of Fe³⁺ are in mutual agreement, confirming the general validity of the stoichiometric calculation introduced by Ercit (1986). However, we prefer the values calculated from stoichi-

ometry for crystal-chemical discussion, because of the ambiguities involved in interpreting our Mössbauer spectra.

The structural formula of ferrotapiolite (Table 1) varies between $A(\text{Fe}^{2+}_{0.93}\text{Fe}^{3+}_{0.04}\text{Mn}_{0.03})_{\Sigma 1.00} B(\text{Ta}_{1.57}\text{Nb}_{0.38}\text{W}_{0.02}\text{Sn}^{4+}_{0.01}\text{Fe}^{3+}_{0.02})_{\Sigma 2.00} \text{O}_{6.00}$ and $A(\text{Fe}^{2+}_{0.85}\text{Fe}^{3+}_{0.12}\text{Mn}_{0.02})_{\Sigma 1.00} B(\text{Ta}_{1.52}\text{Nb}_{0.39}\text{W}_{0.01}\text{Sn}^{4+}_{0.01}\text{Fe}^{3+}_{0.06})_{\Sigma 2.00} \text{O}_{6.00}$ for Sb-free ferrotapiolite, and between $A(\text{Fe}^{2+}_{0.90}\text{Sb}^{3+}_{0.07}\text{Mn}_{0.01})_{\Sigma 1.01} B(\text{Ta}_{1.63}\text{Nb}_{0.33}\text{W}_{0.01}\text{Sn}^{4+}_{0.02})_{\Sigma 1.99} \text{O}_{6.02}$ and $A(\text{Fe}^{2+}_{0.83}\text{Sb}^{3+}_{0.21}\text{Mn}_{0.01})_{\Sigma 1.05} B(\text{Ta}_{1.56}\text{Nb}_{0.35}\text{W}_{0.01}\text{Sn}^{4+}_{0.02})_{\Sigma 1.95} \text{O}_{6.01}$, locally $A(\text{Fe}^{2+}_{0.73}\text{Sb}^{3+}_{0.34}\text{Mn}_{0.01})_{\Sigma 1.08} B(\text{Ta}_{1.53}\text{Nb}_{0.35}\text{W}_{0.01}\text{Sn}^{4+}_{0.03})_{\Sigma 1.92} \text{O}_{6.04}$ for antimonoan ferrotapiolite, respectively.

Unit-cell dimensions of the secondary ferrotapiolite were calculated from X-ray powder-diffraction records (Table 2). The samples studied yielded one of three

TABLE 1. CHEMICAL COMPOSITIONS OF THE LAŠTOVIČKY STIBIOTANTALITE (SB SERIES) AND FERROTAPIOLITE (OTHERS)

	SB TA2	SB TA4	SB TA5	3104	16 TAP	16 TAP	17 TAP	15 TAP	15 TAP	3
WO ₃ wt%	0.45	0.36	0.55	1.61	0.84	0.66	0.57	0.71	0.44	0.34
Nb ₂ O ₅	12.80	5.63	3.90	17.5	10.40	10.10	10.80	9.06	9.57	9.41
Ta ₂ O ₅	40.90	52.60	53.70	66.3	70.60	71.10	69.30	70.20	70.10	67.75
TiO ₂	0.02	0.03	0.02	0.28	0.01	0.04	0.01	0.04	0.02	0.02
SiO ₂	0.00	0.00	0.00	0	0.01	0.00	0.00	0.05	0.02	0.04
SnO ₂	0.53	0.80	0.67	0.00	0.15	0.59	0.42	0.67	0.75	0.80
UO ₃	0.08	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.13	0.03
Sb ₂ O ₃	43.00	40.10	40.60	0.1	0.04	0.04	0.00	4.13	6.12	9.87
Bi ₂ O ₃	0.00	0.00	0.37	0	0.05	0.03	0.00	0.11	0.02	0.06
Fe ₂ O ₃ *	-	-	-	0.00	1.02	1.88	3.09	0.00	0.00	0.00
FeO*	0.00	0.06	0.00	14.19	13.72	13.46	13.05	12.61	12.11	10.51
MnO	0.01	0.00	0.00	0.76	0.38	0.27	0.33	0.21	0.20	0.17
CaO	0.00	0.00	0.00	0.13	0.00	0.05	0.04	0.01	0.04	0.00
BaO	0.00	0.11	0.19	0.00	0.14	0.01	0.02	0.08	0.03	0.00
PbO	0.00	0.00	0.00	0.00	0.13	0.31	0.00	0.15	0.00	0.05
Total	97.79	99.69	100.00	100.86	97.48	98.54	97.71	98.03	99.55	99.05
W ⁶⁺ <i>apfu</i>	0.007	0.005	0.008	0.032	0.018	0.014	0.012	0.015	0.009	0.007
Nb ⁵⁺	0.332	0.150	0.105	0.605	0.384	0.368	0.393	0.339	0.353	0.353
Ta ⁵⁺	0.638	0.842	0.869	1.377	1.567	1.561	1.517	1.580	1.558	1.529
Ti ⁴⁺	0.001	0.001	0.001	0.016	0.001	0.002	0.001	0.002	0.001	0.001
Si ⁴⁺	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.004	0.002	0.003
Sn ⁴⁺	0.012	0.019	0.016	0.000	0.005	0.019	0.013	0.022	0.024	0.026
Sb ³⁺	-	-	-	0.000	0.024	0.036	0.064	0.000	0.000	0.000
Σ_{B} site	0.990	1.018	0.999	2.030	2.000	2.000	2.000	1.962	1.947	1.919
U ⁶⁺	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.002	0.001
Bi ³⁺	0.000	0.000	0.006	0.000	0.001	0.001	0.000	0.002	0.000	0.001
Fe ²⁺	0.000	0.003	0.000	0.907	0.927	0.893	0.855	0.873	0.827	0.729
⁴ Fe ³⁺	0.000	0.000	0.000	0.000	0.038	0.076	0.118	0.000	0.000	0.000
Sb ³⁺	1.017	0.974	0.996	0.003	0.001	0.001	0.000	0.141	0.206	0.337
Mn ²⁺	0.000	0.000	0.000	0.049	0.026	0.018	0.022	0.015	0.014	0.012
Ca ²⁺	0.000	0.000	0.000	0.011	0.000	0.004	0.003	0.001	0.003	0.000
Ba ²⁺	0.000	0.003	0.004	0.000	0.004	0.000	0.001	0.003	0.001	0.000
Pb ²⁺	0.000	0.000	0.000	0.000	0.003	0.007	0.000	0.003	0.000	0.001
Σ_{A} site	1.018	0.980	1.006	0.970	1.000	1.000	1.000	1.038	1.053	1.081
Σ cations	2.008	1.997	2.005	3.000	3.000	3.000	3.000	3.000	3.000	3.000
O ²⁻	4.000	4.000	4.000	6.055	6.000	6.000	6.000	6.012	6.014	6.038
Fe ²⁺ /Fe _{tot}	-	1.000	-	1.000	0.937	0.889	0.824	1.000	1.000	1.000

* The ratio Fe²⁺/Fe³⁺ was calculated on the basis of a charge-balanced formula. Na, K, Cs, and F are below the detection limit.

distinct patterns with different degrees of order and differences in apparent content of Fe^{3+} (Fig. 4). Concentrations of W, Ti and Sn are generally very low, thus the content of Fe^{3+} may be correlated with variations of cation order. However, the structural features do not seem to be simply related to fluctuations in the chemical composition (*cf.* discussion in Wise & Černý 1996).

DISCUSSION

Chemical composition and mechanisms of substitution

Values of $\text{Mn}/(\text{Mn}+\text{Fe})$ in ferrotapiolite are very low (Fig. 5) and comparable to those in ferrotapiolite from less fractionated granitic pegmatites (Černý *et al.* 1992) and rare-metal granites (Wang *et al.* 1997). The volumetrically dominant ferric variety contains Fe^{3+} concentrations, calculated from stoichiometry and confirmed by Mössbauer spectroscopy to be as high as 0.21 *apfu*. The dominant substitution NbTa_{-1} and the minor substitution $\text{Fe}^{3+}_3\text{Fe}^{2+}_2\text{R}^{5+}_{-1}$, which relates end-member ferrotapiolite component ($\text{Fe}^{2+}\text{Ta}_2\text{O}_6$) to a hypothetical rutile-structured $\text{Fe}^{3+}\text{TaO}_4$ component, are inferred. The latter substitution derived from negative correlations $\text{W} + \text{Nb} + \text{Ta}$ versus Fe^{3+} and $\text{Fe}^{2+} + \text{Mn}$ versus Fe^{3+} (Fig. 6) is not mentioned by Wise & Černý (1996). It implies incorporation of Fe^{3+} at both *A* and *B* sites in the ferrotapiolite structure.

The complicated Mössbauer spectrum of the sample studied indicates a disordered structure with most Fe^{2+} in FeO_6 octahedra, and with the Fe^{3+} probably split between the FeO_6 and TaO_6 octahedra, or a domain structure with short-ordered domains of ferrotapiolite but without long-range continuity in terms of cation order. Different Fe^{2+} doublets could result from disorder at one site, where a particular atom of Fe could be surrounded by different cations in second coordination shell (next-nearest-neighbor effect), or it could also suggest incorporation of part of Fe^{2+} into the TaO_6 octahedra. The Mössbauer spectra of ferrotapiolite crystals from Laštovičky were certainly influenced by the highly het-

TABLE 2. UNIT-CELL DIMENSIONS OF FERROTAPIOLITE FROM THE LAŠTOVIČKY PEGMATITE

Sample	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Las1a	4.7506 (7)	9.2412 (21)	208.56 (5)
Las1b	4.7500 (7)	9.2443 (17)	208.57 (4)
Las2	4.7575 (4)	9.2213 (10)	208.72 (2)
Las3	4.7567 (4)	9.2198 (11)	208.61 (3)
Las5*	4.7579 (6)	9.2267 (18)	208.87 (5)
Las6*	4.7459 (3)	9.1976 (10)	207.17 (3)
Las7	4.7459 (3)	9.2013 (12)	207.25 (3)
Las8	4.7457 (5)	9.1986 (15)	207.17 (4)

* Refined from mixture with stibiotantalite.

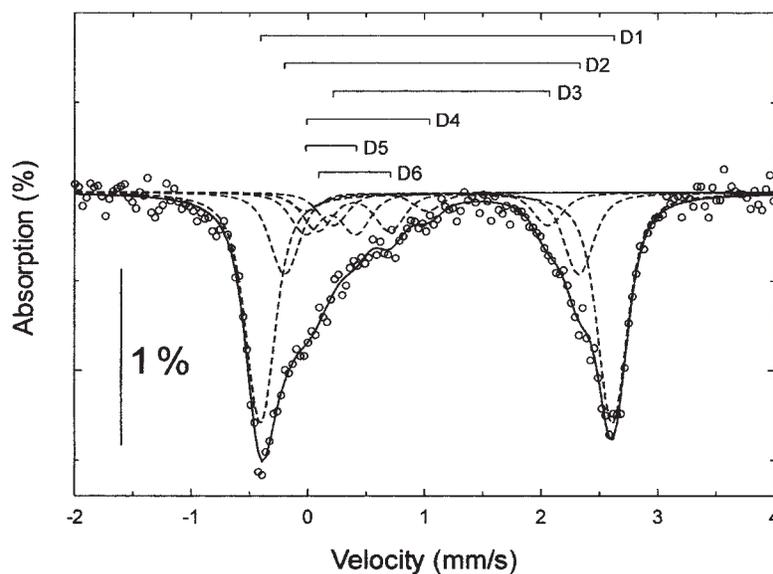


FIG. 3. Representative ^{57}Fe Mössbauer spectrum of Fe^{3+} -rich ferrotapiolite, obtained at room temperature. Open circles: observed data; solid line: the calculated spectrum based on least-squares procedure; dashed lines: the calculated subspectra. D1–D3: Fe^{2+} in octahedral coordinations; D4–D6: Fe^{3+} in octahedral coordinations (D4 could represent charge-balanced iron).

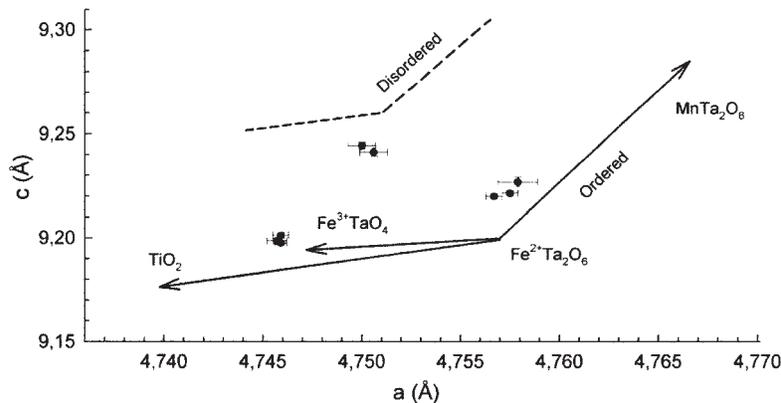


FIG. 4. The a and c unit-cell dimensions of the Laštovičky ferrotapiolite in the grid of Wise & Černý (1996).

erogeneous character of the samples studied, with variable $Ta/(Ta + Nb)$ values, distinct unit-cell dimensions and degree of structural order, as well as likely contamination by included minerals, as well as potential weathering.

The EMP analyses of the very rare antimonian variety yielded up to 9.87 wt.% Sb_2O_3 (0.34 *apfu* Sb), by far the highest content of Sb recorded in ferrotapiolite (*cf.* Wise & Černý 1996, Novák & Černý 1998a); however, the valence state of Sb is not clear. Nevertheless, the presence of Sb^{3+} in the ferrotapiolite structure, as was found in a rutile-type-structure mineral tripuhyite $Fe^{3+}Sb^{5+}O_4$ (Berlepsch *et al.* 2003), is not likely owing to the sum of anions higher than ideal 6 *apfu*. Assuming the presence of Sb^{3+} in the ferrotapiolite structure, the negative correlations $Nb + Ta + W$ versus Sb^{3+} and $Fe^{2+} + Mn$ versus Sb^{3+} (Fig. 6) suggest the substitution $Sb^{3+}_3Fe^{2+}_2R^{5+}_{-1}$. Such a mechanism of substitution leads to the end-member composition $SbTaO_4$.

It is noteworthy that ferrotapiolite with the second highest Sb content (1.20 wt.% Sb_2O_3 , found in a single analyzed spot), from the Tiainen pegmatite, in Finland, contains numerous microscopic inclusions of native antimony (Lahti *et al.* 1983). Consequently, the presence of microscopic inclusions of Sb-rich minerals in ferrotapiolite (native antimony at the Tiainen pegmatite, relics of stibiotantalite at Laštovičky), the nonexistence of $SbTaO_4$ having the rutile structure and the strong stereoactive character of Sb^{3+} , deforming octahedral sites (see Ercit & Foord 1995), suggest that the high contents of Sb_2O_3 found in ferrotapiolite (Lahti *et al.* 1983, Novák & Černý 1998a, this work) probably reflect the presence of microscopic inclusions of a Sb-rich mineral (primary stibiotantalite at Laštovičky), hidden below the polished surface of the analyzed spots. It

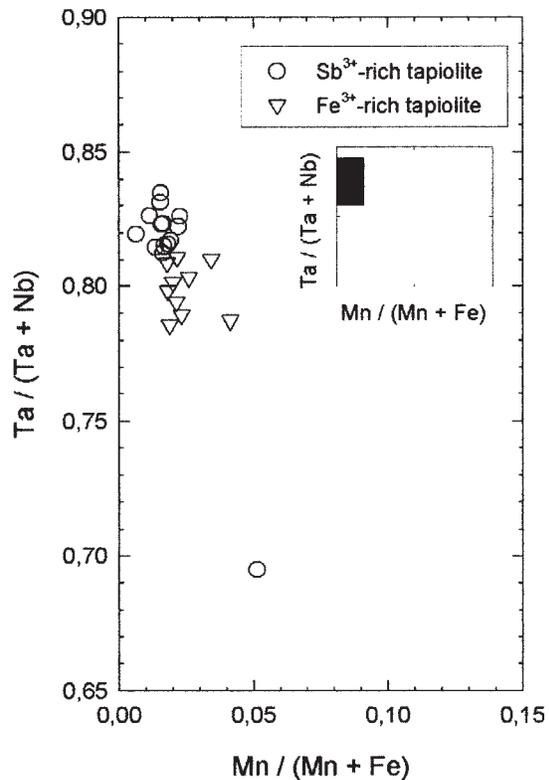


FIG. 5. The Laštovičky ferrotapiolite in the columbite quadrilateral (atom ratios).

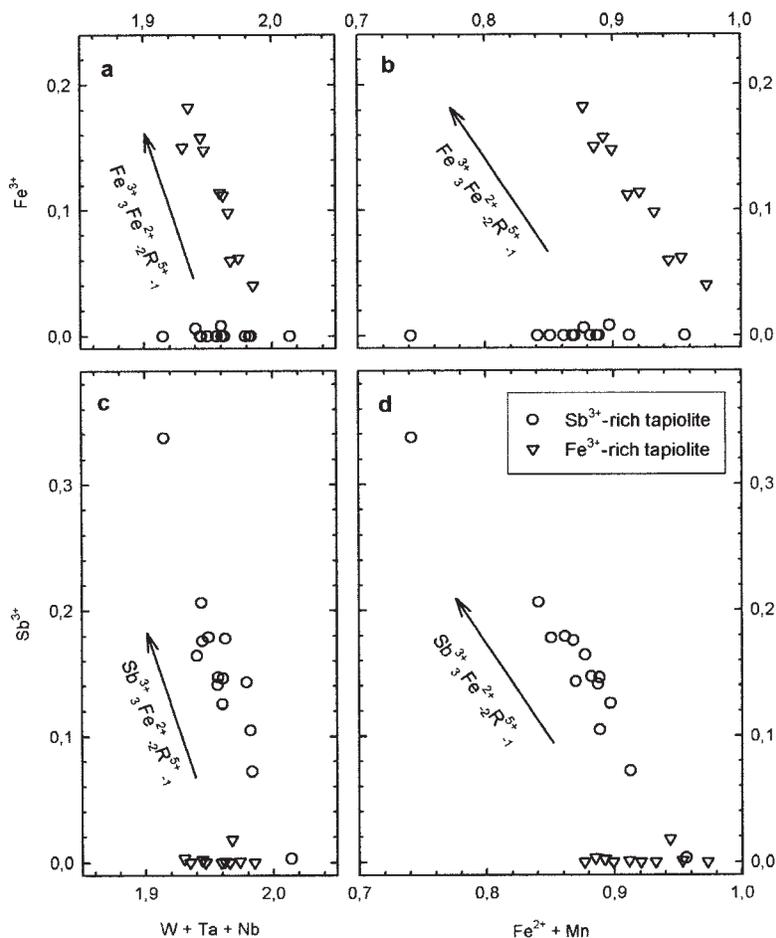
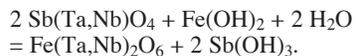


FIG. 6. Composition of the Laštovičky ferrotapiolite: a) W + Nb + Ta versus Fe^{3+} , b) Fe^{2+} + Mn versus Fe^{3+} , c) W + Nb + Ta versus Sb^{3+} , and d) Fe^{2+} + Mn versus Sb^{3+} . Substitution vectors: $\text{Fe}^{3+}_3\text{Fe}^{2+}_2\text{R}^{5+}_{-1}$ (a, b); $\text{Sb}^{3+}_3\text{Fe}^{2+}_2\text{R}^{5+}_{-1}$ (c, d), both leading to $M^{3+}\text{TaO}_4$.

seems likely that Sb does not enter the ferrotapiolite structure, or if so, only in a minor quantity.

Replacement process and mobility of Ta and Nb

Stibiotantalite is replaced by ferrotapiolite along irregularly distributed fractures (Fig. 2). Trace amounts of microlite minerals and cesstibtantite in pseudomorphs show initial low alkali content in altering fluids, followed by strong enrichment in iron. The textural relations between both major minerals and the host quartz or lepidolite suggest the following hypothetical reaction, assuming a constant amount of (Ta,Nb) and the complete removal of Sb from the system, because we did not find any relics of a secondary Sb-phase (*e.g.*, valentinite or senarmontite) in the pores:



Because ferrotapiolite is the only replacement product observed, the reaction requires a 35% decrease of the volume occupied by the precursor. This value is in good agreement with the porosity of fresh, clay-mineral-free portions of the polished sections measured in the BSE image (~28%), but higher in weathered portions of ferrotapiolite with pores filled by clay minerals (~50%).

Textural relations and chemical composition indicate that this reaction represents an example of a dissolution–recipitation reaction [see Putnis (2002) and references therein], where pentavalent cations Ta and Nb are preserved in the system, but Sb is completely removed and Fe is incorporated into the structure of newly formed

ferrotapiolite during the replacement. It involves reorganization of the TaO₆ sheets of stibiotantalite (Černý & Ercit 1989) into the TaO₆ framework octahedra in ferrotapiolite. The porosity estimates, which are in agreement with the above model, show that the mobility of Ta(Nb) in hydrothermal conditions at Laštovičky is low.

The textural pattern of replacement of primary stibiotantalite is similar to that observed in stibiotantalite replaced by microlite, manganotantalite and an undetermined (Fe > Mn, Ta > Nb) phase at Dobrá Voda, where a temperature of ~500–350°C is suggested (Novák & Černý 1998a). High but variable contents of Fe₂O₃ in ferrotapiolite (*cf.* Wise & Černý 1996), as monitored by a Mössbauer study and calculated from stoichiometry (see Figs. 3, 6) should indicate generally elevated *f*(O₂) during the alteration process; however, high variation in Fe₂O₃ suggests strong local variation in *f*(O₂). Consequently, the replacement of stibiotantalite by ferrotapiolite is a hydrothermal, fluid-induced, subsolidus process; however, we are not able to specify its P–T–X conditions. The presence of cookeite and clay minerals in pores indicates that ferrotapiolite formation precedes the formation of such phyllosilicates and clay minerals in the pegmatite, although we do not know whether clay minerals in pores formed during low-temperature hydrothermal process or they were transported to pores during subsurface migration.

Another example of an alteration process similar to that of Laštovičky is provided by the intimate intergrowths of kimrobinsonite and cesstibtantite resulting from weathering of an unknown (Nb,Ta)-oxide mineral (possibly stibiotantalite or cesstibtantite; Nickel & Robinson 1985). Its cryptocrystalline character and soft nature indicate porosity, although it is not mentioned by the authors. Assuming immobile Ta(Nb), the volume of these secondary assemblage would be decreased by approximately 30 vol.%, considering both potential precursors (stibiotantalite or cesstibtantite).

Element fractionation during hydrothermal alteration

The simple assemblage stibiotantalite + ferrian ferrotapiolite is confined to the system Ta₂O₅–Nb₂O₅–Sb₂O₃–Fe₂O₃–FeO. Antimony and Fe are dominant cations at the A sites, with mere traces of Mn, Ca, Sb and Cs (Table 1). Hence, the compositional evolution of late minerals in Laštovičky is relatively simple in contrast to possibilities that involve a wide spectrum of cations such as Ca, Na, Sb, Bi, Cs, Mn, Fe, Pb, Ba, K, Sr, Sn, and U commonly participating during late hydrothermal alteration of stibiotantalite or other primary (Nb,Ta)-oxide minerals such as simpsonite or microlite (*e.g.*, Černý & Harris 1973, Foord & Mrose 1978, Nickel & Robinson 1985, Ercit 1986, Groat *et al.* 1987, Voloshin & Pakhomovskiy 1988, Uher *et al.* 1998, Novák & Černý 1998a). Trace amounts of microlite-subgroup minerals and cesstibtantite in pseudomorphs

suggest initially elevated alkali contents in the fluid phase, followed by strong enrichment in iron. This trend is in agreement with replacement processes affecting primary (Nb,Ta)-oxide minerals in granitic pegmatites from the Moldanubicum (*e.g.*, Dobrá Voda; Novák & Černý 1998a).

The elements at the B site of stibiotantalite include Ta and Nb, besides minor Fe³⁺ and perhaps Fe²⁺, and traces of W and Ti that are considered to enter this site. The stibiotantalite crystals exhibit a simple zonal pattern with an increase in Ta/(Ta + Nb) from core to rim. The variability in Ta/(Ta + Nb) of the parent stibiotantalite is reflected in that of secondary ferrotapiolite. Closely adjacent analyzed spots along contacts of stibiotantalite and ferrotapiolite yielded largely equal, or exceptionally very slightly decreased Ta/(Ta + Nb) values in the secondary ferrotapiolite.

Iron enrichment during late stages of pegmatite crystallization (late magmatic to early subsolidus) has been recorded at some localities, especially in tourmaline (Foord 1976, Zagorskyi & Peretyazhko 1992, Dutrow & Henry 2000, Novák & Taylor 2000) and rarely in micas (Novák & Černý 1998b). However, only a few data have been published about the subsolidus behavior of Mn and Fe in (Nb,Ta)-oxide minerals. An increase of Fe was described in alteration products of simpsonite (Ercit 1986), in manganotantalite replaced by ferrotantalite from the Rubikon pegmatite, Namibia (Baldwin 1989), in holtite replaced by ferrotapiolite (Voloshin & Pakhomovskiy 1988), in products of replacement of stibiotantalite from the Moldanubicum, Czech Republic (Novák & Černý 1998a), and in secondary ferrocolumbite after primary manganocolumbite at Rošná, Czech Republic (Novák & Černý 2001). However, the strong dominance of Fe over other elements, as was found at Laštovičky, is exceptional.

Implications to fractionation of Nb from Ta in the crust

Values of Ta/(Ta + Nb) are typically found to be equal in the products of replacement of primary minerals such as stibiotantalite, simpsonite, manganocolumbite (Černý & Ercit 1985, 1989, Ercit 1986, Ercit *et al.* 1986, Novák & Černý 1998a, 2001, Smeds *et al.* 1999, Černý *et al.* 2004), and they were also retained in pyrochlore-group minerals during geochemical alterations (Lumpkin & Ewing 1992, 1995). Uher *et al.* (1998) and Baldwin (1989) are the only authors to have described minor changes in Ta/(Ta + Nb) between primary and secondary phases.

The secondary phases formed during various stages of hydrothermal alteration, from early subsolidus at T ≈ 500°C to near-surface weathering (Nickel & Robinson 1985, Novák & Černý 1998a). The low mobility of both Nb and Ta is suggested, even over distances of <1 mm, and thus preserve the Ta/(Ta + Nb) values of the precursors in the alteration products. Thus subsolidus

alteration does not affect the apparent degree of fractionation of Ta *versus* Nb attained during primary magmatic crystallization in granitic pegmatites.

The constancy of Ta/(Ta + Nb) from primary minerals to their subsolidus alteration products in both initial alkali-rich and late alkali-poor conditions and in variable P–T conditions from early subsolidus to near-surface weathering is a typical feature of rare-element granitic pegmatites (*e.g.*, Ercit 1986, Novák & Černý 1998a, 2001, Černý *et al.* 2004, this work). Consequently, fluid-induced fractionation of Ta from Nb seems to be negligible in granitic pegmatites. It corroborates experimental work of London *et al.* (1989) with Macusani glass, which revealed that the fractionation in a peraluminous granitic system rich in volatiles is significantly suppressed during the subsolidus hydrothermal stage. It also suggests the low solubility of (Nb,Ta)-oxide minerals in aqueous conditions (Wood 2004).

The ratio Nb/Ta is widely used as an indicator of fractionation chiefly in magmatic rocks [*e.g.*, Linnen & Keppler (1997) and references therein]. Green (1995) suggested that the fluid/melt fractionation of Nb *versus* Ta in granitic pegmatites, with preference for Ta in the fluid, is the principal mechanism in crustal evolution. On the basis of a study of peraluminous granitic rocks from Nova Scotia, Dostal & Chatterjee (2000) considered differences in the Nb/Ta and Zr/Hf due to a fluid-removal mechanism, which decreased the Nb/Ta ratio in rocks (see also Hu *et al.* 1984). This contradicts the absence of hydrothermal (fluid) fractionation of Ta from Nb found in ferrotapiolite from Laštovičky (this work) and in other (Nb,Ta)-oxide minerals from granitic pegmatites (*e.g.*, Ercit 1986, Novák & Černý 1998a) and supports the interpretation of Linnen & Keppler (1997), who considered fractionation in melts sufficient to explain the low Nb/Ta value in the continental crust.

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