

**EFFECTS OF SILLIMANITE-GRADE METAMORPHISM AND
SHEARING ON Nb-Ta OXIDE MINERALS IN GRANITIC PEGMATITES:
MARŠÍKOV, NORTHERN MORAVIA, CZECHOSLOVAKIA**

PETR ČERNÝ

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

MILAN NOVÁK

Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 65937 Brno, Czechoslovakia

RON CHAPMAN

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The (Be,Nb,Ta)-bearing albite-muscovite pegmatites at Maršikov, in the Hrubý Jeseník Mountains pegmatite field of northern Moravia, Czechoslovakia, were subjected to a two-stage, sillimanite-grade, regional metamorphism that reached about 600°C and 4–6 kbar, $P(\text{total}) \gg P(\text{fluid})$. The first stage generated chrysoberyl at the expense of beryl, under relatively static conditions (pegmatite I), whereas extensive shearing during a second stage produced a second generation of chrysoberyl, abundant sillimanite and a foliation (pegmatite III). The primary assemblage of the Nb-Ta oxide minerals consisted of manganocolumbite-manganotantalite displaying oscillatory zoning in terms of Nb and Ta, replaced by fersmite and microlite (rarely pyrochlore). The columbite-tantalite was first recrystallized into "bird's-eye" oscillatory-zoned textures or heterogeneous granular aggregates. The original range of $Ta/(Ta + Nb)$ values was commonly reduced, although locally expanded by contribution of additional Nb or Ta from incipient breakdown of fersmite or microlite, respectively. $Mn/(Mn + Fe)$ largely decreased, by as much as 0.40, by introduction of Fe from the host hornblende gneiss; Mg and Ti also were enriched. During the second metamorphic stage, the $Ta/(Ta + Nb)$ value of columbite-tantalite was locally further homogenized, but $Mn/(Mn + Fe)$ did not change. Fersmite and microlite were almost completely obliterated. Significant ordering of the originally intermediate structural state of columbite-tantalite was promoted during metamorphic recrystallization. This study documents extensive compositional and structural re-equilibration of Nb-Ta oxide minerals at medium-grade regional metamorphic conditions. This pattern of behavior contrasts with their virtual inertness in an environment of mylonitization.

Keywords: niobium, tantalum, columbite-tantalite, fersmite, microlite, granitic pegmatite, regional metamorphism, Moravia, Czechoslovakia.

SOMMAIRE

Les pegmatites granitiques à albite et muscovite, riches en Be, Nb et Ta, situées à Maršikov, faisant partie de l'essaim de pegmatites des montagnes Hrubý Jeseník, dans le nord de la Moravie (Tchécoslovaquie), ont subi deux stades de métamorphisme régional, qui ont atteint le domaine de la sillimanite, à environ 600°C et de 4 à 6 kbar, $P(\text{total}) \gg P(\text{fluide})$. Le premier stade est responsable de la formation du chrysobéryl à partie du béryl dans un milieu relativement statique (pegmatite I). Par contre, un cisaillement répandu a accompagné le deuxième stade et a produit une deuxième génération de chrysobéryl, une abondance de sillimanite, et une foliation (pegmatite III). L'assemblage primaire des oxydes à Nb-Ta est fait de manganocolumbite - manganotantalite montrant une zonation oscillatoire impliquant Nb et Ta, et un remplacement par la fersmite et le microlite (localement, pyrochlore). Les grains de columbite - tantalite ont d'abord été recrystallisés en textures à zonation oscillatoire "en oeil d'oiseau" ou en agrégats granulaires hétérogènes. Cette recrystallisation mène en général à une réduction dans la variabilité des valeurs $Ta/(Ta + Nb)$, sauf exceptions locales où il y a eu addition de Nb ou Ta due à la déstabilisation de la fersmite ou du microlite, respectivement. Les valeurs de $Mn/(Mn + Fe)$ ont diminué en général, la réduction atteignant 0.40, par l'introduction de Fe de l'encaissant, un gneiss à hornblende. Mg et Ti ont aussi été ajoutés. Au cours du deuxième stade, la valeur de $Ta/(Ta + Nb)$ de la columbite - tantalite s'est homogénéisée davantage, sans affecter la valeur du rapport $Mn/(Mn + Fe)$. Fersmite et microlite ont quasiment été éliminés. La recrystallisation métamorphique a favorisé une mise en ordre de la columbite - tantalite, au départ dans un état structural intermédiaire. Notre étude indique un ré-équilibrage important de la composition et la structure des oxydes à Nb-Ta assujetties à des conditions de métamorphisme régional à intensité moyenne. Par contre, ces oxydes semblent relativement inertes dans les zones de mylonitisation.

(Traduit par la Rédaction)

Mots-clés: niobium, tantale, columbite-tantalite, fersmite, microlite, pegmatite granitique, métamorphisme régional, Moravie, Tchécoslovaquie.

INTRODUCTION

Fertile granites, along with their aureole of rare-element pegmatite bodies, are commonly emplaced in the waning stages of orogenic processes, after the culmination of regional metamorphism and deformation or after their cessation (Ginzbourg *et al.* 1979, Černý 1982, 1990). Deformation, recrystallization, mylonitization or metamorphism affecting rare-element pegmatites are usually superimposed, and unrelated to the event that generated the fertile magmas. Regional response to an adjacent younger orogenic event (Anderson 1984) and remobilization along host faults and shears (Eby 1986) are occasionally encountered, whereas extensive deformation during consolidation of the pegmatite is relatively rare (Němec 1989).

So far, the study of effects of deformation has been restricted to rock-forming silicates, on a regional scale (Rossovskiy 1974, Rossovskiy & Bovin 1971, Rossovskiy *et al.* 1976, Simpson 1977, Rossovskiy & Konovalenko 1979) or within the internal structure of a pegmatite body (Grip 1940, Wilson 1980, Eby 1986, Němec 1989). The effects of metamorphism *sensu stricto* were examined only sporadically, as pegmatites commonly behave as competent units that resist pervasive textural or compositional reworking. The few cases investigated in detail concern albite-spodumene pegmatites that show extensive recrystallization but minimal adjustments of mineral assemblages (Luster 1977, Chackowsky 1987, Göd 1989).

The only study focused on metamorphism of accessory minerals that contain rare elements was that of Franz & Morteani (1984), who examined the generation of chrysoberyl and sillimanite at the expense of beryl and muscovite in pegmatites of the Maršíkov area in the northern Moravia, Czechoslovakia. An essentially metamorphic assemblage of exotic Be-bearing minerals from Enderby Land, Antarctica, was generated during roughly coeval emplacement of pegmatite and granulite-facies metamorphism (Grew 1981).

In the present study, we examine effects of static and dynamic metamorphism on the accessory Nb-Ta oxide minerals at Maršíkov. This is, to the best of our knowledge, the first detailed study of this kind, prompted by the results obtained by Černý *et al.* (1986), Lahti (1987) and Voloshin & Pakhomovskiy (1988), which indicate considerable reactivity of Nb-Ta oxide minerals even in static medium- to low-temperature environments. The only observations of recrystallization, chemical equilibration and advanced structural ordering under the influence of deformation were made on ferrotapilolite-ferrotantalite intergrowths from Hercynian, Alpine-overprinted pegmatites (Černý

et al. 1989). As shown below, our expectation of extensive mobilization and re-equilibration of Nb-Ta oxide minerals at conditions of medium-grade metamorphism, spurred by metamorphic zoning of garnet (Novák 1988), was fully justified.

GENERAL CHARACTERISTICS OF THE JESENÍKY PEGMATITE POPULATION

The pegmatites are located in the Šumperk-Maršíkov pegmatite district, in the southern part of the Hrubý Jeseník Mountains pegmatite field of northern Moravia, Czechoslovakia (Fig. 1). Pegmatites of this field were studied by numerous authors since 1824 (Hruschka 1824), as summarized by Novák (1988) and Novák & Rejl (in prep.). These last authors propose the following scheme of classification for the Jeseníky pegmatites: (1) primitive biotite- to muscovite-bearing pegmatites with garnet having $Fe > Mn$, (2) muscovite pegmatites with K-feldspar, garnet with $Fe \cong Mn$ and accessory minerals of Be, Nb-Ta, Zn and B, and (3) muscovite pegmatites without K-feldspar, carrying garnet with $Fe < Mn$ and accessory minerals of Be, Nb-Ta and Zn. Beryl, chrysoberyl, gahnite and columbite-tantalite are typical for types (2) and (3), with rare schorl in the former. Zircon, apatite, triplite, magnetite, bismuth, arsenopyrite and pyrite are observed locally.

Pegmatite dikes and irregular bodies reach 1 to 10 m in width, and are discordant to concordant to the host metapelites (mica schists, two-mica and biotite gneisses), amphibolites and, rarely, granodiorites. The host metamorphic suite, Devonian or Proterozoic in age, was subjected to extensive medium-pressure Barrovian metamorphism (Souček 1978, René 1983: 5-7 kbar, 540-650°C); the pegmatites are found mainly in the staurolite and sillimanite zones.

Except for the biotite-bearing pegmatites hosted by granodiorites, almost all bodies display a metamorphic fabric, expressed locally by distinct foliation and metamorphic mineralogy: chrysoberyl, sillimanite and, exceptionally, andalusite (Franz & Morteani 1984, Novák 1988).

Internal structure, mineralogy and geochemistry of the Jeseníky pegmatites correspond to the beryl-columbite subtype of rare-element pegmatites (e.g., Černý 1991), ranging from Kfs + Ms (in part albitized) bodies to Ab + Ms pegmatites in bulk composition. However, the Barrovian metamorphic facies-series of the host rocks suggests that the muscovite-rich Jeseníky pegmatites should be classified as transitional between the rare-element and muscovite classes [characterized by Shmakin (1976), for example].

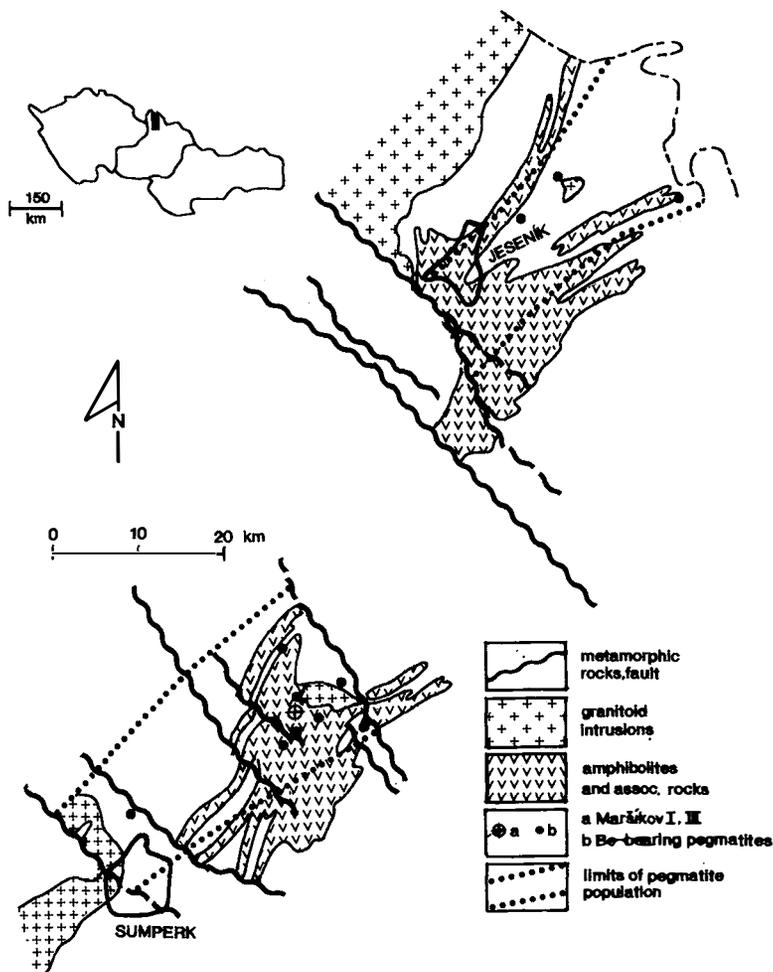


FIG. 1. Location and schematic geology of the Hrubý Jeseník Mountains pegmatite field in northern Moravia, Czechoslovakia.

SPECIFIC FEATURES OF THE PEGMATITES EXAMINED

The best known and most thoroughly examined pegmatites of the Hrubý Jeseník Mountains field crop out on the hill Schinderhübel, some 600 m northeast of the village of Maršíkov (ca. 10 km northeast of Šumperk). Our study of Nb-Ta oxide minerals was aimed at two of these pegmatites, Maršíkov I and III.

Maršíkov I

This zoned dike is hosted by hornblende gneiss. A medium-grained wall zone is composed of albite-oligoclase, quartz, muscovite, minor biotite, and garnet. It grades into an intermediate zone of

coarse-grained albite, quartz and muscovite; garnet is common, subhedral columnar beryl and small platy crystals of chrysoberyl are scarce, as are Nb-Ta oxide minerals, gahnite and rare zircon (Dostál 1964). K-feldspar also is very rare, in grains up to 2 cm in size. Thin layers of saccharoidal albite with garnet and muscovite are observed locally in the intermediate zone. The quartz core contains minor muscovite and albite, and some crystals of beryl. Bavenite, epidote, hematite and chlorite are found in fine fissures.

Maršíkov III

This is the classic locality of sillimanite-bearing pegmatite that yielded the first European occurrence of chrysoberyl (Hruschka 1824). The host

rock is a garnet-bearing biotite-hornblende gneiss, with biotite more abundant than hornblende along the contact with the pegmatite. The pegmatite was thoroughly metamorphosed; its lineation and foliation are concordant with those of the surrounding gneiss (Dostál 1966). The pegmatite attains 1 m in width and shows concentric zoning. The wall zone is aplitic, consisting of albite-oligoclase and quartz, subordinate muscovite and garnet, and rare biotite. A medium- to coarse-grained aggregate of albite + quartz + muscovite forms an intermediate zone as much as 20 cm in width; it carries most of the accessory minerals found in this dike (garnet, second-generation chrysoberyl, gahnite, Nb-Ta oxide minerals, zircon, bismuth). Lineated fibrous sillimanite is abundant here, generated at the expense of muscovite and probably also albite. The central quartz core attains 50 cm in width and contains platy muscovite, fibrous sillimanite, granular albite along its margins, relics of beryl replaced by first-generation chrysoberyl, garnet, gahnite and Nb-Ta oxide minerals. However, the proportion of accessory minerals is much lower than in the intermediate zone. Irregular layers or schlieren of saccharoidal albite with abundant garnet and subordinate muscovite, conformable to the overall fabric of the pegmatite, are found locally along the contacts of the intermediate zone and core (Dostál 1966). Bavenite, chlorite and epidote are rarely observed in fissures or in cleavage planes of muscovite flakes.

Mineral assemblages constituting both pegmatite dikes are shown in Figure 2, subdivided according to mode of formation.

Geochemical features

A few representative samples of muscovite were analyzed by atomic absorption spectrometry from the two pegmatites, and a single K-feldspar sample from dike III. Three muscovite samples from pegmatite I show average K/Rb and K/Cs ratios of 19.5 and 543, respectively, a Li content of 3830 ppm, and surprisingly low concentrations of Ba and Sr (in low tens of ppm to below detection limits of 5 ppm each). The respective averages for four muscovite samples from dike III are 19.4, 641, 3800 ppm, and Ba and Sr as low as in K-feldspar. The K-feldspar from dike III has a K/Rb of 64.2, K/Cs of 2980, 5 ppm Li, 36 ppm Ba, and 8 ppm Sr. Parts of the primary core of garnet crystals from both pegmatites show overlapping compositions in the $Alm_{18.9}Sps_{78.6}$ to $Alm_{33.8}Sps_{63.2}$ range, with minor Prp (0.8–4.1) and Grs (0–1.4) (Novák 1988, unpubl. data). These data, although sparse, suggest that the overall levels of fractionation are similar in both bodies.

	I *			III **		
	PEG	PM	RM	PEG	PM	RM
quartz	●			●	•	
albite	●		+	●		
muscovite	●			●		
sillimanite		+				●
beryl	•			•		
chrysoberyl		+				•
garnet	●			●		
Nb, Ta-oxide minerals	•			•		
gahnite	+			•		
zircon	+			+		
bavenite			•			+
epidote			•			+
biotite	•			•		
chlorite			+			+

● rock-forming ● subordinate
• minor + rare

FIG. 2. Mineral associations constituting three stages of evolution of the Maršikov I and III pegmatites. PEG: magmatic and postmagmatic crystallization of the pegmatites, PM: products of prograde metamorphism, RM: minerals generated by retrograde processes. Pegmatite I also contains rare apatite, magnetite, bismuth and bismuthinite; dike III also carries rare K-feldspar, pyrite and goethite.

Metamorphism of the pegmatites

Both of the dikes were subjected to various degrees of metamorphic reworking. Two metamorphic events can be distinguished: a prograde process followed by retrograde effects. The prograde metamorphism generated distinct foliation and lineation parallel to those of the enclosing rocks (Dostál 1966), and led to the formation of chrysoberyl and sillimanite (Franz & Morteani 1984). Our study suggests a two-fold division of the prograde event according to different intensities of shearing stress. The first stage (I) produced thick tabular pale green chrysoberyl I (Fig. 3A) at the expense of beryl, approximately,

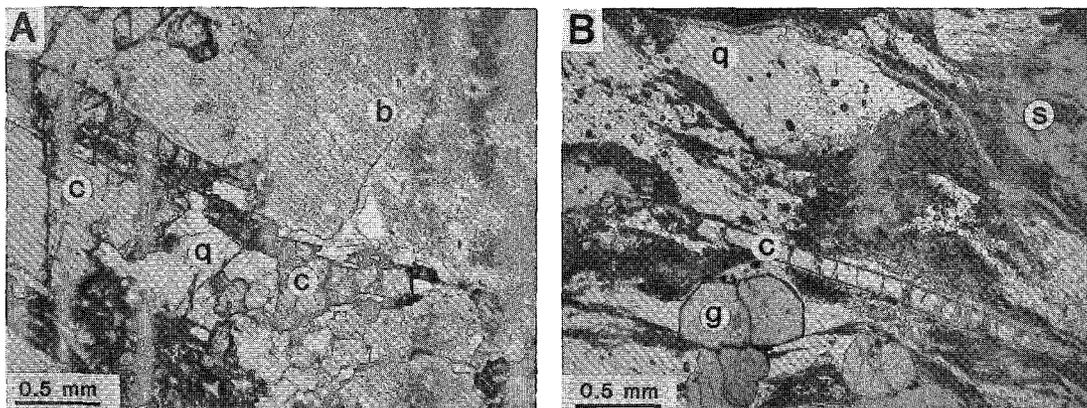
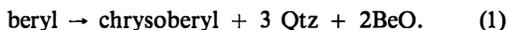
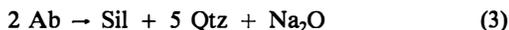
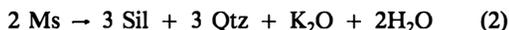


FIG. 3. Tabular chrysoberyl I (c) + quartz (q) replace beryl (b; clouded, with mica inclusions). Marškov I, thin section, plane-polarized light. B. Thin platy chrysoberyl II (c) associated with quartz (q), subhedral garnet (g) and fibrous aggregates of sillimanite (s). Marškov III, thin section, plane-polarized light. The scale bars are 0.5 mm long.



Stress was probably minor, as this generation of chrysoberyl shows minimal, if any, preferred orientation. In contrast, stress and shearing were very pronounced in the second stage (II), which generated abundant lineated fibrous sillimanite at the expense of muscovite and probably also albite:



Chrysoberyl I recrystallized during this substage into thin plates of yellow-green chrysoberyl II, typically associated with sillimanite and oriented parallel to its foliation (Fig. 3B). Recrystallization of other minerals also was enhanced by this event, as shown later on the example of Nb-Ta oxide minerals.

Garnet developed a Fe-rich outer zone during the first stage. Its crystallization could have been extended into the second stage, but the compositional range of this outer zone is about the same in garnet from both sheared and unsheared assemblages. The composition ranges from $\text{Alm}_{29.1}\text{Sp}_{67.0}$ to $\text{Alm}_{41.0}\text{Sp}_{57.0}$, with minor Prp (0.1–4.6) and Grs (0–2.8) (Novák 1988, unpubl. data).

Experimental data summarized in Figure 4 permit an estimate of metamorphic conditions of the above reactions, earmarked by loss of alkalis and dehydration: the temperature of equilibration is inferred to have been between 570 and 630°C, at a P(total) of about 2.5–4 kbar. The reaction first proceeded in a fluid-poor static environment (P

total \gg P fluid), and was extensively promoted by stress and shearing during the second stage (P total \cong P stress). At $a(\text{H}_2\text{O})$ close to 0, reaction (1) would probably be shifted to a higher pressure of about 5 kbar (Barton 1986). In such a case, the P–T conditions of crystallization of the chrysoberyl + sillimanite assemblage would correspond to those derived for the host region by René (1983).

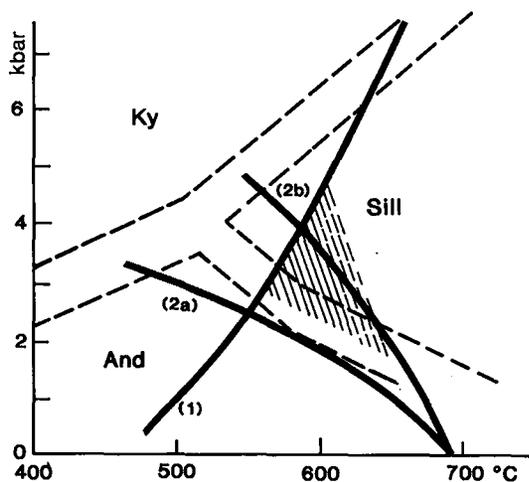


FIG. 4. Probable conditions of metamorphism of the Marškov pegmatites I and III (subvertical ruling). Stability fields of Al_2SiO_5 polymorphs after Robie & Hemingway (1984); (1) $\text{Ms} + \text{Qtz} \rightleftharpoons \text{Kfs} + \text{Al}_2\text{SiO}_5 + \text{H}_2\text{O}$ at $a(\text{H}_2\text{O}) = 0.5$, after Chatterjee & Johannes (1974); (2) $\text{beryl} + 2\text{Al}_2\text{SiO}_5 \rightleftharpoons 3 \text{ chrysoberyl} + 8 \text{ Qtz}$ at $a(\text{H}_2\text{O}) = 0$ (2a) and 0.5 (2b), after Barton (1986).

Prominent foliation and lineation in some pegmatites, their virtual absence in other dikes, and a very limited regional extent of thorough metamorphic reworking strongly suggest the presence of localized shear-zones.

Retrogression of the above assemblages is not widespread. The mineral assemblage generated by this event can be likened to Ginzbourg's (1960) "alpine vein" stage of pegmatite evolution, marked by hydrous Fe^{3+} -bearing phases indicative of increased $f(\text{O}_2)$: epidote, bavenite, chlorite and, locally, hematite.

Although both bodies were subjected to both prograde and retrograde metamorphism, the extent of each differs. In dike I, prograde metamorphism is moderate, mainly because of low intensity of shearing: foliation and lineation are minimal, chrysoberyl and sillimanite are rather uncommon, and recrystallization of premetamorphic phases is very restricted because of a low input of energy and limited flow of fluid. In contrast, the retrograde event is prominent; epidote and bavenite are relatively widespread. In dike III, evidence of prograde metamorphism is very extensive, particularly for the second stage. Foliation and lineation are extensive, chrysoberyl and sillimanite are abundant, and recrystallization of magmatic assemblages is very thorough. The retrograde assemblage, however, is very restricted.

OXIDE MINERALS OF Nb AND Ta

It is evident from the preceding description of the pegmatites examined that Nb-Ta oxide minerals can be expected to exhibit more pronounced effects of metamorphism in dike III than in dike I. The following text and illustrations confirm this expectation.

General characteristics of the mineral assemblages

In dike I, Nb-Ta oxide minerals are relatively common in the intermediate albite + quartz + muscovite zone, but they were not encountered in any other unit. In hand specimens, black to brownish black tabular crystals, up to 20 mm in size, show neither preferred orientation nor effects of deformation. Microscopic and electron-microprobe examination shows the presence of columbite-tantalite as a dominant phase, largely in primary zoned crystals, with only minor recrystallization. Subordinate phases include fersmite, microlite and, only rarely, pyrochlore.

In dike III, the Nb-Ta oxide minerals are also concentrated in the intermediate Ab + Qtz + Ms unit, but some are encountered in the quartz core. The wall zone and saccharoidal albite units are devoid of them. Thin platy, black, and generally

subhedral crystals 2-5 mm in size are common, rarely reaching 1 X 8 mm. The orientation of the platy crystals largely conforms to the foliation of the silicate matrix. The crystals are locally deformed, enclosed in quartz or albite, and rarely in sillimanite; they are commonly associated with chrysoberyl II and gahnite, rarely with zircon or native bismuth. Microscopic and electron-microprobe study indicates the presence of columbite-tantalite, with extremely rare microscopic relics of fersmite and microlite. Slight deformation of primary zoned columbite-tantalite is observed only locally, but extensive recrystallization is widespread. The aggregates of secondary columbite-tantalite obliterate most of the textural and compositional features of the primary crystals.

Figure 5 illustrates typical textural features of the primary assemblage, and some compositional characteristics as well. Oscillatory growth-zoning is a typical, widespread feature of primary columbite-tantalite (Figs. 5A, B). Fersmite forms fibrous to platy aggregates aligned parallel to the pinacoidal planes of the surrounding columbite-tantalite; it has never been observed outside this host phase (Figs. 5A, B). The relationship suggests an epitaxial intergrowth between the isostructural host and guest phases. However, it is uncertain whether the intergrowth originated by simultaneous crystallization, filling of primary intracrystal cavities by fersmite, or replacement of the columbite-tantalite host, largely along structurally controlled fractures. The last of these three possibilities seems most probable, considering the pattern of fersmite aggregates, their association with near-homogeneous cross-cutting blocks of columbite-tantalite with intermediate electron density, and small-scale textural details (Figs. 5A, B, D, respectively). In contrast to fersmite, microlite tends to fill microscopic vugs and cross-cutting fissures (Figs. 5B, C), but it also exhibits replacement relationships. It corrodes both columbite-tantalite and fersmite (Figs. 5C, D) and also is seen to "follow" fersmite within its aggregates, behind their outer parts that shield microlite from direct contact with the host (Fig. 5A). Oscillatory zoning is characteristic of metasomatic as well as cavity-grown microlite (Figs. 5C, D).

Figure 6 portrays characteristic textural patterns of secondary, recrystallized columbite-tantalite and some aspects of its chemistry. Recrystallization proceeds locally in two stages: a patchy, concentrically zoned "bird's-eye" pattern replaces specific zones of primary oscillatory phases, and may precede homogenization affecting larger volumes of primary material (Fig. 6A). In many cases, however, the patchy stage is not developed, and massive homogenization may leave only a few relics of the primary zoned mineral intact (Fig. 6B). In

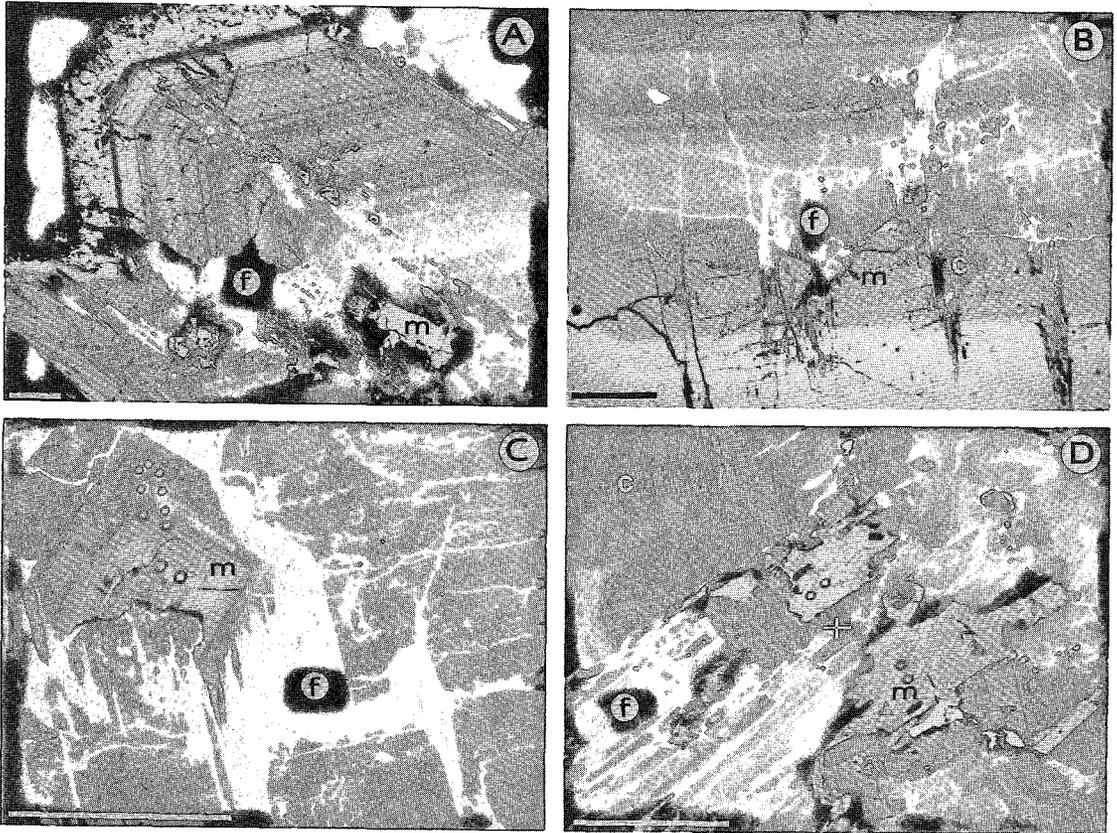


FIG. 5. Textural relationships of Nb-Ta oxide minerals in the Maršůkov pegmatite I, in BSE images that reflect the Ta/(Ta+Nb) ratio. A. Oscillatory zoning of primary euhedral columbite-tantalite, cross-cut by streaks of fersmite (f) with anhedral to subhedral microlite (m); sample MM-120, *cf.* Fig. 11A for chemistry. B. Oscillatory zoning in primary columbite-tantalite cross-cut by fersmite (f) associated with parallel slabs of homogeneous columbite (c), and by zoned fracture-filling microlite (m); sample MMM-11, *cf.* Fig. 11B. C. Nearly homogeneous columbite-tantalite veined and replaced by fersmite (f), both corroded and replaced by subhedral microlite (m) with oscillatory zoning; sample MM-27, *cf.* Fig. 11C for chemistry. D. Secondary columbite-tantalite (c) with laths of fersmite (lamellar, f) corroded and replaced by oscillatory-zoned microlite (m); sample MM-9, *cf.* Fig. 11D for chemistry. Circular spots in C and D are burn marks in the carbon coating. All scale bars are 200 μm long.

complex aggregates of subparallel zoned crystals, recrystallization commonly produces a heterogeneous patchwork of highly variable electron density, with low-density phases apparently the last to crystallize (Fig. 6C). These last products of recrystallization are locally associated with fracture-filling veinlets of quartz, albite or sericitic mica that criss-cross the less affected or primary phases (Fig. 6D).

Chemical composition

Electron-microprobe analyses were carried out in the wavelength-dispersion mode on a Cameca

Camebax SX50 instrument, with beam diameter of 1–2 μm and an accelerating potential of 15 kV. For all minerals except microlite, a sample current of 20 nA measured on Faraday cup and a counting time of 20 s were used for Fe, Mn, Sn, Ti, Nb, and Ta. For Mg, Ca, Sb, As, Bi, Sc, Zr, and U, 40 nA and 50 s were used. The following standards were used: manganotantalite ($\text{TaM}\alpha$), FeNb_2O_6 ($\text{FeK}\alpha$), MnNb_2O_6 ($\text{NbL}\alpha$, $\text{MnK}\alpha$), SnO_2 ($\text{SnL}\alpha$), rutile ($\text{TiK}\alpha$), ZrO_2 ($\text{ZrL}\alpha$), $\text{NaScSi}_2\text{O}_6$ ($\text{ScK}\alpha$), MgNb_2O_6 ($\text{MgK}\alpha$), BiTaO_4 ($\text{BiM}\alpha$), mimetite ($\text{AsL}\alpha$), CaNb_2O_6 ($\text{CaK}\alpha$), stibiotantalite ($\text{SbL}\alpha$) and UO_2 ($\text{UM}\alpha$). For microlite, a sample current of 20 nA and a counting time of 20 s were used for Na, Ca,

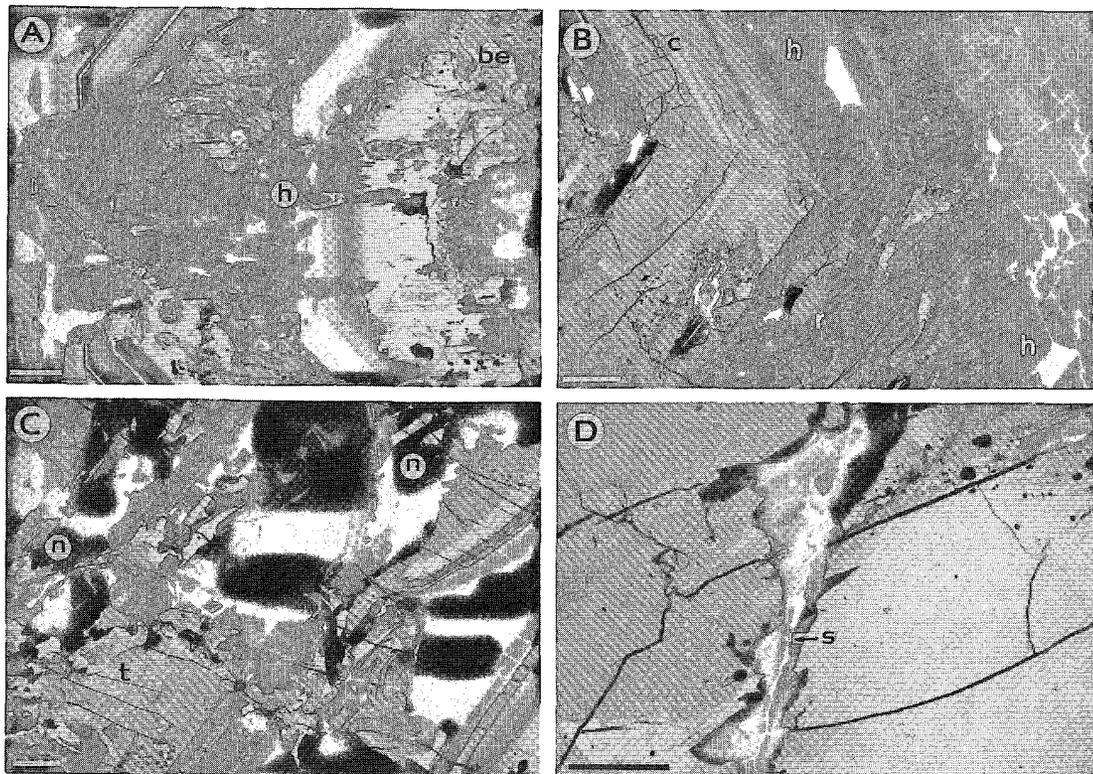


FIG. 6. Textural relationships of Nb-Ta oxide minerals in the Maršikov pegmatite III, in BSE images that reflect the Ta/(Ta+Nb) ratio. A. Oscillatory zoning of primary columbite-tantalite disturbed by early "bird's-eye" recrystallization (be), with its own oscillatory zoning, and both cross-cut by a nearly homogeneous product of late recrystallization (h); sample MM-8, *cf.* Fig. 12A for constant Mn/(Mn+Fe). B. Oscillatory zoning of primary columbite (c), largely obliterated by early heterogeneous recrystallization (r) and late homogenization (h); sample MM-48, *cf.* Fig. 12B for decrease in Mn/(Mn+Fe) during recrystallization. C. Oscillatory zoning in subhedral subparallel laths of primary columbite-tantalite, extensively recrystallized into Fe-enriched secondary columbite-tantalite with highly variable Ta/(Ta+Nb) (n: Nb-rich, t: Ta-rich); sample MM-28, *cf.* Fig. 12C for chemistry. D. Secondary, recrystallized columbite matrix cut by a veinlet of sericite and albite (s), which is rimmed by a third generation, Ta-poor, Fe-enriched columbite replacing the host columbite; sample MM-31, *cf.* Fig. 12D for compositional relationships. All scale bars are 200 μ m long.

Nb, Ta, and F. For K, Cs, Sr, Ba, Fe, Mn, Pb, Sb, Bi, Sn, Ti, and U, 40 nA and 50 s were used. In addition to, or instead of the above standards, microlite was analyzed using manganotantalite ($MnK\alpha$), YAG ($YL\alpha$), $Ba_2NaNb_5O_{15}$ ($BaL\alpha$), $SrBaNb_4O_{10}$ ($SrL\alpha$), pollucite ($CsL\alpha$), orthoclase ($KK\alpha$) and mimetite ($PbM\alpha$). Data were reduced using the PAP routine of Pouchou & Pichoir (1985).

Figure 7 shows a summary of compositional data on columbite-tantalite from the pegmatites examined. Primary compositions of zoned crystals range from marginal Mn-rich ferrocolumbite through manganocolumbite to niobian man-

ganotantalite, with extensive overlap of compositions from both localities. The broad trend is marked by enrichment in Mn and Ta. In contrast to the primary crystals, products of recrystallization display extensive compositional variations in both Fe-Mn and Nb-Ta. Prominent enrichment in Fe is evident relative to the primary trends, and a few of the Fe-rich compositions also are enriched in Ta, reaching the composition of Mn,Nb-rich ferrotantalite. Table 1 presents examples of typical compositions of the columbite-tantalite minerals of different genetic affiliations.

Besides the main components of the primary zoned crystals illustrated in the columbite quad-

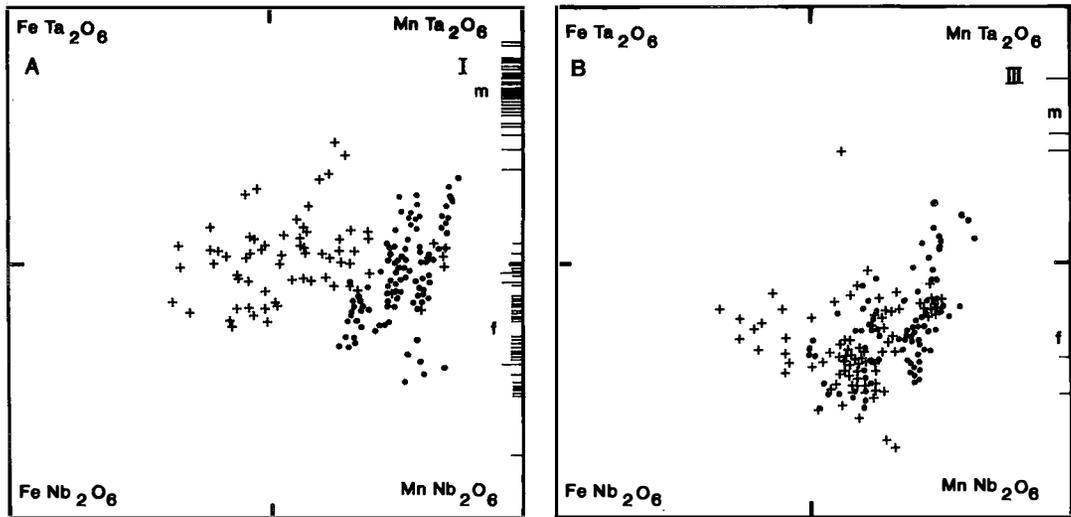


Fig. 7. Summary of compositions of the primary (dots) and recrystallization-related (crosses) columbite-tantalite, and of fersmite (f) and microlite (m) in the Maršikov pegmatites I (A), and III (B), in terms of the columbite quadrilateral (atomic ratios). The Ta/(Ta+Nb) ratios of fersmite (short dashes) and microlite (long dashes) are marked on the Mn-sideline for convenience, with no reference to their Mn/(Mn+Fe).

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF COLUMBITE-TANTALITE AND FERSMITE (SAMPLE M00-11)

	Columbite-tantalite					Fersmite	
	G3-77	G2-P28	G1-P6	G2-P18	G2-P8	G1-P11	G1-P10
Nb ₂ O ₅ wt.%	36.90	23.95	46.26	28.55	28.26	66.69	34.05
Ta ₂ O ₅	45.26	58.93	34.04	53.54	52.75	15.97	48.43
TiO ₂	0.07	0.17	0.28	1.08	1.74	0.09	1.09
SnO ₂	-	-	-	-	0.07	-	-
UO ₂	0.02	0.10	0.01	0.01	-	0.06	-
As ₂ O ₃	0.02	0.04	-	-	-	n.d.	n.d.
Sb ₂ O ₃	-	-	0.03	-	-	0.02	0.04
Bi ₂ O ₃	0.05	-	-	0.02	-	0.01	0.05
Fe ₂ O ₃ *	0.47	0.51	0.34	0.89	1.47	0.03	0.27
MgO	-	0.01	-	0.27	0.60	n.d.	n.d.
CaO	0.02	0.01	0.18	0.01	0.03	16.33	14.15
MnO	12.72	12.35	15.17	10.08	5.16	0.16	0.21
FeO	4.20	3.27	2.55	6.33	9.22	-	-
total	99.73	99.24	98.86	100.78	99.30	99.36	98.29
Nb	4.578	3.198	5.540	3.657	3.601	6.926	4.108
Ta	3.377	4.733	2.400	4.125	4.044	0.998	3.516
Ti	0.014	0.038	0.055	0.230	0.369	0.014	0.221
Sn	-	-	-	-	0.008	-	-
U	0.001	0.007	0.001	0.001	-	0.004	-
As	0.004	0.007	-	-	-	-	-
Sb	-	-	0.003	-	-	-	0.004
Bi	0.004	-	-	0.001	-	-	0.004
Fe ³⁺	0.097	0.113	0.067	0.190	0.311	0.007	0.054
Mg	-	0.004	-	0.114	0.252	-	-
Ca	0.006	0.003	0.050	0.003	0.009	4.018	4.048
Mn	2.956	3.089	3.332	2.179	1.232	0.029	0.046
Fe ²⁺	0.963	0.808	0.553	1.499	2.174	-	-
total	12.000	12.000	12.000	12.000	12.000	11.996	12.001
Mn/(Mn+Fe)	0.74	0.77	0.84	0.56	0.33	-	-
Ta/(Ta+Nb)	0.42	0.60	0.30	0.53	0.53	0.13	0.46

Calculated on the basis of 24 atoms of oxygen p.f.u.; *Fe₂O₃ calculated to eliminate cation surplus over 12.000.
 G3-77, G2-P28 and G1-P6: primary oscillatory zoned manganocolumbite-manganotantalite.
 G2-P18 and G2-P8: secondary, homogenized, Fe-, Ti- and Mg-enriched manganotantalite and ferrotantalite, respectively.
 G1-P11 and G1-P10: adjacent lamellae of fersmite with contrasting Ta contents.

rilateral (Fig. 7), no other constituents show any regular trends or correlations. The only exception is a rough positive correlation of Ti (≤ 0.193 atoms per formula unit) and Mg (≤ 0.084 a.p.f.u.) with Fe, all particularly enriched in the secondary columbite-tantalite. Very low concentrations are typical of Ca, Bi, Sn, U and Zr (maxima at 0.053 Ca, 0.004 Bi, 0.019 Sn, 0.006 U, 0.008 Zr, all a.p.f.u.). Contents of Sc, As and Sb are consistently at or below detection limits (0.03–0.04 wt.% oxide). Adjustments of compositions showing excess of cations over available sites with ΣFe as Fe^{2+} , calculated on the basis of cation plus anion normalization, show only a minor concentration of Fe^{3+} in a restricted number of compositions, mainly those of the secondary Fe-rich phases.

Fersmite is commonly heterogeneous, in a lamellar pattern. Overall, it varies from 0.24 to 0.49 in Ta/(Ta+Nb), but the range in individual grains is less than 0.15. Two microscopic grains show Ta/(Ta+Nb) slightly above 0.50. They should represent a different species: either a Ta > Nb counterpart of fersmite proper (Nb > Ta), or rynersonite. However, the structural type of these grains could not be verified by X-ray diffraction because of their extremely small size. Consequently, all $\text{Ca}(\text{Nb} \geq \text{Ta})_2\text{O}_6$ compositions encountered in our study are referred to as fersmite, the identity of the grains having been established by X-ray powder

diffraction in a mixture with dominant columbite-tantalite.

Low Fe, Mn, Sn and Ti contents are characteristic of the Maršikov I fersmite, the latter two elements being on average lower than in columbite-tantalite. Uranium was found only rarely in minor amounts, whereas Y was not detected. Table 1 shows the typical chemistry of fersmite, and its most Nb-enriched composition. Both compositions also show a slight deviation from the ideal AB_2 stoichiometry, with excess of the *A* cations in general, and Ca in particular. Analytical error seems to be improbable as an explanation of this deviation. Assuming full occupancy of cationic sites, (OH) substitution for O may balance the deficit of cation charges; fluorine was not detected.

Microlite shows a broad compositional range, from 0.68 to 0.93 in $Ta/(Ta + Nb)$. This ratio shows extensive variations among different specimens, and locally also within individual zoned crystals. Pyrochlore is found only rarely, with $Ta/(Ta + Nb)$ from 0.31 to 0.49, separated by a gap of 0.19 from

the compositions of microlite proper. Figure 8 shows ratios of the main *A* and *B* cations of the pyrochlore family of minerals, and Table 2 presents representative compositions.

In the *A* site, Ca is dominant over Na, which rarely exceeds 0.05 a.p.f.u., and may locally become undetectable. Uranium also is low, mostly less than 0.022 a.p.f.u. Compositions approaching uranmicrolite do occur, but they are extremely rare; high U is commonly accompanied by high Na. Lead is mostly below 0.005 a.p.f.u., rarely up to 0.068, and it shows no correlation with uranium. Similarly, Sn is largely less than 0.004 a.p.f.u., but occasionally increases to 0.023. Contents of Fe and Mn are typically variable, but generally they are much lower than 0.21 a.p.f.u. Concentrations at or below the detection limit characterize K, Cs, Sr, Ba, Sb and Bi; Y was not detected.

Besides Ta and Nb (and potentially, some Sn), the only other significant cation in the *B* site is Ti. It is generally present in concentrations below 0.048 a.p.f.u., but some grains of microlite contain as

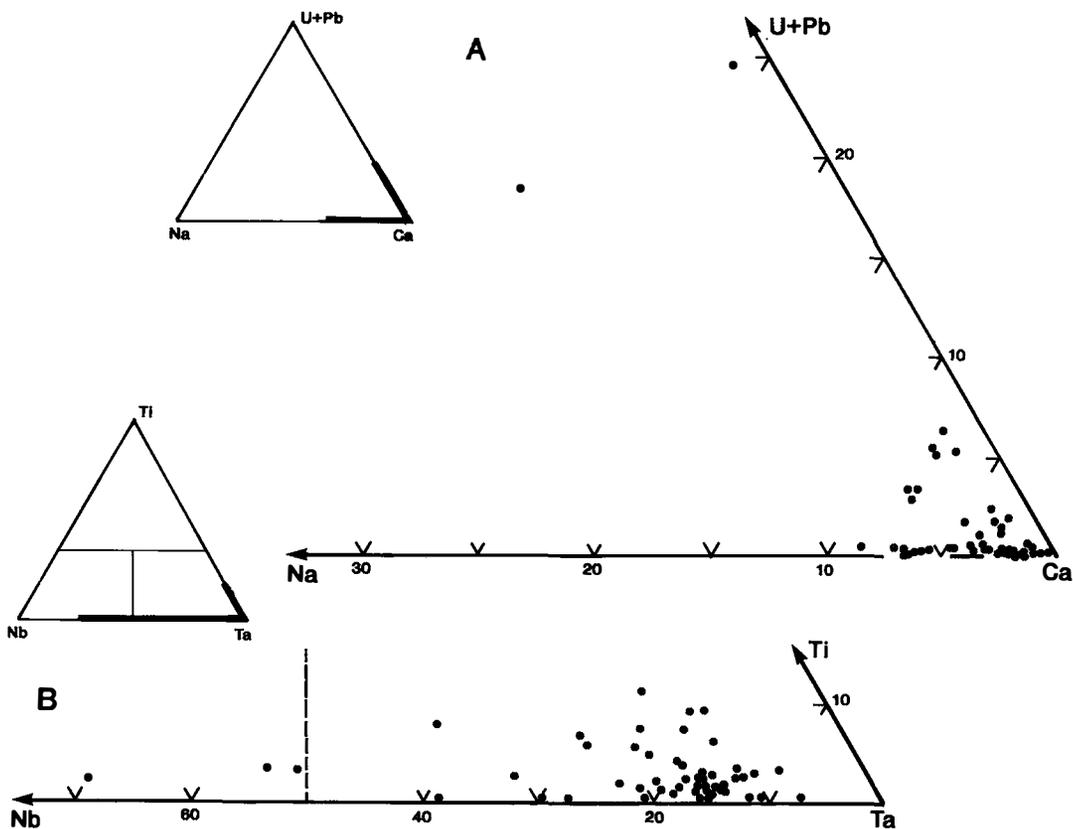


FIG. 8. Composition of the Maršikov I microlite (pyrochlore) in the Na-Ca-(U+Pb) (at.) triangle (A), and in the Nb-Ta-Ti (at.) diagram (B) of Hogarth (1977). Note the dominance of Ca, locally to the exclusion of Na, the generally low abundances of U, and the low content of Ti.

TABLE 2. CHEMICAL COMPOSITION OF MICROLITE AND PYROCHLORE (SAMPLE MPM-11)

	G1-P15	G3-P1	G2-P1
	microkite	uranian microkite	pyrochlore
Nb ₂ O ₅ wt. %	8.24	5.18	45.92
Ta ₂ O ₅	64.45	61.42	33.65
TiO ₂	3.64	2.54	0.97
SnO ₂	0.06	0.75	-
UO ₂	0.43	14.76	0.11
Sb ₂ O ₃	0.01	-	-
Bi ₂ O ₃	0.05	-	-
CaO	17.60	11.58	16.09
BaO	-	-	0.07
MnO	0.42	0.39	0.22
FeO	0.31	0.78	0.45
PbO	-	0.51	-
Na ₂ O	0.86	1.32	0.19
K ₂ O	0.02	0.04	0.01
CS ₂ O	0.01	-	0.02
F	1.73	0.37	0.65
total	97.83	99.64	98.35
-O = F	0.73	0.16	0.27
	97.10	99.48	98.08
Nb	0.310	0.222	1.355
Ta	1.460	1.586	0.598
Ti	0.228	0.182	0.047
Sn	0.002	0.010	-
U	0.008	0.312	0.010
Sb	-	-	-
Bi	0.001	-	-
Ca	1.572	1.178	1.125
Ba	-	-	0.002
Mn	0.030	0.031	0.012
Fe	0.021	0.062	0.025
Pb	-	0.013	-
Na	0.139	0.243	0.025
K	0.002	0.004	0.001
O	6.200	6.860	6.000
OH	0.343	0.032	0.265
F	0.457	0.110	0.082
	-	-	0.653
ΣA cat.	1.775	1.843	1.200
ΣB cat.	2.000	2.000	2.000

calculated on the basis of ΣB cations (Nb,Ta,Ti,Sn) = 2.

much as 0.230. Uranium-rich compositions usually show Ti in the 0.05–0.10 range. Sn also was assigned to the B site as Sn⁴⁺, because its negligible contents do not permit a meaningful calculation of probable valency state(s) (*cf.* Ercit *et al.* 1987). The concentration of fluorine is commonly below 0.123 a.p.f.u., with a maximum of 0.457, *i.e.*, fluorine populates less than 50% of the (F,OH,O) site.

The composition of pyrochlore generally conforms to the microkite pattern above (Table 2). Titanium seems to be somewhat enriched relative to most of the microkite data, and Fe plus Mn are also higher than normally encountered.

Figure 9 summarizes partitioning data on Nb and Ta in associated pairs of Nb–Ta oxide species. As established in previous studies, microkite is enriched in Ta relative to the primary columbite–tantalite. Our data also indicate that, with a few exceptions,

tantalum has a slight preference for columbite–tantalite as compared to fersmite, and microkite is consistently Ta-rich relative to the latter. It should be noted, however, that the associated pairs did not necessarily coexist at equilibrium. As noted earlier and discussed below, the timing of crystallization of fersmite and microkite is an open question, with textural evidence favoring replacement of columbite–tantalite by these two minerals, and microkite replacing fersmite. In such a case, compositional differences among the three minerals may be a function of evolution of parent fluids “contaminated” by the replaced minerals, rather than of crystal-chemical preferences among truly coexisting phases.

Structural state

The identity of fersmite and microkite–pyrochlore, indicated by chemical composition, was confirmed by X-ray powder diffraction. However, this line of study could not advance beyond a mere identification because these minerals are not separable from the host columbite–tantalite phase.

Unit-cell dimensions of columbite–tantalite were refined for samples selected to represent the primary and recrystallized material. Refinements were done using the FIX program for reduction of systematic error in positional data of X-ray powder-diffraction maxima to $\pm 0.01^\circ 2\theta$ (Ercit 1986), and the CELREF least-squares program of Appleman & Evans (1973) for treatment of data obtained on the Philips PW1710 automated powder diffractometer at $0.60^\circ 2\theta/\text{min}$, with graphite-monochromatized CuK α radiation at 40 kV and 40 mA. Annealed CaF₂ [*a* 5.46379(4) Å] calibrated against a NBS silicon reference (batch 640; *a* 5.430825 Å) was used as an internal standard.

The unit-cell dimensions derived in the above manner cannot be correlated with individual compositions established by microprobe technique (such as those in Tables 1 and 2), as they were obtained on compositionally heterogeneous mixtures. However, they can be taken as representative averages of the main phases constituting individual grains. It is thus significant that samples consisting dominantly of primary zoned crystals show intermediate levels of disorder, whereas those that are largely recrystallized are more highly ordered (Fig. 10).

Textural and compositional trends

The summary of compositional data shown in Figures 7A and 7B indicates gross shifts in chemistry from primary to secondary columbite–tantalite. However, the specific nature of the

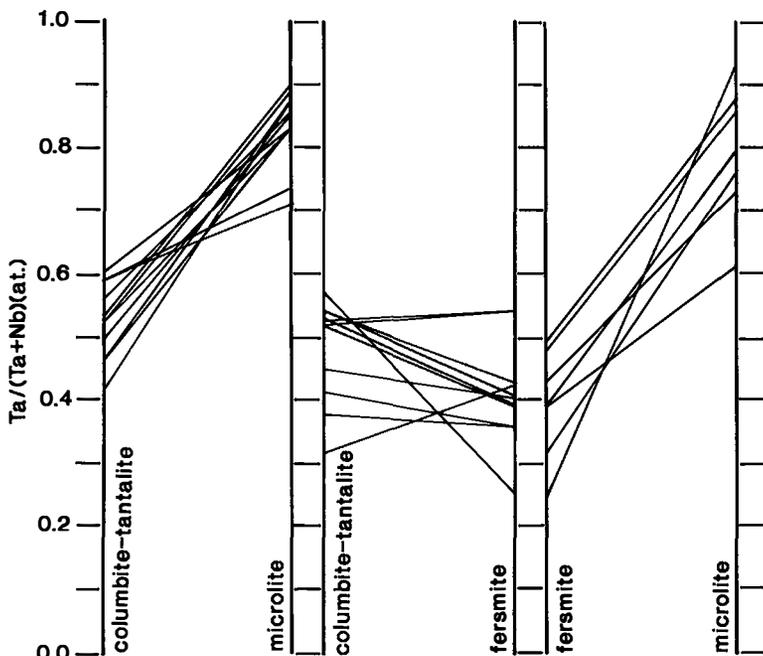


FIG. 9. The Ta/(Ta+Nb) ratio of associated (but not necessarily coexisting) columbite-tantalite + microlite, columbite-tantalite + fersmite, and fersmite + microlite.

changes is concealed in these compilations because of significant variations among the primary phases of different grains. The consequent spread of

secondary compositions inevitably dilutes any trend due to recrystallization, systematic as it may be in relation to the individual primary chemistries.

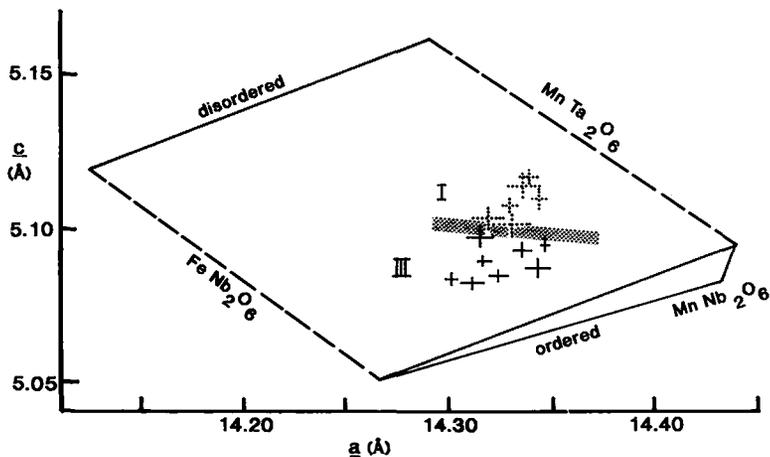


FIG. 10. Structural state of columbite-tantalite from the Maršikov pegmatites I (solid error bars) and III (dotted error bars) in the a - c diagram of Cerný & Turnock (1971), as modified by Wise *et al.* (1985). The dotted band marks the approximate boundary between the largely secondary, relatively ordered phases and the primary crystals with intermediate disorder.

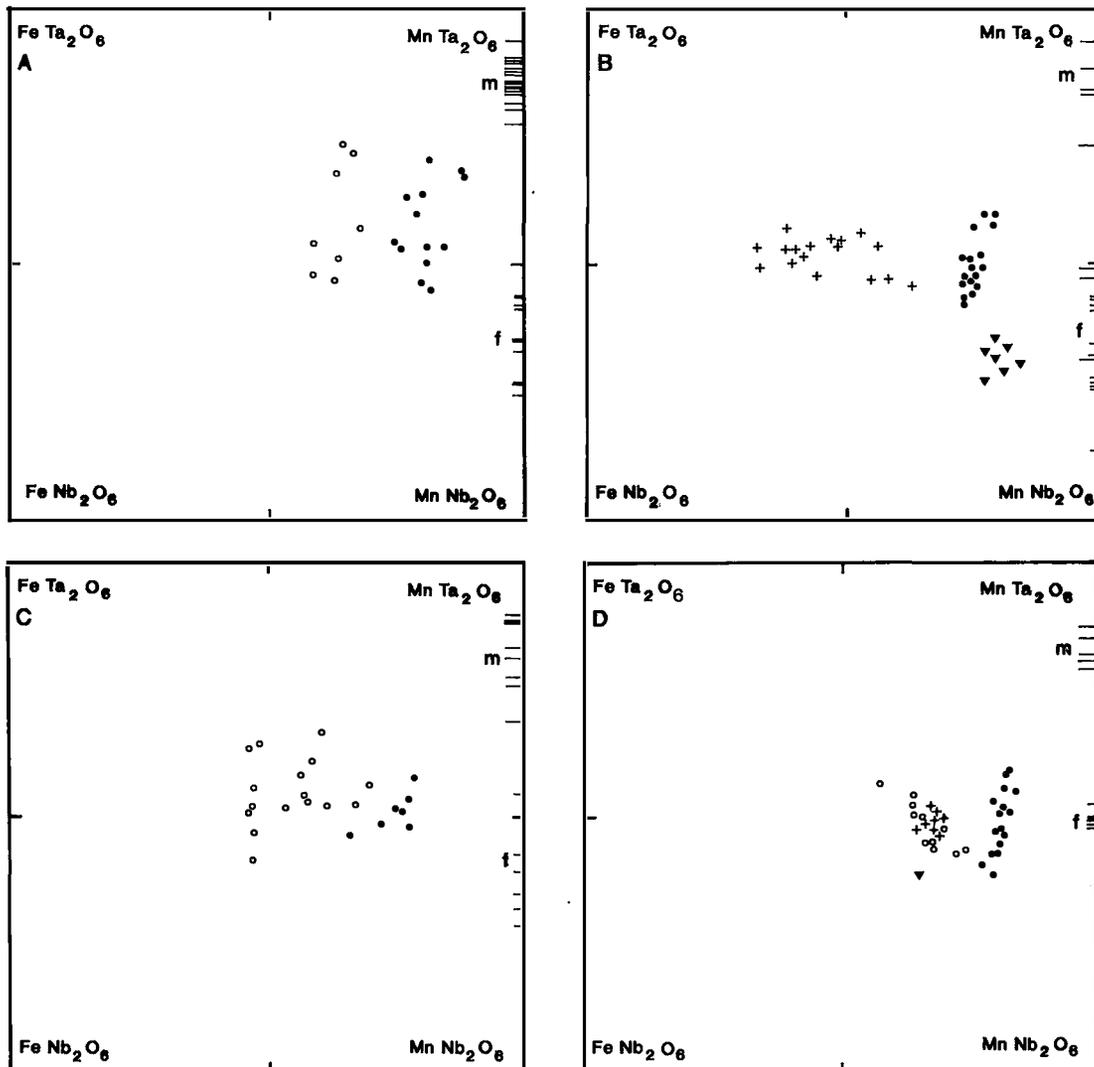


FIG. 11. Compositional evolution of Nb-Ta oxide minerals in the Maršikov I pegmatite, in terms of $Ta/(Ta+Nb)$ versus $Mn/(Mn+Fe)$ (at.). Fersmite (f) and microlite (pyrochlore) (m) are marked on the $Ta/(Ta+Nb)$ sideline for convenience, without any reference to their actual $Mn/(Mn+Fe)$ ratio. Dots: primary oscillatory-zoned columbite-tantalite; circles: secondary early, heterogeneous, "bird's-eye" or granular columbite-tantalite; crosses: secondary late, homogeneous columbite-tantalite; triangles: homogeneous slabs of columbite associated with fersmite; inverted triangle: columbite rimming microlite. A. Enrichment of recrystallized columbite-tantalite in Fe, within the primary range of $Ta/(Ta+Nb)$; sample MM-120, *cf.* Fig. 5A. B. Extensive enrichment in Fe during recrystallization of columbite-tantalite, with considerable homogenization of $Ta/(Ta+Nb)$, and Ta-poor manganocolumbite associated with fersmite; sample MMM-11, *cf.* Fig. 5B. C. Broadening of range in $Ta/(Ta+Nb)$ and enrichment in Fe in early stages of recrystallization; sample MM-27, *cf.* Fig. 5C. D. Gradual decrease in range of both $Ta/(Ta+Nb)$ and $Mn/(Mn+Fe)$ values in early and late secondary columbite-tantalite, and Ta-poor, Fe-rich manganocolumbite rimming microlite; sample MM-9, *cf.* Fig. 5D.

Similarly, the compositional summaries in Figures 7A and 7B conceal the specific relationships among columbite-tantalite, fersmite and microlite-pyrochlore in individual aggregates of these

minerals. To understand the characteristic features of compositional relations among these three phases, and of the compositional shifts associated with recrystallization of columbite-tantalite, in-

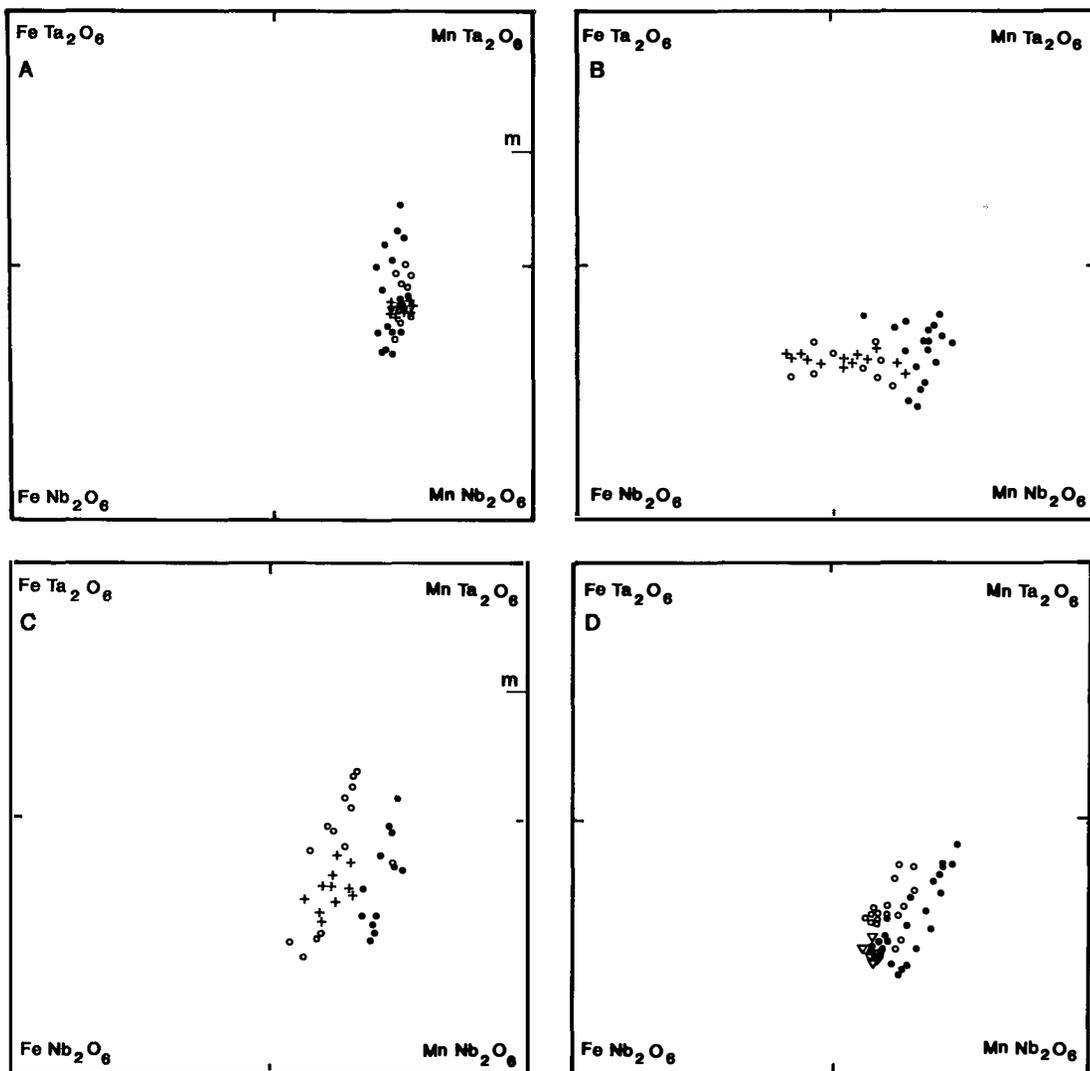


FIG. 12. Compositional evolution of Nb-Ta oxide minerals in the Maršíkov III pegmatite, in terms of Ta/(Ta + Nb) versus Mn/(Mn + Fe) (at.). Fermite (f) and microlite (m) are marked on the Ta/(Ta + Nb) sideline for convenience, disregarding their actual Mn/(Mn + Fe) ratio. Symbols as in Figure 11; inverted open triangle: late Fe-rich, Ta-poor manganocolumbite associated with cross-cutting silicate veinlets. A. Gradual homogenization of Ta/(Ta + Nb) during recrystallization of primary columbite-tantalite at constant Mn/(Mn + Fe); sample MM-8, *cf.* Fig. 12A. B. Gradual homogenization of Ta/(Ta + Nb) in recrystallized columbite, combined with enrichment in Fe; sample MM-48, *cf.* Fig. 12B. C. Extension of the range in Ta/(Ta + Nb) in early recrystallization of columbite-tantalite, coupled with enrichment in Fe, and followed by homogenization of Ta/(Ta + Nb) at near constant Mn/(Mn + Fe); sample MM-28, *cf.* Fig. 12C. D. Heterogeneous recrystallization of manganocolumbite combined with enrichment in Fe, and followed by cross-cutting veinlets of silicate rimmed by late Fe-rich, Ta-poor manganocolumbite; sample MM-31, *cf.* Fig. 6D.

dividual assemblages such as those shown in Figures 5 and 6 must be examined separately. Figures 11 and 12 illustrate compositional and evolutionary details of the mineral assem-

blages shown in the above-mentioned back-scattered electron images and, in some cases, also the broader relationships within the surrounding material.

With the exception of sample MM-48 (Figs. 6B, 12B), oscillatory zoning of primary columbite-tantalite shows extensive variation in $Ta/(Ta + Mn)$ (Δ up to 0.30), but a more restricted range in $Mn/(Mn + Fe)$ (Δ from 0.06 to 0.14). This observation explains the subvertical arrays of primary compositions observed in Figure 7, particularly in its part B: trends of primary fractionation within individual pegmatites largely consist of laterally stacked and vertically shifted arrays representative of individual crystals or their local aggregates, rather than of continuous sequences of overlapping compositional ranges.

Despite the moderate slope of tie lines connecting associated pairs of columbite-tantalite and fersmite (Fig. 9B), the bulk range of fersmite chemistry is in most cases very distinctly Ta-poor relative to primary columbite (Figs. 11A, B, C). However, structurally controlled streaks of nearly homogeneous manganocolumbite associated with fersmite in sample MMM-11 (Figs. 5B, 11B) and primary columbite-tantalite of sample MM-9 (Figs. 5D, 11D) have about the same bulk $Ta/(Ta + Nb)$ as the associated fersmite.

In contrast, compositions of microlite are in almost all cases considerably enriched in Ta relative to columbite-tantalite. The only exception is the sample MMM-11 (Figs. 5B, 11B), which is the only one with pyrochlore compositions that extend the $Ta/(Ta + Mn)$ range of microlite-type minerals well into that of fersmite, and below the range of primary columbite-tantalite.

Secondary recrystallization of columbite-tantalite shows two dominant features: homogenization in terms of $Ta/(Ta + Nb)$ (Figs. 11B, D; 12A, B, D), and enrichment in Fe, Mg and Ti, coupled with considerable extension of the overall $Mn/(Mn + Fe)$ range (Figs. 11, 12A, B, C). Notable exceptions from the general tendency toward more uniform $Ta/(Ta + Nb)$ ratios (e.g., Figs. 11A, C, 12C) are found mainly (although not exclusively) in the Maršikov I pegmatite. In these cases, the overall $Ta/(Ta + Nb)$ range of the recrystallized mineral may significantly exceed that of the primary zoned phase, with lower minimum and higher maximum values. Exceptions from enrichment in Fe are rare (cf. Fig. 12A).

Recrystallization of columbite-tantalite is a gradual, possibly multistage process. Initially, a patchy "bird's-eye" texture develops with a concentric oscillatory zoning of its own (Figs. 6A, B, 12A, B). In other cases, a random aggregate of irregular, ragged grains is formed; individual grains are virtually homogeneous internally but highly variable from one to the other, with ambiguous textural relationships (Figs. 6C, 12C). The granular and "bird's-eye" aggregates pass in later stages into columbite-tantalite that is close to being

homogeneous, at least in terms of $Ta/(Ta + Nb)$ (Figs. 6A, B, 12A, B, C).

As to the $Mn/(Mn + Fe)$ ratio, no clearcut relationship is observed between the level of enrichment in Fe (plus Mg, Ti) and the degree of homogenization of $Ta/(Ta + Nb)$. The shift toward high contents of Fe is close to being uniform at all stages of recrystallization. The apparent (and rare) exceptions, such as that shown in Figure 12D, seem to result from insufficient analytical sampling rather than actual differences in ranges of $Mn/(Mn + Fe)$. The extent of Fe enrichment must be emphasized: the secondary columbite-tantalite ranges to values of $Mn/(Mn + Fe)$ that are lower by as much as 0.40 than the Fe-rich side of the primary clusters of data (Fig. 11B), and differences in the range of 0.15 to 0.20 are common (Figs. 11A, C, D, 12B, C).

DISCUSSION

Premetamorphic state of the Maršikov pegmatites I and III

Available data indicate that prior to metamorphism, the two pegmatite bodies examined were very similar in overall geochemistry and mineralogy. This inference is supported by the bulk composition of the dikes, the minor- and trace-element contents of rock-forming silicates, the bulk composition of the garnet, and the scarcity of K-feldspar.

Primary columbite-tantalite shows essentially the same compositional range in both pegmatites, with a slight shift toward a higher degree of fractionation in dike I. Fersmite and microlite (+ pyrochlore) are distinctly more abundant in dike I at present, but the scarcity of these minerals in dike III is not necessarily representative of their abundance prior to metamorphism. The relict nature of these phases in dike III suggests that they could have been much more widespread (although not necessarily as much as in dike I), but were largely obliterated by metamorphic processes.

Thus we can conclude that the two pegmatite bodies were closely analogous before the onset of metamorphism, in terms of mineral assemblages and mineral chemistries, although abundances of individual minerals could have been somewhat different.

Effects of metamorphism on the Nb-Ta oxide minerals

Four phenomena observed in the preceding sections should be considered to interpret metamorphism as a factor modifying the assemblage and individual constitutions of Nb-Ta oxide minerals:

initial premetamorphic state of these phases, reconstitution of columbite-tantalite, destruction of fersmite and microlite, and changes in structural state of columbite-tantalite.

(i) The oscillatory zoning of the primary columbite-tantalite crystals and their considerably disordered structure represent a state of high free energy, even at the late-magmatic stage of their crystallization. The discrepancy between their free energy and the equilibrium state increased after consolidation and cooling of the pegmatite hosts. Thus it is not surprising that columbite-tantalite was subject to extensive reconstitution during metamorphism, with the whole mineral assemblage being modified. Prograde metamorphic conditions supplied the activation energy (P, T, shearing) and generated at least a modest flow of fluid (dehydration reactions, influx of fluids from country rocks), which promoted adjustment of the Nb-Ta oxide minerals.

(ii) Columbite-tantalite underwent gradual recrystallization concomitant with homogenization of the Ta/(Ta+Nb) ratio, and moderate to considerable enrichment in Fe, with some increase in Mg and Ti.

Recrystallization progressed essentially through two stages. "Bird's-eye" structures developed initially, as ellipsoidal to angular patches with concentric oscillatory zoning, or random aggregates of anhedral ragged grains with widely different compositions. Both textural types cover the same range of Ta/(Ta+Nb), commonly about the same as shown by the primary mineral, or somewhat smaller. In later stages, columbite-tantalite became homogenized, with rare relics of the "bird's-eye" or granular texture. The reasons for the textural differences at the early stage of recrystallization are not known; the mechanism generating oscillatory zoning is rather obscure, even in primary crystals (*cf.* Lahti 1987). It should be noted, however, that the initial compositionally heterogeneous product of recrystallization is typical mainly of the Maršíkov I pegmatite, whereas the advanced homogenization is observed predominantly at the Maršíkov III locality. Thus the increasing intensity of metamorphic effects seems to have promoted increasing degrees of Nb-Ta redistribution.

It must be stressed that the above homogenization in the distribution of Nb and Ta proceeds at a very local scale, within individual mm-sized crystals and their small aggregates. We have no reason to suspect long-range migration of these elements between grains of Nb-Ta oxide minerals that are commonly separated by decimeters to meters of silicate host-rock.

Enrichment in Fe, Mg and Ti proceeded simultaneously with the above recrystallization and homogenization of the content of Nb and Ta. In

contrast to the internal and extremely local redistribution of Nb and Ta, these three elements had to be introduced from the country-rock hornblende gneiss. Novák (1988) reached the same conclusion about the origin of the Fe-rich outermost zone of garnet crystals from the pegmatites examined; the Mn/(Mn+Fe) in the rim is lower by as much as 0.50 relative to the interior. The only possible exception to the external provenance is Ti, which could be in part contributed by the breakdown of microlite. There does not seem to be any significant difference in the Mn/(Mn+Fe), Mg or Ti ranges at the two stages of redistribution of Nb and Ta. Consequently, pervasive flow of pore fluids from the metamorphic suite through the pegmatites had to have taken place already in the early stages of metamorphism.

(iii) Fersmite and microlite are largely intact in dike I, but they decomposed during the advanced, shear-accentuated metamorphism of dike III. Mechanical instability and a gradient in chemical potentials of Ca and F between the affected minerals and the intergranular fluid may be among the factors destabilizing them. The high friability of microlite is well known from ore beneficiation, and the behavior of fersmite seems to be close to that of microlite in this respect.

The Nb, Ta and Ti liberated during the breakdown of fersmite and microlite were probably coupled with some of the Fe and Mg (plus Ti) introduced from country rocks, and incorporated into the reconstituted columbite-tantalite. It is significant in this respect that in some cases the range of Ta/(Ta+Nb) of the heterogeneous products of initial recrystallization is larger than that of the primary crystals (*e.g.*, Figs. 11C, 12C). The presence of microlite, yielding Ta dominant over Nb locally, and fersmite, contributing Nb dominant over Ta, could have initially expanded the primary Ta/(Ta+Nb) span to higher and lower values, respectively, in a process that otherwise reduces the range encountered in primary columbite-tantalite.

(iv) In natural columbite-tantalite, the degree of structural order is highly variable, and depends on several factors, such as bulk composition and heterovalent substitutions (*e.g.*, Černý *et al.* 1984, Černý & Ercit 1985, 1989). Well-defined ranges of structural order are commonly characteristic of regional populations of granitic pegmatites, or of specific units within complex pegmatites (*e.g.*, Černý & Ercit 1985, Ercit 1986). The metastable persistence of intermediate to disordered structural states in columbite-tantalite is well known from experimental work, particularly at medium to low temperatures (*e.g.*, Komkov & Dubik 1974). High-temperature treatment is required to achieve ordering of columbite-tantalite within reasonable

time (e.g., 1000°C/16 hrs; Černý & Turnock 1971, Wise *et al.* 1985).

In view of the above, the intermediate structural state typical of primary columbite-tantalite from the Maršíkov pegmatites is not surprising, as it seems to be the rule rather than exception among natural members of this group of minerals (Černý & Ercit 1985, 1989). It is also understandable that metamorphism of the Maršíkov columbite-tantalite promoted substantial ordering. The long duration of metamorphic temperatures above ~500°C, combined with compositional reconstitution of primary columbite-tantalite, resulted in a distinctly more ordered secondary phase.

SUMMARY

The (Be,Nb,Ta)-bearing Ab + Qtz + Ms pegmatites at Maršíkov contain a primary assemblage of oscillatory-zoned columbite-tantalite (dominantly manganocolumbite), veined by fersmite (with a few compositions having Ta > Nb) and microlite (rarely also pyrochlore). Silimanite-grade metamorphism of the pegmatites strongly affected these primary phases (Fig. 13). Although no sharp boundaries can be defined that would separate the sequence of events, it seems probable that different effects can be correlated

with each of the two stages of prograde regional metamorphism.

During the first stage, under relatively static conditions, initial reconstitution of columbite-tantalite generated a "bird's-eye" structure and granular aggregates with highly variable Ta/(Ta+Nb). Considerable enrichment in Fe and some increase in Mg and Ti proceeded simultaneously. Whereas redistribution of Nb, Ta and Ti was an internal process, the Fe, Mg (and some Ti) were introduced by fluids mobilized from host rocks. Fersmite and microlite largely survived this first metamorphic stage. However, initial breakdown of these two minerals probably contributed to the extensive range of Ta/(Ta+Nb) values in some aggregates of secondary columbite-tantalite; extreme compositions exceed both the minimum and maximum values of their primary precursors.

The second metamorphic stage, marked by extensive shearing, resulted in a thorough homogenization of Ta/(Ta+Nb) in secondary columbite-tantalite, although the ranges of Mn/(Mn+Fe), Mg and Ti remained at the previous levels. Oscillatory zoning and other growth-related features of the primary columbite-tantalite were locally entirely erased. Fersmite and microlite were almost completely obliterated.

Changes in the structural state of columbite-tantalite could not be tracked down in much detail.

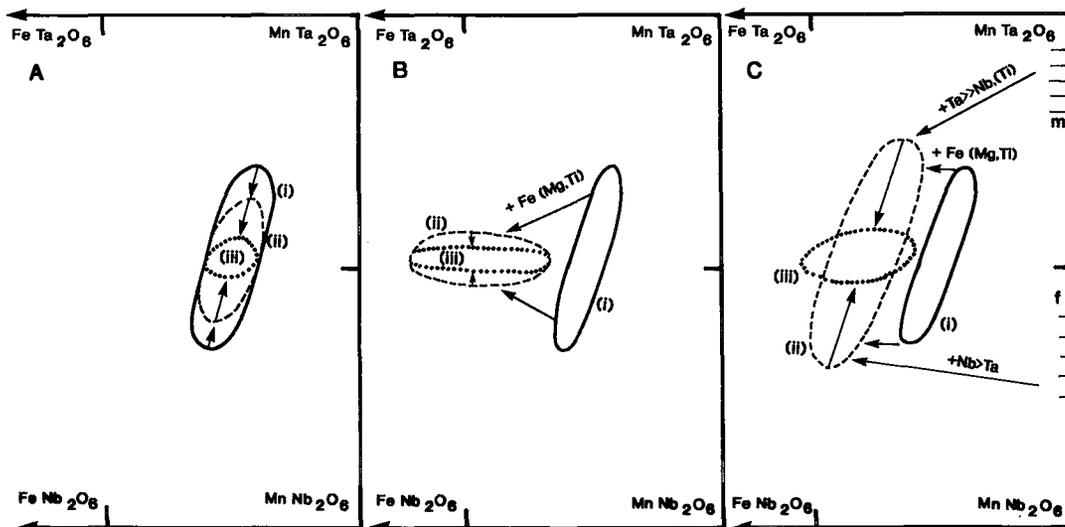


FIG. 13. Schematic three-stage evolutionary trends of columbite-tantalite in Maršíkov pegmatites I and III. A. Gradual homogenization of Ta/(Ta+Nb) with no substantial change in Mn/(Mn+Fe) (rather exceptional). B. Same, with enrichment in Fe(Mn,Ti) in early stages (most common). C. Same, combined with expansion of the Ta/(Ta+Nb) range in early stages by breakdown of microlite and fersmite (common). (i) Primary oscillatory-zoned columbite-tantalite, (ii) secondary "bird's-eye" or granular heterogeneous assemblage, (iii) secondary phase with homogenized Ta/(Ta+Nb).

However, there is no doubt about a general increase in degree of structural order, promoted during metamorphism and compositional reconstitution of the mineral.

In conclusion, the conspicuous difference between "autometasomatic" alteration of columbite-tantalite and the metamorphic effects at Maršíkuv should be pointed out. The late-magmatic to subsolidus processes of pegmatite consolidation invariably lead to diversification of the mineralogy of Nb and Ta, introducing a multitude of additional cations and OH, F into its composition. Overgrowths, veining and replacements of columbite-tantalite by (Nb-Ta)-bearing minerals with Na, Ca, Sb, Bi, Pb, Sn, Al or Cs are commonplace (e.g., Ercit 1986, Černý *et al.* 1986, Voloshin & Pakhomovskiy 1988, Černý & Ercit 1989). In contrast, the metamorphic effects described here destabilize the (Na,Ca,F,OH)-bearing minerals, reduce the primary magmatic assemblage of (Nb-Ta)-bearing phases to columbite-tantalite alone, and homogenize the composition of this mineral. This contrast is illustrative of the differences between the parent environments: disequilibrium conditions of relatively rapid crystallization of pegmatite (and metastable survival of most of the resulting mineral assemblages) on one hand, and long-lasting metamorphic processes promoting equilibration on the other.

The present study of the Maršíkuv pegmatites is the first to explore the influence of regional metamorphism on Nb-Ta oxide minerals. Consequently, there are no other cases available for comparison, and no generalizations can be offered on the basis of a single locality. We can only state that regional metamorphism does affect the minerals of Nb and Ta, and very profoundly so. This is in considerable contrast to the brittle and chemically unreactive behavior of these phases in an environment of mylonitization, even under conditions that promote recrystallization of quartz and some silicates (unpubl. data of PC). Any other locality that may provide further insight into the metamorphic reactions of Nb-Ta oxide minerals is well worth a thorough examination.

ACKNOWLEDGEMENTS

The authors acknowledge the financial and logistical support from the Moravian Museum during the field studies (MN), and the NSERC Operating and Major Installation Grants that funded the laboratory work (PC). Ing. A. Kašpárek made specimen MM-48 available for our study, and Mr. N. Ball provided extensive help with the X-ray-diffraction study. The manuscript was much improved thanks to constructive comments of T.S. Ercit, E.E. Foord and R.F. Martin.

REFERENCES

- ANDERSON, A.J. (1984): *Geochemistry, Mineralogy and Petrology of the Cross Lake Pegmatite Field, Manitoba*. M.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Comp. Contr.* **20** (NTIS Doc. **PB2-16188**).
- BARTON, M.D. (1986): Phase equilibria and thermodynamic properties of minerals in the BeO-Al₂O₃-SiO₂-H₂O (BASH) system, with petrologic applications. *Am. Mineral.* **71**, 277-300.
- ČERNÝ, P. (1982): Petrogenesis of granitic pegmatites. In *Granitic Pegmatites in Sciences and Industry* (P. Černý ed.) *Mineral. Assoc. Can., Short-Course Handbook* **8**, 405-461.
- _____ (1990): Distribution, affiliation and derivation of rare-element granitic pegmatites in the Canadian Shield. *Geol. Rundschau* **79**, 183-226.
- _____ (1991): Fertile granites of Precambrian rare-element pegmatite fields: is geochemistry controlled by tectonic setting or source lithologies? *Precamb. Res.* **51**, 429-468.
- _____, CHAPMAN, R., CHACKOWSKY, L.E. & ERCIT, T.S. (1989): A ferrotantalite-ferrotapiolite intergrowth from Spittal a.d. Drau, Carinthia, Austria. *Mineral. Petrol.* **41**, 53-63.
- _____ & ERCIT, T.S. (1985): Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. *Bull. Minéral.* **108**, 499-532.
- _____ & _____ (1989): Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. In *Lanthanides, Tantalum and Niobium* (P. Möller, P. Černý & F. Saupé, eds.). Springer-Verlag, New York (27-79).
- _____, _____ & WISE, M.A. (1984): Compositional and structural variability in columbite-tantalite and tapiolite. *Geol. Soc. Am., Abstr. Programs* **16**, 466.
- _____, GOAD, B.E., HAWTHORNE, F.C. & CHAPMAN, R. (1986): Fractionation trends of the Nb- and Ta-bearing oxide minerals in the Greer Lake pegmatitic granite and its pegmatite aureole, southeastern Manitoba. *Am. Mineral.* **71**, 501-517.
- _____ & TURNOCK, A.C. (1971): Niobium-tantalum minerals from granitic pegmatites at Greer Lake, southeastern Manitoba. *Can. Mineral.* **10**, 755-772.
- CHACKOWSKY, L.E. (1987): *Mineralogy, Geochemistry and Petrology of Pegmatitic Granites and Pegmatites at Red Sucker Lake and Gods Lake, Northeastern*

- Manitoba*. M.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- CHATTERJEE, N.D. & JOHANNES, W. (1974): Thermal stability and standard thermodynamic properties of synthetic $2M_1$ muscovite, $KAl_2AlSi_3O_{10}(OH)_2$. *Contrib. Mineral. Petrol.* **48**, 89-114.
- DOSTÁL, J. (1964): *Geological and Petrographic Study of the Maršikov Area – Mineralogical Study of Actinolite from Sobořín*. M.Sc. thesis, Faculty of Sci., Charles Univ., Prague (in Czech).
- (1966): Mineralogische und Petrographische Verhältnisse von Chrysoberyl-Sillimanit-Pegmatit von Maršikov, *Acta Univ. Carolinae – Geol.* **4**, 271-287.
- EBY, R. (1986): *A Structural and Petrofabric Study of Sheared Pegmatite Dikes, Red Cross Lake, Manitoba*. Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- ERCIT, T.S. (1986): *The Simpsonite Paragenesis. The Crystal Chemistry and Geochemistry of Extreme Ta Fractionation*. Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- , ČERNÝ, P. & SHIVOLA, J. (1987): The composition of stannomicrolite. *Neues Jahrb. Mineral., Monatsh.*, 249-252.
- FRANZ, G. & MORTEANI, G. (1984): The formation of chrysoberyl in metamorphosed pegmatites. *J. Petrol.* **25**, 27-52.
- GINZBOURG, A.I. (1960): Specific geochemical features of the pegmatitic process. *Int. Geol. Congress, 21st (Norden)* **17**, 111-121.
- , TIMOFEYEV, I.N. & FELDMAN, L.G. (1979): *Principles of Geology of the Granitic Pegmatites*. Nedra, Moscow (in Russ.).
- GÖD, R. (1989): The spodumene deposit at "Weinebene", Koralpe, Austria. *Miner. Deposita* **24**, 270-278.
- GREW, E.S. (1981): Surinamite, taaffeite and beryllian sapphirine from pegmatites in granulite-facies rocks of Casey Bay, Enderby Land, Antarctica. *Am. Mineral.* **66**, 1022-1033.
- GRIP, E. (1940): A lithium pegmatite on Kluntarna in the archipelago of Pitea. *Geol. Fören. Stockholm Förh.* **62**, 380-390.
- HOGARTH, D.D. (1977): Classification and nomenclature of the pyrochlore group. *Am. Mineral.* **62**, 403-410.
- HRUSCHKA, W. (1824): Vorkommen und Kristallisation einiger mährischen Fossilien. I. Chrysoberyll. *Mitt. der Mähr.-Schles. Gesellschaft* **52**, 413-415.
- KOMKOV, A.I. & DUBIK, O.YU. (1974): Experimental examination of polymorphic and isomorphic relationships in the system $FeNb_2O_6$ - $FeTa_2O_6$ - $MnTa_2O_6$ - $MnNb_2O_6$. In *Kristalloghimiya: Strukturnaya Mineralogiya* (V.A. Frank-Kamenetskiy, ed.). Nauka, Leningrad (82-93; in Russ.).
- LAHTI, S.I. (1987): Zoning in columbite-tantalite crystals from the granitic pegmatites of the Eräjärvi area, southern Finland. *Geochim. Cosmochim. Acta* **51**, 509-517.
- LUSTER, G.R. (1977): *Lithologic Variability of the Kings Mountain Pegmatite, North Carolina*. M.Sc. thesis, Pennsylvania State Univ., University Park, Pennsylvania.
- NEJEC, D. (1989): Lithium aluminosilicates in pegmatites affected by stress. *Chem. Erde* **49**, 167-172.
- NOVÁK, M. (1988): Garnets from pegmatites of the Hrubý Jeseník Mts. (northern Moravia, Czechoslovakia). *Acta Mus. Moraviae, Sci. Nat.* **73**, 3-28 (in Czech).
- POUCHOU, J.L. & PICHOU, F. (1985): "PAP" procedure for improved quantitative microanalysis. *Microbeam Anal.* **20**, 104-105.
- RENÉ, M. (1983): Geochemistry and petrology of metapelites in the envelope of the core of the Desná dome in northern Moravia. *Cas. pro Mineral. a Geol.* **28**, 277-286 (in Czech).
- ROBIE, R.A. & HEMINGWAY, B.S. (1984): Entropies of kyanite, andalusite and sillimanite: additional constraints on the pressure and temperature of the Al_2SiO_5 triple point. *Am. Mineral.* **69**, 298-306.
- ROSSOVSKIY, L.N. (1974): Regular orientation of minerals as an indicator of the conditions of formation of rare-metal pegmatites. *Zap. Vses. Mineral. Obshchest.* **103**(1), 44-51 (in Russ.).
- & BOVIN, YU.P. (1971): Formation of rare-metal pegmatites under conditions of high lateral pressure. *Geol. i Geof. Moscow* **5**, 1322-1327 (in Russ.).
- , CHMYREV, V.M. & SALAKH, A.S. (1976): Genetic relationship of aphanitic spodumene dikes to lithium-pegmatite veins. *Dokl. Acad. Sci. USSR, Earth-Sci. Sect.* **226**, 170-172.
- & KONOVALENKO, S.I. (1979): Features of the formation of the rare-metal pegmatites under conditions of compression and tension (as exemplified by the Hindu Kush region). *Int. Geol. Rev.* **21**, 755-764.
- SHMAKIN, B.M. (1976): *Muscovite and Rare-Metal Muscovite Pegmatites*. Nauka, Novosibirsk (in Russ.).
- SIMPSON, M.G. (1977): *Structural Analysis of the Kings Mountain Belt, Kings Mountain, North Carolina*. M.Sc. thesis, Univ. South Carolina, Columbia, South Carolina.

- SOUČEK, J. (1978): Metamorphic zones of the Vrbno and Rejviz Series, Hrubý Jeseník Mts., Czechoslovakia. *Tschermaks Mineral. Petrogr. Mitt.* **25**, 195-217.
- VOLOSHIN, A.V. & PAKHOMOVSKIY, YA.A. (1988): *Minerals of Tantalum and Niobium in Rare-Metal Pegmatites*. Nauka, Leningrad (in Russ.).
- WISE, M.A., TURNOCK, A.C. & ČERNÝ, P. (1985): Improved unit cell dimensions for ordered columbite-tantalite end-members. *Neues Jahrb. Mineral., Monatsh.*, 372-378.
- WILSON, C.J.L. (1980): Shear zones in a pegmatite: a study of albite-mica-quartz deformation. *J. Struct. Geol.* **2**, 203-209.

Received February 19, 1991, revised manuscript accepted July 7, 1992.