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THE CRYSTAL CHEMISTRY OF THE TAPIOLITE SERIES

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ABSTRACT

Ferrotapiolite–manganotapiolite-group minerals [(Fe,Mn)Ta_2O_6] are formed as accessory phases in rare-element granitic pegmatites exhibiting moderate to high degrees of fractionation. Despite their relative paucity, 94 sets of unit-cell parameters and 194 chemical compositions were compiled to characterize the crystal chemistry of the tapiolite series. X-ray-diffraction studies indicate that the degree of order and compositional variations strongly influence unit-cell dimensions of tapiolite. Natural tapiolite shows wide ranges of structural state. Crystallization of disordered phases at low temperatures is suggested; however, the available data are not unambiguous. Tapiolite chemistry is typically uniform (Fe > Mn, Ta > Nb), and compositional variations are the result of limited, but effective homovalent and heterovalent substitutions: (1) $Mn^{2+}Fe^{2+}_{-1}$; (2) $Nb^{5+}Ta^{5+}_{-1}$; (3) $Fe^{3+}(Ti,Sn)^{4+}Fe^{2+}_{-1}(Ta,Nb)^{5+}_{-1}$ and (4) $(Ti,Sn)^{4+}_3(Fe,Mn)^{2+}_{-1}(Nb,Ta)^{5+}_{-2}$. In association with other Nb,Ta,Sn-bearing minerals, tapiolite shows a distinct preference for Fe^{2+} and Ta over Mn and Nb. Enrichment in Nb, Ti and Sn appears to be common in tapiolite from moderately fractionated pegmatites, whereas extreme Mn enrichment is typical of highly fractionated pegmatites of the petalite subtype or metasomatic units.

Keywords: tapiolite series, crystal chemistry, order – disorder, tantalum, granitic pegmatite.

SOMMAIRE

Les minéraux de la série ferrotapiolite – manganotapiolite [(Fe,Mn)Ta_2O_6] se présentent sous forme d'accessoires des pegmatites granitiques à éléments rares faisant preuve d'un degré de fractionnement intermédiaire à élevé. Malgré leur rareté, les résultats de 94 affinements de la maille élémentaire et de 194 analyses chimiques sont disponibles, et servent à caractériser la cristallochimie des minéraux de cette série. Les études par diffraction X permettent de voir que le degré d'ordre et les variations compositionnelles affectent fortement les paramètres réticulaires. L'ensemble des échantillons témoigne d'une grande variété du degré d'ordre. Nous préconisons une cristallisation des phases désordonnées à faibles températures, quoique les données disponibles sont assez ambiguës. La composition des minéraux de ce groupe est typiquement uniforme (Fe > Mn, Ta > Nb); les variations en composition peuvent s'expliquer par le degré des substitutions homovalentes et hétérovalentes suivantes, somme tout assez restreint: (1) $Mn^{2+}Fe^{2+}_{-1}$, (2) $Nb^{5+}Ta^{5+}_{-1}$, (3) $Fe^{3+}(Ti,Sn)^{4+}Fe^{2+}_{-1}(Ta,Nb)^{5+}_{-1}$, et (4) $(Ti,Sn)^{4+}_3(Fe,Mn)^{2+}_{-1}(Nb,Ta)^{5+}_{-2}$. Tout comme les autres minéraux porteurs de Nb, Ta et Sn qui lui sont associés, les minéraux de cette série semblent préférer le Fe^{2+} et le Ta au Mn et au Nb. Un enrichissement en Nb, Ti et Sn semble assez courant dans les minéraux de cette série dans les pegmatites granitiques à degré de fractionnement intermédiaire, tandis qu'un enrichissement extrême en Mn est typique de roches granitiques pegmatitiques fortement évoluées, du sous-type de la pétalite, ou bien d'unités métasomatiques.

(Traduit par la Rédaction)

Mots-clés: minéraux de la série de la tapiolite, chimie cristalline, ordre – désordre, tantale, pegmatite granitique.

INTRODUCTION

Minerals of the tapiolite series, (Fe,Mn)Ta_2O_6, occur primarily as accessory phases in rare-element granitic pegmatites that display moderate to high levels of fractionation, and rarely in some Ta-mineralized granites. Commonly associated with columbite – tantalite, wodginite and cassiterite, tapiolite is difficult to identify in hand specimens. Consequently, its presence is often overlooked. However, recent systematic studies of the mineralogy of Nb and Ta suggest that tapiolite, although subordinate to columbite – tantalite in overall abundance, is more common than was previously believed (Černý & Ercit

1985, Wise 1987). As part of an ongoing systematic study of Nb and Ta minerals, we aim here to provide a review of the mineralogy, crystal chemistry and geochemistry of the tapiolite series.

PREVIOUS WORK

Until recently, most studies on the tapiolite minerals were merely descriptive reports on its occurrences, with little or no X-ray-diffraction and chemical information given. The tapiolite structure was first solved by Goldschmidt (1926), but later refined by von Heidenstam (1968), Weitzel & Klein (1974), and Wise (1987). Hutchinson (1955) and Hutton (1958) were the first to identify an order – disorder relationship in natural tapiolite minerals. Clark & Fejer (1978) and Wise (1987) provided a thorough study on the composition and unit-cell dimensions of tapiolite minerals from various localities.

Moreau & Tramasure (1965), Schröcke (1966) and Turnock (1966) have attempted to experimentally define compositional fields for tapiolite. Furthermore, Turnock (1966), Komkov & Dubik (1974a), and Zhao *et al.* (1977) investigated the conditions for the stability of tapiolite. However, the present state of experimental evidence is far from satisfactory (Černý *et al.* 1992).

EXPERIMENTAL METHODS

We used X-ray powder-diffraction methods to characterize the degree of cation order in unheated and heated tapiolite minerals. Heating induces order in disordered and partially disordered members of the series. Samples were scanned on an automated Philips powder-diffractometer system (PW 1710) at 6° 2θ/minute for the purpose of mineral identification and at 0.60° 2θ/minute for the refinement of unit-cell dimensions, with graphite-monochromated Cu*K*α radiation, operating voltage of 40 kV and operating current of 40 mA. Annealed CaF_2 [a = 5.46379(4) Å] calibrated against a NBS silicon reference standard (batch 640a; a = 5.430825 Å) was used as an internal standard in all slow scans. Peak positions and intensities were determined with the automated PW 1710 system using a computer-controlled continuous scanning program (CSP), which searches for the tops of diffraction peaks. The gross positions of peaks were calibrated to true $CuK\alpha_1$ positions ($CuK\alpha_1$ = 1.54064 Å) and calibrated against the internal standard using the computer program FIX, which reduces systematic error in positional data to ±0.01° 2θ (Ercit 1986). Fifteen to twenty-five corrected reflections were used for the indexing and unit-cell refinement using a modified version of the CELREF least-squares refinement computer program of Appleman & Evans (1973).

Fragments of ferrotapiolite crystals 2 to 5 mm in size were placed in silica "boats" lined with Ag–Pd foil and heated in a Fisher Isotemp muffle furnace (Model 186) in air at 1000°C at 1 atm for 16 hours. After heating, samples were cooled to room temperature, X-rayed, and their unit-cell parameters refined.

The chemical data for this study were obtained by electron-microprobe analysis at our laboratories, and selected data were collected from the literature. Electron-microprobe analyses were obtained at the University of Manitoba using a model MAC 5 electron microprobe in the energy-dispersion mode (ED). The principal data-set was augmented by data obtained on an ARL–SEMQ electron microprobe in wavelength-dispersion mode (WD) at the Smithsonian Institution. Operating conditions for (ED) microanalysis were: accelerating voltage 15 kV, beam diameter 1–2 mm, and collection time 200 seconds for each spectrum. The following standards were used for the study: chromite and fayalite (Fe*K*α), $CaNb_2O_6$ and $Ba_2NaNb_5O_{15}$ (Nb*L*α), manganotantalite (Mn*K*α, Ta*M*α), cassiterite (Sn*L*α), rutile and ilmenite (Ti*K*α), and $CaNb_2O_6$ and microlite (Ca*K*α). Energy-dispersion spectra were collected with a KEVEX Micro–X 7000 ED spectrometer and reduced with KEVEX computer software utilizing the MAGIC V computer program of Colby (1980). WD analyses were carried out at an operating voltage of 20 kV and a sample current of 0.015 nA, with 20-s counts. The following standards were used: $MnNb_2O_6$ (Mn*K*α, Nb*L*α), $CaTa_4O_{11}$ (Ca*K*α, Ta*M*α), cassiterite (Sn*L*α), ilmenite (Fe*K*α, Ti*K*α), Sc_2TiO_5 (Sc*K*α) and $MnWO_4$ (W*M*α). Data reduction was done using the procedure of Bence & Albee (1968). Back-scattered electron imagery was frequently used for examining textural features such as exsolution lamellae and inclusions, as well as for routine checks for compositional inhomogeneity and zoning. At least two data sets (rim and core) were collected for each crystal. In most cases, however, three to six points were analyzed across the mineral grain. Compositions of some grains occasionally showed cation sums in excess of structurally available sites if all the iron is calculated as Fe^{2+}. Recalculation of the unit-cell contents was adjusted by converting as much Fe^{2+} to Fe^{3+} as required to eliminate the cation surplus, *i.e.*, ferric iron for ferrotapiolite was calculated by normalizing to 12 oxygen atoms and 6 cations.

CRYSTAL CHEMISTRY

The general formula of tapiolite minerals can be expressed as AB_2O_6 where A represents Fe^{2+} and Mn^{2+}, and B, Ta^{5+} and Nb^{5+} (Ta > Nb). Ferric iron, titanium and tin occur in minor quantities in both sites. The present nomenclature of the tapiolite series is based on a study by Lahti *et al.* (1983). Ferrotapiolite refers to the Fe^{2+} end-member $FeTa_2O_6$, whereas manganotapiolite refers to the Mn-rich member. Of the more than 20 elements reported to occur in tapiolite minerals, only six of these, (Fe, Mn, Ta, Nb, Ti and Sn)

TABLE 1. MAXIMUM OXIDE CONTENTS REPORTED IN NATURAL TAPIOLITE

Oxide	Wt. %	Reference
Ta_2O_5	86.00	Ercit (1986)
Nb_2O_5	11.11	Wise (1987)
MnO	10.20	Lahti et al. (1983)
FeO	16.20	Lahti et al. (1983)
Fe_2O_3	5.80	Litovchenko (1966)
TiO_2	7.17	This study
SnO_2	3.92	Wise (1987)
CaO	1.96	Simpson (1917)
U_3O_8	0.28	Litovchenko (1966)
SiO_2	1.31	Lavrinenko et al. (1971)
Al_2O_3	0.29	Khvostova & Arkhangelskaya (1971)
WO_3	0.30	Lahti et al. (1983)
ZrO_2	0.20	von Knorring & Fadipe (1981)
Sc_2O_3	0.21	von Knorring & Fadipe (1981)
Sb_2O_3	1.40	Lahti et al. (1983)
Y_2O_3	0.01	von Knorring & Fadipe (1981)
MgO	0.61	Khvostova & Arkhangelskaya (1971)
CO_2	0.24	Rudovskaya (1962)
RE_2O_3	0.16	Litovchenko (1966)
CuO	0.14	Nordenskiold (1863)
H_2O^+	0.90	Lavrinenko et al. (1971)
H_2O^-	0.05	Chukhrov & Bonshtedt-Kupletskaya (1967)

are of any quantitative importance (Table 1). Representative chemical compositions of selected tapiolite minerals are provided in Table 2.

Tapiolite minerals are rarely pure, and typically contain some Nb (Fig. 1). The niobium content is generally less than 10% Nb_2O_5, although Permingeat (1955) reported on ferrotapiolite containing 21.2% Nb_2O_5. However, the compositions of apparently coexisting tantalite and ferrotapiolite analyzed in his study are not in agreement with recent data and

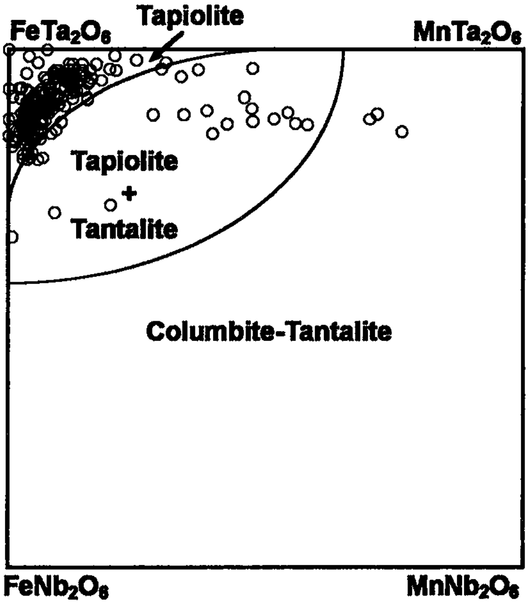

FIG. 1. Composition of natural tapiolite minerals in the columbite quadrilateral. The two-phase field marks the approximate extent of single-phase, non-paired compositions of tapiolite and columbite – tantalite. The new data reported here are complemented by those of Černý & Harris (1973), Clark & Fejer (1978), Lahti *et al.* (1983), and Wise (1987).

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF TAPIOLITE

	1	2	3	4	5	6	7	8	9	10
MnO, wt.%	0.38	0.70	0.89	0.90	1.22	1.60	2.28	4.27	6.02	10.20
FeO	11.90	11.93	13.20	12.83	11.81	11.49	11.29	9.45	7.22	3.20
Fe_2O_3	2.97	0.94	0.00	0.52	1.52	1.61	0.91	0.45	1.71	0.00
Sc_2O_3	0.00	0.04	0.06	0.00	0.00	0.06	0.00	0.00	0.00	0.00
TiO_2	4.87	7.17	0.49	0.00	0.12	0.93	0.10	0.00	0.57	0.00
SnO_2	0.00	1.16	0.07	3.92	2.79	0.28	0.67	0.00	0.29	1.00
Nb_2O_5	6.98	4.74	4.07	4.57	1.99	4.70	1.43	0.00	4.75	8.50
Ta_2O_5	72.17	72.60	81.65	78.38	81.14	77.47	83.78	85.97	78.76	76.30
Total	99.27	99.28	100.43	101.12	100.59	98.14	100.91	100.15	99.32	99.20
					Cations based on 12 oxygen atoms					
Mn^{2+}	0.050	0.091	0.124	0.124	0.171	0.224	0.323	0.616	0.837	1.409
Fe^{2+}	1.533	1.533	1.820	1.748	1.635	1.591	1.580	1.345	0.992	0.436
Fe^{3+}	0.344	0.109	0.000	0.063	0.190	0.201	0.115	0.058	0.211	0.000
Sc^{3+}	0.000	0.005	0.009	0.000	0.000	0.009	0.000	0.000	0.000	0.000
Ti^{4+}	0.564	0.828	0.061	0.000	0.015	0.116	0.013	0.000	0.070	0.000
Sn^{4+}	0.000	0.071	0.005	0.255	0.184	0.018	0.045	0.000	0.019	0.065
Nb^{5+}	0.486	0.329	0.303	0.337	0.149	0.352	0.108	0.000	0.353	0.627
Ta^{5+}	3.023	3.033	3.661	3.427	3.654	3.488	3.814	3.981	3.517	3.384
Total	5.999	5.999	5.982	5.999	5.999	5.999	5.999	6.001	5.999	5.921

(1) PEG Claim, Northwest Territories (Wise 1987), (2) NMNH #14439: Kararfvet mine, Sweden, (3) NMNH #168546: Alto do Giz mine, Brazil, (4) BIN pegmatite, Northwest Territories (Wise 1987), (5) BIGHILL pegmatite, Northwest Territories (Wise 1987), (6) NMNH #157839: Rio Grande do Norte, Brazil, (7) Tanco, Manitoba (Ercit 1986), (8) Alto do Giz mine, Brazil (Ercit 1986), (9) NMNH #146411: Tabba Tabba, Australia, (10) Tiainen pegmatite, Erajarvi, Finland (Lahti *et al.* 1983).

likely cannot be taken seriously. Although the Ta/Nb ratio varies greatly in natural specimens, it is never less than 1.0.

An alleged Nb-dominant member of the tapiolite series was described as "mossite", from Berg, near Moss, Norway (Brögger 1897). The crystals examined by Brögger were described as being tetragonal, but they were not analyzed. Holotype material chosen by Brögger (1906) for chemical analysis was found to contain 51.92% Ta_2O_5 and 31% Nb_2O_5 [Mn/(Mn + Fe) = 0 and Ta/(Ta + Nb) = 0.50]. "Mossite" also was reported by Pryce & Chester (1978) from the Greenbushes deposit in Australia. Their X-ray powder-diffraction data confirmed the tapiolite structure, and a measured density of 5.9 led them to believe that the material is Nb-rich. No chemical data for this material were reported. Bowley (1923) reported the occurrence of "manganomossite" from the Yinnietarra mine, Western Australia. Analysis of this material gave Mn/(Mn + Fe) = 0.72 and Ta/(Ta + Nb) = 0.44.

Re-examination of "mossite" and "manganomossite" has led to the discreditation of these minerals (Hutton 1959, Ewing 1976, Dunn *et al.* 1979). The material from Norway was shown by X-ray powder-diffraction studies to be a ferrotapiolite – ferrocolumbite mixture (Dunn *et al.* 1979). Chemical analysis of "mossite" from the Greenbushes deposit showed it to have Fe > Mn and, more importantly, Ta > Nb. Hutton's (1959) and Ewing's (1976) studies of "manganomossite" showed this material to be metamict manganocolumbite. Thus it appears that the formation of tetragonal $FeNb_2O_6$ is unlikely in nature.

Divalent manganese commonly replaces ferrous iron, but the extent of substitution is limited. Compositions close to the manganotapiolite end-member are not known. The amount of Mn occurring in natural tapiolite minerals is typically less than 2.0% MnO, but may reach up to 5.96%. Lahti *et al.* (1983) found tapiolite minerals with Mn > Fe (up to 10.2% MnO) and proposed the name *manganotapiolite*. However, if plotted on the columbite quadrilateral, most of their data plot within the tapiolite + tantalite region defined by natural samples and some experimental data. Textural evidence suggests that manganotapiolite may be a product of metastable crystallization, as it is only found in microscopically fine-grained mixtures with wodginite (Černý & Ercit 1985).

Data on the levels of ferric iron in tapiolite minerals are scarce. Although Fe^{2+} is predominant, Litovchenko (1966) found up to 5.80% Fe_2O_3 in a sample from the Ukraine. Litovchenko attributed the presence of Fe^{3+} to the oxidation of Fe^{2+} during albitization. Khvostova & Arkhangelskaya (1971) and Wise (1987) also have shown Fe^{3+} to be an important component in some cases.

Tapiolite compositions with *A*-site populations greater than the ideal value of 2.00 are generally considered to contain ferric iron. In our data base, where Fe_2O_3 was not determined and the cation sum in the *A* site was found to exceed 2.00, the excess Fe was recalculated to Fe^{3+}, and the Fe^{2+}/Fe^{3+} ratio determined by stoichiometry. This procedure was proven legitimate during the study of wodginite, conducted under similar analytical conditions and checked by Mössbauer spectroscopy (Ercit 1986, Ercit *et al.* 1992). On this basis, we find that most samples contain minor amounts of Fe^{3+}, and that the average content is about 2.5% Fe_2O_3 (0.3 atoms per formula unit Fe^{3+}).

Most samples of ferrotapiolite–manganotapiolite contain minor to trace amounts of titanium, the average of all compositions being 1.0% TiO_2 (0.12 atoms per formula unit Ti^{4+}). Electron-microprobe analysis of ferrotapiolite from Kararfvet, Sweden showed Ti contents of 7.17% TiO_2 (0.83 atoms per formula unit Ti^{4+}). The close similarity of the ionic radius of Ti^{4+}, Fe^{3+} and Ta^{5+} enables titanium to enter the tapiolite structure *via* the complementary substitution $Ti^{4+}_3(A^{2+}B^{5+}_2)_{-1}$. Tapiolite minerals enriched in Ti are generally poor in Mn.

Tapiolite minerals commonly contain minor to trace amounts of Sn. Although 3.92% SnO_2 (0.26 atoms per formula unit Sn^{4+}) was found in ferrotapiolite from the Yellowknife pegmatite field (Wise 1987), the SnO_2 content rarely exceeds 2.0%. The existence of a ferrotapiolite – cassiterite isomorphous series has been suspected from numerous finds of $FeTa_2O_6$-rich cassiterite and "staringite" (Černý & Ercit 1985, Groat *et al.* 1992); however, cases of Sn-rich tapiolite have yet to be found.

Calcium has been detected in a few cases and probably substitutes for divalent Fe in the *A* site. Calcium contents are generally minor, and samples with elevated Ca contents are also associated with microlite. It is quite possible that the Ca found in many analyses is due to submicroscopic inclusions of microlite.

The Si, Al, U, W, Zr, Sc, Sb, Mg, the rare-earth elements (*REE*) and H_2O contents are negligible, and their presence in the tapiolite structure is not considered established. Silicon and aluminum contents are easily attributed to contamination, whereas H_2O is likely due to the presence of iron or manganese hydroxides. Spectroscopic analyses of ferrotapiolite also showed traces of Be, Bi, Cu, Mo, Na, Ni, Pb, Sr, Te, V, Y, Yb and Zr (Rudovskaya 1962, Chen & Sidorenko 1962, Barsanov *et al.* 1964, Litovchenko 1966, Čech 1973).

As a general rule, the bulk composition of tapiolite minerals is fairly restricted. Although both Mn and Fe^{3+} are known to substitute for Fe^{2+}, the extent of substitution is limited (Fig. 2a). Compositions lie predominantly along the Fe^{2+}–Fe^{3+} join and, with few exceptions, rarely show extensive Mn enrichment. The uniform chemistry of tapiolite minerals is further

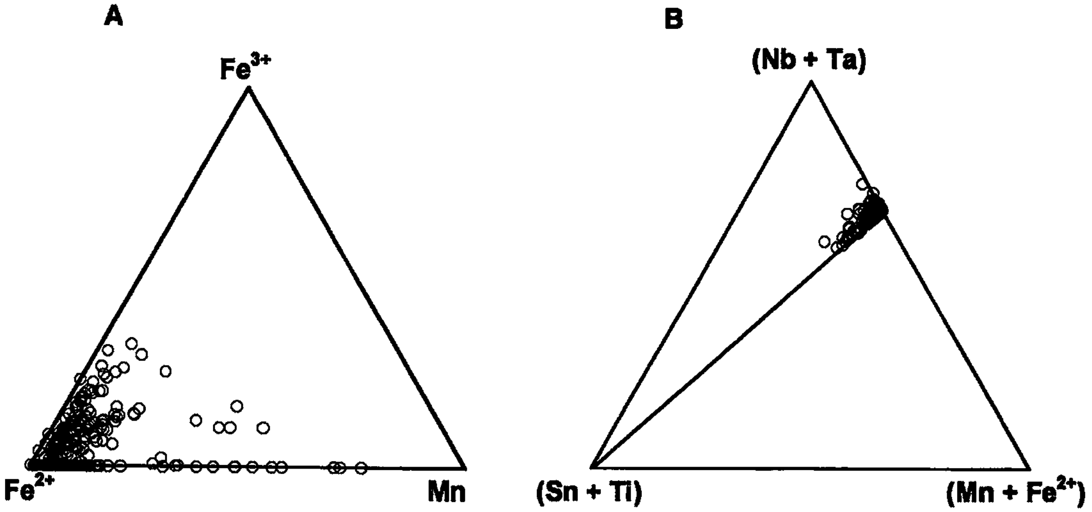

FIG. 2. Bulk composition (atomic) of tapiolite in the Fe^{2+} – Mn – Fe^{3+} triangle (A) and the (Nb,Ta) – (Sn,Ti) – (Fe^{2+}–Mn) triangle (B).

emphasized by Ta-rich compositions showing only minor enrichment in Ti and Sn (Fig. 2b).

CRYSTALLOGRAPHY

Crystal structure

Minerals of the tapiolite series are tetragonal, space group $P4_2/mnm$, $Z = 2$. Goldschmidt (1926) solved the structure of ferrotapiolite and showed it to be related to the rutile structure (Fig. 3). Both the Fe^{2+} and Ta cations occupy unique positions in the ordered structure (equivalent to the Ti sites in rutile) and are coordinated by six atoms of oxygen in a distorted octahedral arrangement. The oxygen atoms form hexagonal-closest-packed layers that lie parallel to (001). The oxygen atoms occupy the same positions as in the rutile structure, and each is surrounded by three cations.

The prominent feature of the structure is the presence of distorted, edge-sharing octahedra that form straight chains parallel to [001] (Fig. 3). These chains have an intrachain stacking sequence, ...*A–B–B–A–B–B*..., where *A* represents Fe^{2+} and *B* represents Ta in the ideal structural formula. Adjacent chains are linked by shared corners of the octahedra. This structure has been termed the trirutile structure by Goldschmidt (1926).

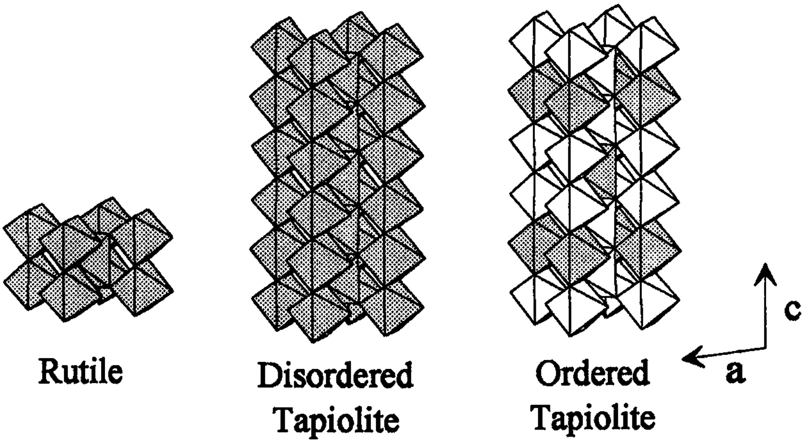

FIG. 3. Comparison of the rutile, disordered tapiolite and ordered tapiolite structures. Shaded octahedra represents Ti-bearing polyhedra in the rutile structure, Fe- and Ta-bearing polyhedra in the disordered structure, and Fe-bearing polyhedra in the ordered structure. Unshaded octahedra represents Ta-bearing polyhedra.

Structural order – disorder relationship

The trirutile structure described by Goldschmidt represents the ordered tapiolite structure, in which ordering of the Fe^{2+} and Ta cations in two unique sites (*A* and *B*, respectively) results in a tripling of the rutile cell along the *c* axis. The positions of the oxygen atoms remain essentially unchanged, whereas the cations order to form the previously described stacking sequence. If the Fe^{2+} and Ta cations become randomly distributed (disordered) over both the *A* and *B* sites, the two sites become equivalent in a larger unit-cell equivalent to that of rutile (monorutile structure).

The effects of order – disorder on natural samples is reflected in their X-ray powder-diffraction records (Fig. 4, Table 3). Disordered tapiolite has a diffraction pattern with supercell reflections weakened or missing, *i.e.*, *hkl* reflections where $l \neq 3n$. With increasing disorder, both the a and c cell dimensions increase, c increasing at a much greater rate than a. Disordered tapiolite typically shows unit-cell dimensions $a = 4.75$ and $c = (3 \times 3.08)$ 9.24 Å, compared to $a = 4.74$ and $c = 9.19$ Å for ordered tapiolite.

The departure from complete order was first noted by Hutchinson (1955) in specimens from the Ross Lake area, N.W.T. Hutton (1958) also noted similar relationships in ferrotapiolite from the Skogböle pegmatite, Finland. His detailed study of several fragments extracted from a single crystal showed either a trirutile-type pattern with weak subcell reflections or a monorutile-type pattern. Hutton's findings indicate that domains of varying degrees of order may exist within a single crystal. The data of Clark & Fejer (1978) confirm the large variation in structural state present in the tapiolite series. In addition, Wise (1987) noted varying degrees of order among different specimens from a single pegmatite body.

Hutton (1958) found that order may be restored by heating disordered ferrotapiolite in air at 500–1200°C. However, we have found that heating above 1000°C in air causes oxidation of Fe^{2+} and produces minor FeTaO$_4$ along with ordered tapiolite. Heat treatment of natural samples in air for 16 hours at 1000°C induces order with very limited oxidation of Fe^{2+}. When tapiolite minerals are heated (ordered), significant shifts in the relative positions of the diffraction peaks occur. In addition, weak or diffuse supercell reflections become more intense and sharper (this, Hutton felt, was clearly indicative of an order – disorder relationship).

The cause of structural disorder in tapiolite minerals is not well understood. Disorder due to compositional variations or temperature changes have been suggested, but thus far these hypotheses have

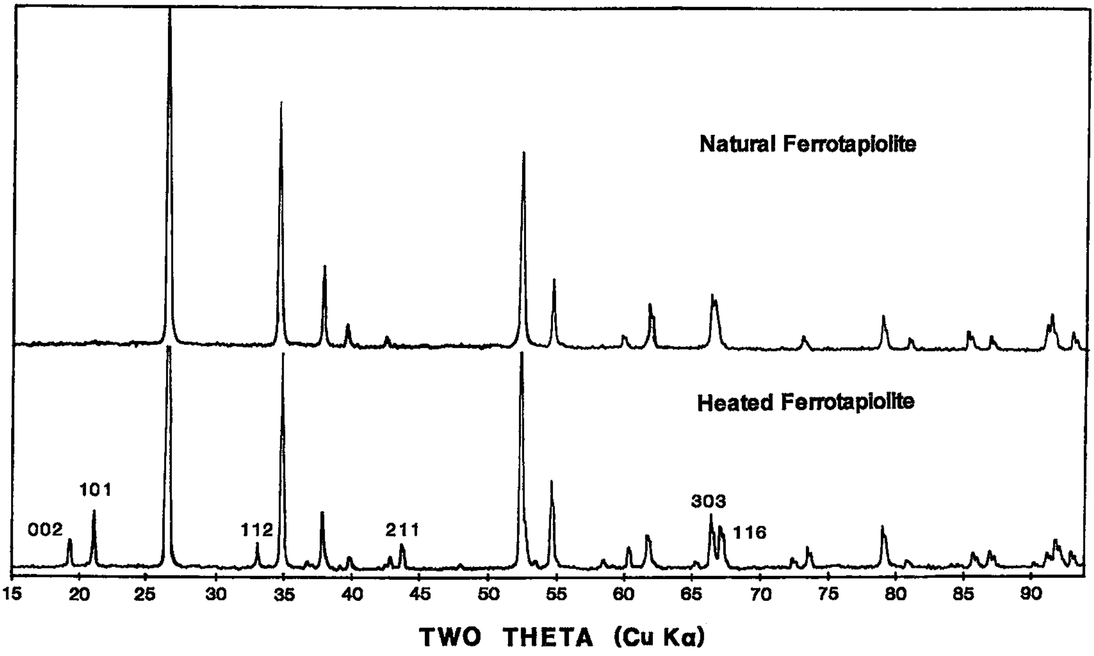

FIG. 4. Comparison of X-ray powder-diffraction patterns of natural (disordered) and heated (ordered) ferrotapiolite from the Yellowknife pegmatite field [sample PEG–319–1 of Wise (1987)].

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC AND NATURAL TAPIOLITE

	Synthetic $FeTa_2O_6$		Synthetic $(Mn_{.6}Fe_{.4})Ta_2O_6$		Disordered Ferrotapiolite		Ordered Ferrotapiolite	
hkl	I	d(obs)	I	d(obs)	I	d(obs)	I	d(obs)
002	15	4.603	14	4.654	2	4.621	9	4.610
101	27	4.230	31	4.248	2	4.231	16	4.229
110	98	3.366	99	3.374	100	3.366	100	3.365
112	17	2.715	14	2.727	2	2.719	9	2.711
103	100	2.577	100	2.594	44	2.592	57	2.575
200	28	2.378	25	2.383	16	2.377	16	2.376
004	4	2.300	3	2.318	-	-	2	2.299
113	6	2.265	7	2.279	5	2.275	6	2.263
210	4	2.127	-	-	3	2.126	3	2.125
202	7	2.112	7	2.120	-	-	4	2.108
211	10	2.072	15	2.077	-	-	7	2.070
114	6	1.898	6	1.910	-	-	3	1.895
213	83	1.747	80	1.754	40	1.751	83	1.745
105	7	1.716	8	1.728	-	-	4	1.715
220	19	1.682	35	1.684	23	1.680	32	1.678
204	-	-	5	1.662	-	-	-	-
222	7	1.579	7	1.584	-	-	4	1.577
301	5	1.562	4	1.565	-	-	3	1.559
006	16	1.533	10	1.546	3	1.546	7	1.532
310	21	1.504	27	1.507	10	1.503	15	1.502
312	7	1.430	7	1.433	-	-	4	1.427
303	24	1.408	20	1.413	13	1.410	10	1.406
116	19	1.395	20	1.406	10	1.406	12	1.393
224	4	1.358	-	-	-	-	3	1.355
313	3	1.350	-	-	2	1.352	-	-
321	5	1.306	6	1.309	-	-	3	1.303
206	14	1.289	15	1.297	4	1.296	5	1.287
107	3	1.267	4	1.277	-	-	2	1.265
314	5	1.259	5	1.264	-	-	3	1.257
323	17	1.212	23	1.216	9	1.213	12	1.210
305	5	1.201	4	1.207	-	-	3	1.199
400	7	1.189	8	1.192	3	1.189	3	1.187
402	4	1.151	4	1.154	-	-	2	1.149
411	5	1.144	5	1.147	-	-	-	-
226	14	1.133	11	1.139	3	1.138	15	1.131
330	8	1.121	8	1.123	5	1.208	8	1.119
118	4	1.089	5	1.097	-	-	3	1.087
413	17	1.080	17	1.083	6	1.080	6	1.078
316	18	1.074	19	1.080	4	1.078	8	1.072
420	8	1.064	9	1.066	7	1.063	4	1.062

Data for synthetic ferrotapiolite and manganotapiolite determined from synthetic products of Turnock (1966). Disordered (unheated) and ordered (heated) ferrotapiolite from the PEG Claim (Wise 1987).

been inadequately investigated. Compositionally dependent degree of order or disorder was studied on the related systems $CoNb_2O_6$–$CoTa_2O_6$ and $NiNb_2O_6$–$NiTa_2O_6$ by Felten (1967). At temperatures above 1400°C, Nb-dominant species crystallized with the rutile structure, whereas the Ta-dominant phases have the trirutile structure. Felten found that as the Nb content increases, the peak height of the supercell reflections decreases, and the peak broadens. He attributed the broadening of the supercell reflections to the crystallization of trirutile domains within the rutile structure, the domains becoming larger as the Ta content increases. Whether or not this holds true for naturally occurring tapiolite requires further study.

Crystals of synthetic $FeNb_2O_6$ grown between 850 and 1400°C were shown to have a disordered tapiolite structure (Aruga *et al.* 1985, Tokizaki *et al.* 1986). However, the crystals were formed under conditions that are unlikely to occur during formation of granitic pegmatite (*i.e.*, strongly reducing conditions and high temperatures in a dry system).

The influence of minor amounts of Nb, Mn, Ti and Sn on the order – disorder transformation has yet to be determined. Although Clark & Fejer (1978) found that the *a* dimension decreases with increasing Ti and Nb, they found no obvious correlation between degree of order and composition.

Temperature-related studies are only in their infancy. A single study by Komkov & Dubik (1974b) suggests that the degree of order may be temperature-dependent. Under hydrothermal conditions at 200–600°C, they found that the degree of order of $FeTa_2O_6$, based on the relative intensities of the (101) and (200) reflections, decreased with decreasing temperature. However, because of the strong compositional influence on the intensities of these reflections, we question the validity of this method and its conclusions.

A fundamental problem in adequately describing the tapiolite structure is the determination of the degree of order in natural specimens. The first attempt to quantify degree of order in the tapiolite series was that of Komkov (1974), who noted that the intensities of the (200) and (101) reflections diminished with increasing disorder. In general, all *hkl* reflections in which $l \neq 3$ show diminished intensities with increasing disorder. Because of its great sensitivity to structural changes, the $I(101)/I(200)$ ratio of ferrotapiolite was used as an indicator of order. However, we have found this method to be unsatisfactory, owing to the strong influence of Mn and Ti on the intensity of the (200) reflection. Clark & Fejer (1978) noted that the *c* dimension of disordered tapiolite minerals is significantly larger than that of ordered tapiolite. Ferrotapiolite was considered disordered if *c* is greater than 9.24 Å. However, examination of numerous sets of unit-cell dimensions of chemically analyzed samples showed this conclusion to be partly erroneous. High Mn contents also can produce high *c* values in tapiolite minerals that have a fully ordered structure. Thus a quick and simple means of determining the degree of order is not available at present, and we must rely on detailed refinement of the structure to obtain this information.

Unit-cell dimensions

The unit-cell dimensions of ferrotapiolite – manganotapiolite vary over a wide range; their variation is due to variable degree of order and variable chemical composition. Disordered tapiolite has larger *a* and *c* dimensions (and subsequently larger unit-cell volume) than ordered tapiolite (Hutton 1958). This is further shown by heating the disordered tapiolite, which causes the structure to order, resulting in reductions in *a*, *c* and *V*.

Chemical substitution also accounts for variations in the unit cell, although its role is not well understood. Clark & Fejer (1978) investigated the variations in cell dimensions with composition and found trends with extent of Nb, Ti and Mn incorporation. The effects of Mn and Fe^{3+} in synthetic tapiolite were examined by Turnock (1966) and Wise (1987). They showed that Mn-for-Fe substitution strongly affects *a*, *c* and *V*, whereas Fe^{3+} primarily affects the *a* dimension. Unfortunately, compositional effects are generally masked by variable degree of order. Our understanding of the overall variation in cell parameters remains somewhat unclear.

In order to clarify the above relationships, data on synthetic and natural phases were used to characterize the compositional dependence of the unit-cell dimensions of tapiolite. The primary substituting constituents are Mn^{2+}, Fe^{3+}, Ti^{4+}, Sn^{4+} and Nb^{5+}.

Manganese

Manganotapiolite and Mn-rich ferrotapiolite are rare in nature; as a result, we have had to rely upon synthetic phases to characterize the effect of Mn on the cell dimensions. Turnock (1966) synthesized tapiolite between the compositions $FeTa_2O_6$ and $(Fe_{0.4}Mn_{0.6})Ta_2O_6$. New, improved unit-cell dimensions were determined for Turnock's synthetic

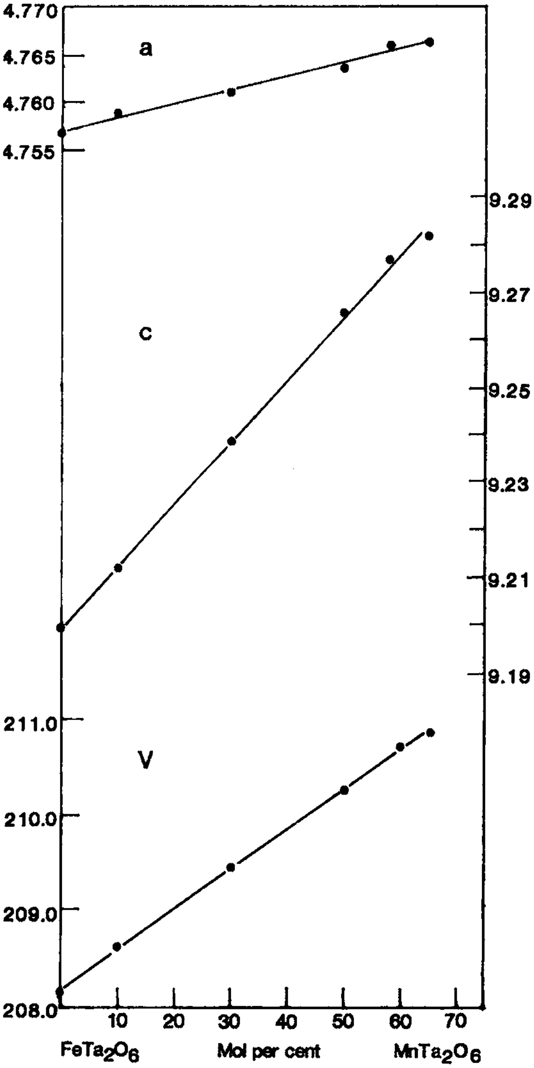

FIG. 5. Variation in unit-cell dimensions and cell volume of synthetic tapiolite with proportion of Mn. Unit-cell data refined from the materials synthesized by Turnock (1966). Errors on our data are about the size of the symbols.

TABLE 4. UNIT–CELL DIMENSIONS OF SYNTHETIC TAPIOLITE

	a (Å)	*c* (Å)	*V* (Å³)
Ferrotapiolite			
$FeTa_2O_6$	4.7570(4)	9.1992(9)	208.17(3)
Manganoan tapiolite and manganotapiolite			
$(Fe_{0.9}Mn_{0.1})Ta_2O_6$	4.7587(3)	9.2122(9)	208.61(2)
$(Fe_{0.7}Mn_{0.3})Ta_2O_6$	4.7611(2)	9.2393(6)	209.44(2)
$(Fe_{0.5}Mn_{0.5})Ta_2O_6$	4.7637(3)	9.2660(8)	210.28(2)
$(Fe_{0.4}Mn_{0.6})Ta_2O_6$	4.7660(2)	9.2772(6)	210.73(2)
$(Fe_{0.35}Mn_{0.65})Ta_2O_6$	4.7665(2)	9.2817(7)	210.87(2)
Ferric tapiolite			
$(Fe^{2+}_{0.92}Fe^{3+}_{0.08})Ta_2O_6$	4.7548(4)	9.1996(10)	207.99(3)
$(Fe^{2+}_{0.8}Fe^{3+}_{0.2})Ta_2O_6$	4.7478(3)	9.1943(7)	207.26(2)
Titanian tapiolite			
$(Fe_{1.9}Ti_{0.1})(Ta_{3.8}Ti_{0.2})O_{12}$	4.7138(4)	9.142(1)	203.12(4)

products (Fig. 5, Table 4). The results show a steep increase in the *c* dimension and a moderate increase in *a* with increasing Mn content. Tapiolite described by Čech (1973) and Lahti *et al.* (1983) show cell parameters typical of manganotapiolite. However, it should be stressed that large values of *c* in natural tapiolite are more likely the result of structural disorder. Caution thus is advised when estimating the Mn content of tapiolite using cell dimensions.

Ferric iron

Variations in the unit cell due to incorporation of ferric iron are not well characterized owing to the lack of Fe^{3+} determinations in chemical analyses. The ionic radius of Fe^{3+} (0.66 Å) is much smaller than that of Fe^{2+} (0.78 Å), and thus its effect would probably cause a decrease in the cell size. This assumption was verified by Turnock (1965), who synthesized Fe^{3+}-bearing ferrotapiolite. New unit-cell dimensions are shown in Figure 6. The experimental data show a gradual decrease in the *a* dimension and a more limited decrease in the *c* and *V* parameters with increasing proportion of ferric iron.

Titanium and tin

The effect of titanium incorporation on the unit cell of ferrotapiolite is similar to that of ferric iron (Fig. 7), *i.e.*, *a*, *c* and *V* all decrease with increasing Ti content (Wise *et al.* 1988). In contrast, preliminary investigations of the ferrotapiolite – cassiterite system shows that the incorporation of Sn into the tapiolite structure causes a decrease in *a* and an increase in both *c* and *V* (unpubl. data of M. Wise).

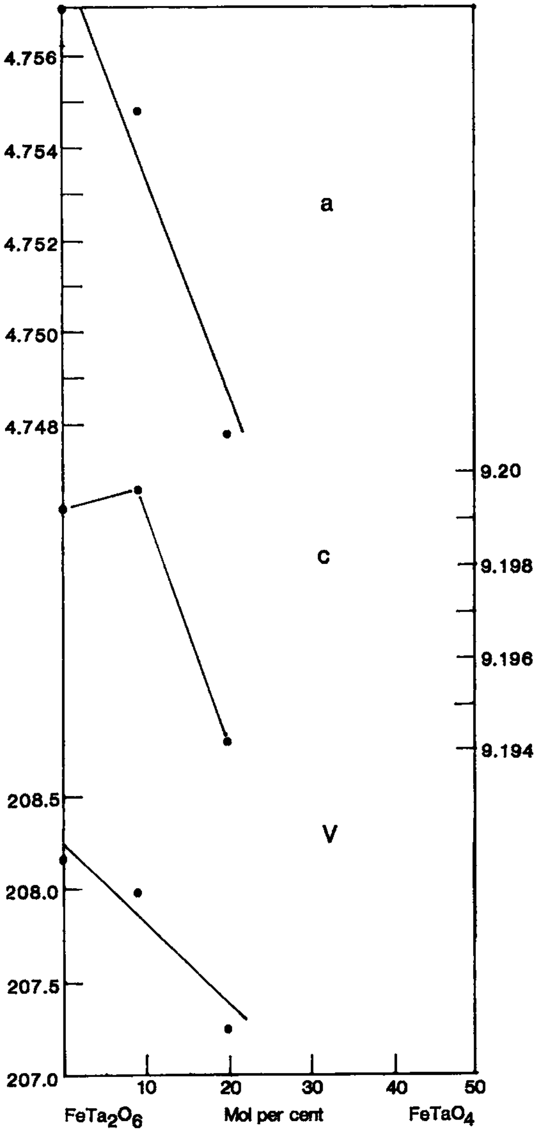

FIG. 6. Variation in unit-cell dimensions and cell volume of synthetic tapiolite with proportion of Fe^{3+}. Unit-cell data refined from the materials synthesized by Turnock (1965). Errors on our data are about the size of the symbols.

The a–c plot

A plot of the *a versus c* cell dimensions may be considered a convenient method of representing the degree of order for natural samples (Fig. 8a). However, the complex interdependence of cell dimensions of tapiolite minerals on composition and degree of order makes such a simple graphical representation of

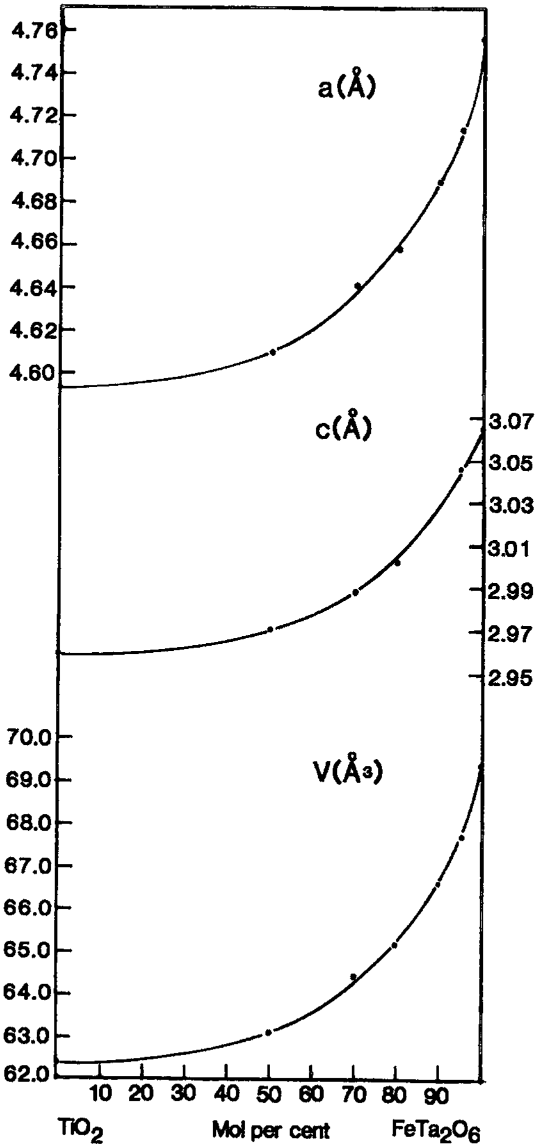

FIG. 7. Variation in unit-cell dimensions and cell volume of synthetic tantalian rutile and titanian tapiolite (Wise *et al.* 1988). For tapiolite (95 and 100 mol.% $FeTa_2O_6$), *c* and *V* are divided by 3 for a direct comparison to the rutile unit-cell. Materials synthesized at 1100°C, P = 1 atm, $CO/CO_2 = 3$ gas flow. Errors on our data are about the size of the symbols.

structural state difficult to interpret. Superimposed on the *a–c* plot are data for synthetic ordered phases outlining the effect of Mn, Fe^{3+} and Ti on the *a* and *c* dimensions. The data for disordered $FeTa_2O_6$ taken from Komkov & Dubik (1974b) are used here as a reference point for the extrapolation of Mn- and Fe^{3+}-rich disordered phases. Almost all of the available data for natural samples fall well within these bounding lines.

The relative degree of order in natural specimens can be seen by the comparison of the unit-cell dimensions for natural and heated samples. Tie-lines joining these points represent a heating vector or path of ordering (Fig. 8b). However, the general direction of these tie-lines is significantly different from that generated by the synthetic disordered phases, and it is difficult to determine which ordering trend is correct. Consequently, the determination of the degree of order in the tapiolite series remains unresolved until synthetic disordered phases are produced and an accurate method of quantifying degree of order in natural samples can be derived.

PHASE RELATIONS

Our present understanding of phase stabilities among ferrotapiolite–manganotapiolite and coexisting Nb,Ta-bearing oxide minerals is poor. A number of authors have attempted to characterize the stability range of the tapiolite series through experimental studies (Moreau & Tramasure 1965, Turnock 1966, Schröcke 1966, Komkov & Dubik 1974a). Despite their efforts, the picture remains hazy (Černý *et al.* 1992). Although a few studies have been conducted hydrothermally (Komkov & Dubik 1974a), most of the experimental work has been conducted in dry systems and under geologically unrealistic conditions. Ferrotapiolite was produced under controlled fugacities of oxygen by Turnock (1966) and Komkov & Dubik (1974a).

Solid solution between $FeTa_2O_6$ and $FeNb_2O_6$ is limited. Beugnies & Mozafari (1968) found that the incorporation of $FeNb_2O_6$ is limited to 36 mol.% in ferrotapiolite, although approximately 20 mol.% $FeNb_2O_6$ is the maximum amount found so far in natural tapiolite. The solubility of $FeNb_2O_6$ in synthetic $FeTa_2O_6$ is virtually nil at 885°C. Its limit has been determined to be 20 mol.% at 1050°C (Moreau & Tramasure 1965). At higher concentrations of Nb, intergrowths of ferrotapiolite + ferrocolumbite were observed. In contrast, Schröcke (1966) found that the $FeNb_2O_6$ solubility increases to 56 mol.% at 1100°C.

Solid solution toward $MnTa_2O_6$ has been shown to increase significantly with increasing temperature (Turnock 1966). His data show that the maximum extent of solid solution varies from near 58% at 1000°C to about 68% at 1500°C, at atmospheric pressure. A two-phase region of tapiolite + tantalite exists at concentrations greater than these limits in natural tapiolite; Mn-for-Fe substitution extends to about 40 mol.%, although most samples show less than 20 mol.% of the Mn end-member.

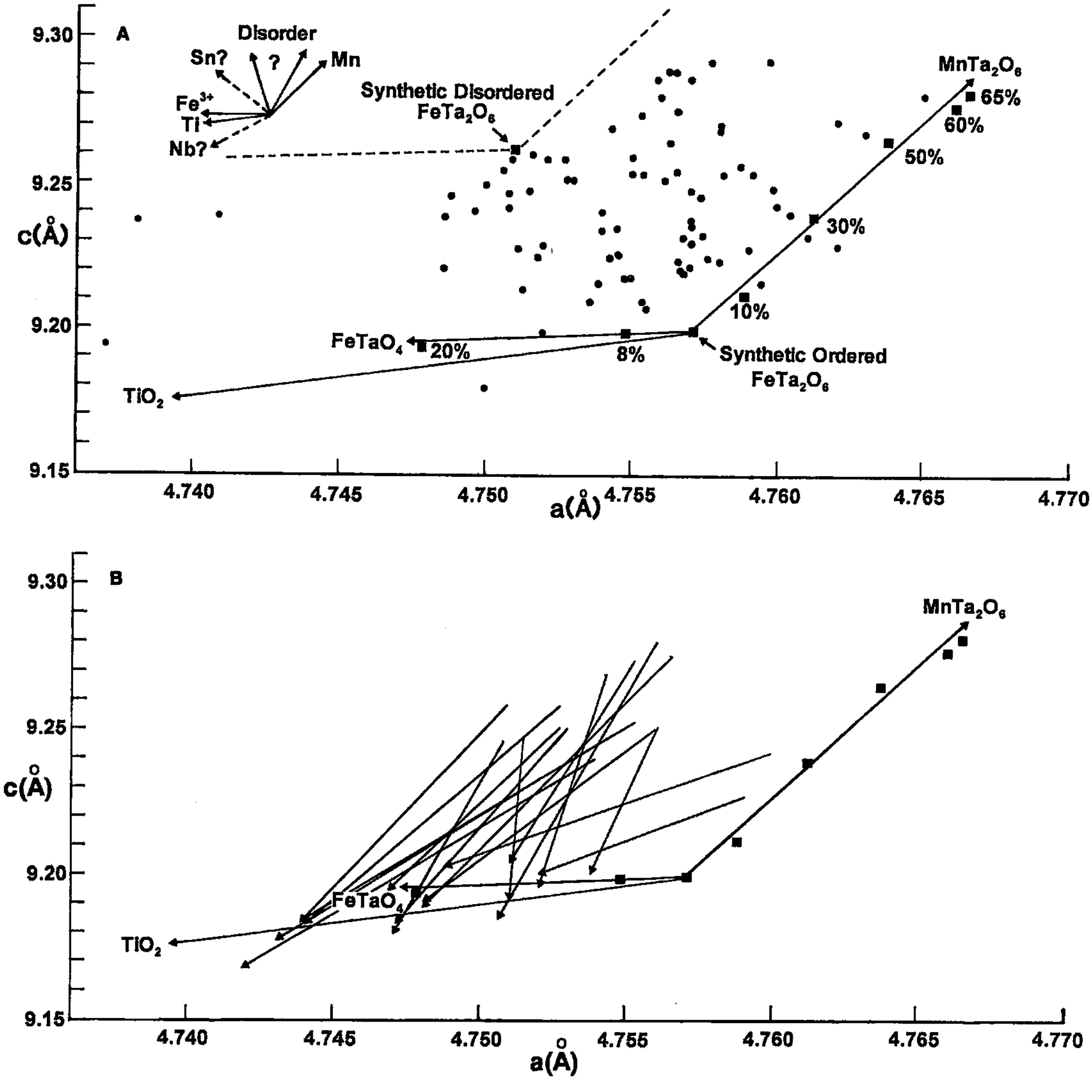

FIG. 8. The *a–c* plot for the tapiolite series, illustrating the probable degree of order. (A) Vectors indicate general change in *a* and *c* dimensions caused by chemical substitution. The data on synthetic ordered $FeTa_2O_6$, $FeTaO_4$ and Mn-substituted tapiolite of Turnock (1966) were refined by Wise (1987). The synthetic disordered $FeTa_2O_6$ is that of Komkov & Dubik (1974b). Dashed line represents extrapolation for Mn- and Fe^{3+}-rich disordered phases. Plots of natural tapiolite from Anderson (1984), Barsanov *et al.* (1964), Burke *et al.* (1969), Čech (1973), Černý & Harris (1973), Chen & Sidorenko (1962), Chukhrov & Bonshtedt-Kupletskaya (1967), Clark & Fejer (1978), Ercit (1986), Khvostova & Arkhangelskaya (1971), von Knorring *et al.* (1969), Lahti *et al.* (1983), Vorma (1965), Wise (1987), and unpublished data of the authors. (B) General trend of ordering of tapiolite from the Yellowknife pegmatite field. Arrowheads represent ordered (heated) tapiolite. Data of Wise (1987).

Under conditions of increasing temperature, pressure and oxygen fugacity, tapiolite-group minerals may become oxidized and incorporate Fe^{3+}. Synthetic tapiolite was found to take up to 22 mol.% $FeTaO_4$ into solid solution (Turnock 1966). A rutile-type phase occurs at higher concentrations of $FeTaO_4$. The amount of Fe^{3+} present in tapiolite is dependent on the partial pressure of oxygen under which the tapiolite crystallized and the degree of Mn incorporation in the structure.

Solid phases in the binary system $FeTa_2O_6$–TiO_2 have been synthesized at 1000–1300°C. The system shows complete solid-solution between the rutile and ferrotapiolite end-members. In the $Ti_{1-x}Fe_{x/3}Ta_{2x/3}O_2$ phases, the rutile structure converts to the trirutile structure only in the 0.95–1.00 range of x at 1100°C (Wise *et al.* 1988).

Experimental data for the system $FeTa_2O_6$–SnO_2 are nonexistent. Solid solution between ferrotapiolite and cassiterite has been suggested (Åmark 1941), but so far has not been studied. At very high temperatures, ferrotapiolite – cassiterite solid solution may exist, but at lower temperatures, the tapiolite phase would be expected to exsolve cassiterite (Edwards 1940). The extent of Sn in natural tapiolite is approximately 4 mol.% SnO_2. Åmark (1941) found that up to 25 mol.% of ferrotapiolite might enter the cassiterite structure. According to Quensel (1957), elevated Ta contents favor the solubility of Sn in Nb,Ta oxide minerals. He further suggested that substantial Nb reduces the miscibility between SnO_2 and the "columbite" component, and the result is a mixture of separate phases.

Coexisting phases

Tapiolite minerals rarely occur as the only Nb,Ta-bearing mineral in a given pegmatite. A mineral of this series is usually accompanied by columbite – tantalite or wodginite and, less commonly, cassiterite or microlite. The influence of coexisting phases on tapiolite composition is at present unknown. Insufficient chemical data on coexisting pairs has hindered the understanding of element partitioning. The little that we do know is inferred from only a handful of analyses. Figures 9 and 10 summarize the present understanding of Fe, Mn, Nb and Ta partitioning in pairs of coexisting minerals.

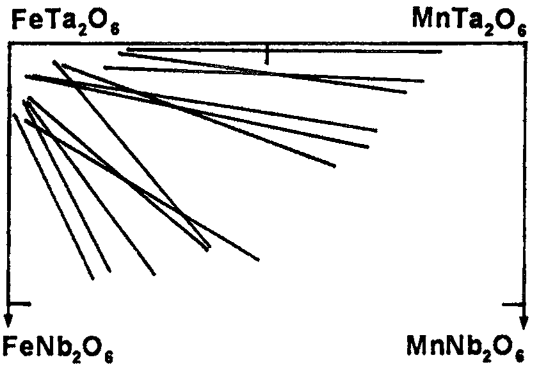

FIG. 9. Compositions of coexisting (or associated) natural ferrotapiolite and tantalite pairs. After Černý *et al.* (1992).

Ferrotapiolite versus tantalite

Ferrotapiolite is invariably conspicuously enriched in Ta and Fe in comparison to coexisting tantalite. Compositional data for ferrotapiolite + tantalite pairs show very restricted Mn-for-Fe^{2+} substitution in ferrotapiolite, and only slightly greater substitution of Nb-for-Ta (Fig. 9). In contrast, the coexisting orthorhombic phase shows a broad range of Mn/(Mn + Fe) values (0.20–0.90), along with an extensive range of Ta/(Ta + Nb) values (0.52–0.98) (Černý *et al.* 1992). Tie-lines linking coexisting grains of ferrotapiolite and tantalite sweep across the two-phase region and vary greatly in their slope. Internal consistency in slopes of tie-lines linking ferrotapiolite – ferrotantalite pairs is best represented by material from Spittal and Nyanga #2 (*cf.* Černý *et al.* 1992), suggesting near-equilibrium conditions. In contrast, strongly divergent slopes and crossing tie-lines suggestive of disequilibrium are typical of the Finnis River, Scheibengraben and Yellowknife data (*cf.* Černý *et al.* 1992). Compositions of ferrotapiolite – manganotantalite pairs from Tanco, Bikita and Alto do Giz are similar, suggesting similar conditions of crystallization (Ercit 1986).

Weitzel (1976) suggested that the preference of Fe and Ta for the tetragonal phase relative to the orthorhombic phase is due to the difference in polarizing effect of Ta^{5+} and Nb^{5+}. In addition, the difference in ionic radius between Mn^{2+} and Fe^{2+} (0.83 and 0.78 Å for Mn and Fe, respectively; Shannon 1976) apparently controls their preference for a particular structure-type. The Mn cation is too large to be easily accommodated by the tapiolite structure, and therefore enters the orthorhombic structure of columbite [the average *A*–O distances for ferrotapiolite and manganotantalite are 2.07 Å (von Heidenstam 1968) and 2.18 Å (Grice *et al.* 1976), respectively].

Ferrotapiolite versus wodginite and ixiolite

In pairs of coexisting ferrotapiolite + wodginite, ferrotapiolite preferentially accepts Fe^{2+} and Ta, whereas wodginite prefers Sn, Mn and Nb (von Knorring *et al.* 1969, Vorma & Siivola 1967, Ercit 1986). Ixiolite, which seems to be closely related to wodginite compositionally, also show similar partitioning tendencies. This mineral pair is scarce, and the available data indicate a strong preference of Mn for ixiolite relative to ferrotapiolite (Fig. 10a). Partitioning of Ta between the two phases is essentially equal.

Ferrotapiolite versus cassiterite and microlite

Data for ferrotapiolite + cassiterite pairs also are scarce. In general, Fe^{2+} is concentrated in cassiterite relative to slightly manganiferous ferrotapiolite,

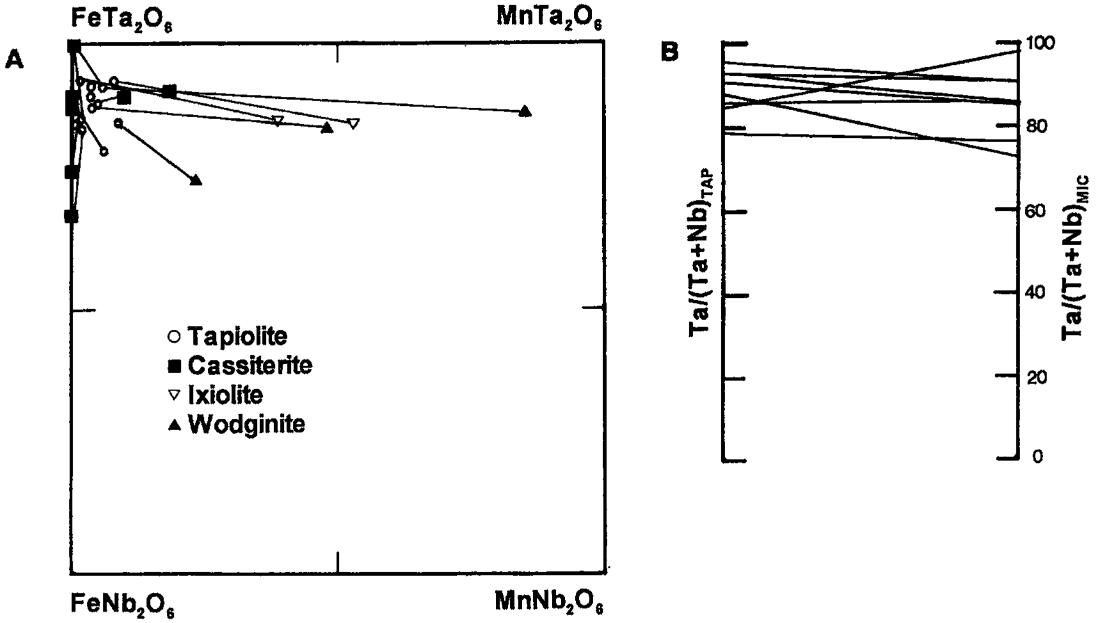

FIG. 10. Compositions of natural ferrotapiolite coexisting with (A) cassiterite, ixiolite and wodginite, and (B) with microlite.

whereas the behavior of Ta and Nb is quite erratic (Fig. 10a). In pairs of this type, Sn is conspicuously absent or occurs in minor quantities only in ferrotapiolite. In coexisting ferrotapiolite and microlite, the Ta content is slightly higher in ferrotapiolite than microlite (Fig. 10b), although some ferrotapiolite + microlite pairs show impartial Ta distribution.

Paragenesis

Primary tapiolite-series minerals

Tapiolite minerals are restricted to rare-element granitic pegmatites that show moderate to high degrees of fractionation, to placers derived from granitic pegmatites and, rarely, to some Ta-mineralized granites characterized by low levels of F and limited enrichment in Fe and Mn. Granitic pegmatites of the beryl-columbite and complex (Li, Be, Ta≧Nb) or (Li, Rb, Cs, Ta>Nb) subtypes (Černý 1991) commonly carry tapiolite, although the less fractionated pegmatites of the gadolinite subtype and the highly fractionated spodumene subtype may also carry a tapiolite-series mineral as a minor constituent. Ferrotapiolite occurs as a rare accessory mineral in the intermediate zone and core margin of zoned pegmatites, commonly intimately associated with albite, muscovite, beryl, spodumene, tourmaline, triphylite, triplite and other Nb,Ta,Sn-bearing minerals (columbite – tantalite, wodginite, cassiterite, microlite). Rarely is ferrotapiolite the sole representative of Ta mineralization in a pegmatite (von Knorring & Fadipe 1981).

Tapiolite minerals are usually found in muscovite + quartz + albite zones or in replacement bodies of lithian muscovite of Li-poor or Li-enriched granitic pegmatites (von Knorring & Fadipe 1981). Manganotapiolite – ferrotapiolite occurs in the fine-grained albite + quartz + muscovite border zone of the Tianinen pegmatite, Finland (Lahti *et al.* 1983). Manganese-rich ferrotapiolite from the Maršikov pegmatite, Czech Republic, belongs to a late albite metasomatic complex (Čech 1973). Manganoan compositions are typical of ferrotapiolite belonging to the simpsonite paragenesis of low-pressure, petalite-subtype pegmatites, which may also include wodginite, manganotantalite and microlite. These samples of tapiolite are chemically more evolved than those not associated with the simpsonite paragenesis, *i.e.*, they are strongly depleted in Nb, Ti and Sn, but Mn- and Ta-enriched (Ercit 1986). In *REE*-bearing mica-bearing granitic pegmatite, ferrotapiolite is reportedly associated with *REE* phosphates (monazite and xenotime), epidote and allanite (Hutton 1958, Rudovskaya 1962).

Ferrotapiolite may occur as inclusions within wodginite (Vorma & Siivola 1967, von Knorring *et al.* 1969), as subhedral grains in stibiotantalite (Černý & Harris 1973) or as grains within columbite – tantalite or cassiterite. The association ferrotapiolite – stibiotantalite – antimonian microlite of the Odd West pegmatite, Manitoba, occurs in a highly fractionated Li-enriched pegmatite in a relatively early assemblage of albite + quartz + muscovite + tourmaline + cassiterite (Černý & Harris 1973). Numerous homogeneous samples of ferrotapiolite were shown to be associated with contemporaneous or secondary microlite (Adusumilli 1980, von Knorring & Fadipe 1981). Others are intimately associated with "staringite" (Burke *et al.* 1969, Adusumilli 1980). Ta-rich cassiterite may also contain inclusions of ferrotapiolite (Vorma & Siivola 1967, Černý *et al.* 1986, Wise 1987). Ferrotapiolite intergrown with tantalian rutile was found associated with saccharoidal albite, beryl and Ti-rich columbite – tantalite (Anderson 1984).

Exsolution of ferrotapiolite

Exsolution of ferrotapiolite from an unstable homogeneous precursor was described by Černý *et al.* (1989a) from Uganda. Other possible occurrences of similar exsolution were reported from Australia (Jutz 1986) and Austria (Černý *et al.* 1989b); however, deformation of the ferrotapiolite – ferrotantalite aggregates disturbed the primary textural relationship in the latter case. Another occurrence of an exsolved ferrotapiolite – ferrotantalite pair was recently examined from the Chantrey Inlet, Northwest Territories pegmatite field (Tomascak *et al.* 1994).

Microscopic rounded grains of ferrotapiolite in Fe,Ta-bearing cassiterite were interpreted as products of exsolution by Ramdohr (1955). More recent observations of this exsolution include, for example, those of Černý *et al.* (1981, 1985), Groat *et al.* (1992), and unpublished data of the authors.

Late secondary tapiolite

The formation of ferrotapiolite by late hydrothermal or metasomatic alteration of pre-existing Nb–Ta minerals seems to be an uncommon process. At present, only two replacement-induced sequences have been documented. Ferrotapiolite, possibly recrystallized from remnants of an earlier generation of tapiolite, is found in cavities of massive microlite from the Bulema pegmatite, Uganda (von Knorring & Fadipe 1981). Ercit & Černý (1982), Voloshin (1983) and Voloshin & Pakhomovskyi (1983) found tapiolite replacing simpsonite.

The alteration of tapiolite minerals to secondary Nb, Ta-bearing minerals also does not appear to be a common process. The replacement of tapiolite minerals by microlite has been documented by Pough (1945) and Eid & von Knorring (1976). Fibrous microlite replaces ferrotapiolite along its margins and continues along fractures until most of the mineral is replaced.

CONCLUDING REMARKS

X-ray-diffraction studies have provided valuable information regarding the structural variations of the tapiolite series. Although we are able to recognize order – disorder relationships in natural specimens, the mechanisms responsible for such structural changes are still undefined, primarily because of the pronounced effect of composition on the unit cell. The latter is not well documented, and the present data only underscore the difficulty in separating compositional factors from those caused by the degree of order. Comparison of chemical and experimental data suggests that the degree of order may be controlled by the crystallization history and only slightly affected by chemical variations. An experimental approach emphasizing changes in temperature, rate of cooling, pressure, *etc.*, complemented by structure refinement of disordered phases, obviously is needed.

Limited but effective homovalent and heterovalent substitutions, acting in most cases concomitantly, and competition of coexisting phases play dominant roles in defining the compositional range of tapiolite. Major deviations from the typical compositions are due not only to the bulk Nb/Ta value of the crystallizing melt or fluid, but also to the progress of pegmatite fractionation and the presence of associated Nb,Ta phases.

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