

## Hidden story of tapiolite

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### ABSTRACT

The crystal chemistry of tapiolite is more complicated than previously recognized. Perusal and synthesis of relatively recent publications reveals a ‘hidden’ story about tapiolite, one that: (1) permits quantification of the effects of Mn, Fe<sup>3+</sup>, Ti (and Sn) upon the unit-cell parameters of maximally ordered tapiolite; (2) shows that the effect of Nb = Ta substitution upon unit-cell parameters is insignificant; (3) casts doubt on the usefulness of heating experiments for accurately evaluating cation order in tapiolite; (4) suggests that rutile exsolves from tapiolite upon heating in air at lower temperatures than previously established; (5) shows that the maximum solubility of TiO<sub>2</sub> in FeTa<sub>2</sub>O<sub>6</sub> tapiolite during the later stages of crystallization of granitic pegmatites is ~1 mol.%; (6) shows that the heating paths for at least some natural tapiolite samples are not necessarily linear, consisting of two sequential steps; (7) sheds doubt on the usefulness of unit-cell parameters as quantitative measures of long-range cation order,  $Q$ , in tapiolite; but (8) does show that the intensity ratio  $I_{011}/I_{110}$  can provide an accurate and reasonably precise measure of cation order in tapiolite.

**KEYWORDS:** tapiolite, order-disorder, solid solution, granitic pegmatites.

### Introduction

TAPIOLITE is a supergroup of minerals, ideal formula  $AB_2O_6$ , which includes the tantalum oxide species tapiolite-(Fe) Fe<sup>2+</sup>Ta<sub>2</sub>O<sub>6</sub>, tapiolite-(Mn) (Mn,Fe<sup>2+</sup>)Ta<sub>2</sub>O<sub>6</sub> and the antimony oxide species byströmite, MgSb<sub>2</sub>O<sub>6</sub> and ordoñezite, ZnSb<sub>2</sub>O<sub>6</sub>. No measurable degree of solid solution exists between the Ta oxide and Sb oxide groups, and limited solid solution exists between the Ta-oxide members and their hypothetical Nb equivalents (Wise and Černý, 1996). Considerable solid solution exists between tapiolite-(Fe) and tapiolite-(Mn), although geological metastability has been inferred for the most Mn-enriched compositions (Wise and Černý, 1996).

The tapiolite structure is a cation-ordered derivative of the rutile structure. All cations are octahedrally coordinated, and the MO<sub>6</sub> polyhedra are linked *via* edge sharing to form straight chains

along *c*, with adjacent chains cross-linked by shared corners. Cation ordering within each chain results in the pattern ... Fe<sup>2+</sup>–Ta–Ta ... along *c* (Fig. 1), which triples the *c* cell edge of the rutile subcell, hence the alternate name for the structure, ‘trirutile’. At high temperature, extensive solid solution exists between tapiolite and rutile-structured TiO<sub>2</sub> and SnO<sub>2</sub> (*e.g.* Wise *et al.*, 1988); however, behaviour under conditions typical of tapiolite in geological settings (those of rare-element granitic pegmatites) is much less well known. The only evidence is anecdotal (Groat *et al.*, 1994) and it implies that solid solution may be highly limited under such conditions.

In reviewing relatively recent publications on tapiolite (Wise and Černý, 1996; Kinast *et al.*, 2002; Zema *et al.*, 2006), the present author began to suspect that the crystal chemistry of tapiolite is more complicated than previously reported or suspected *vis-à-vis* the role of cation ordering. The present paper is mostly a re-interpretation and synthesis of the combined results of these studies.

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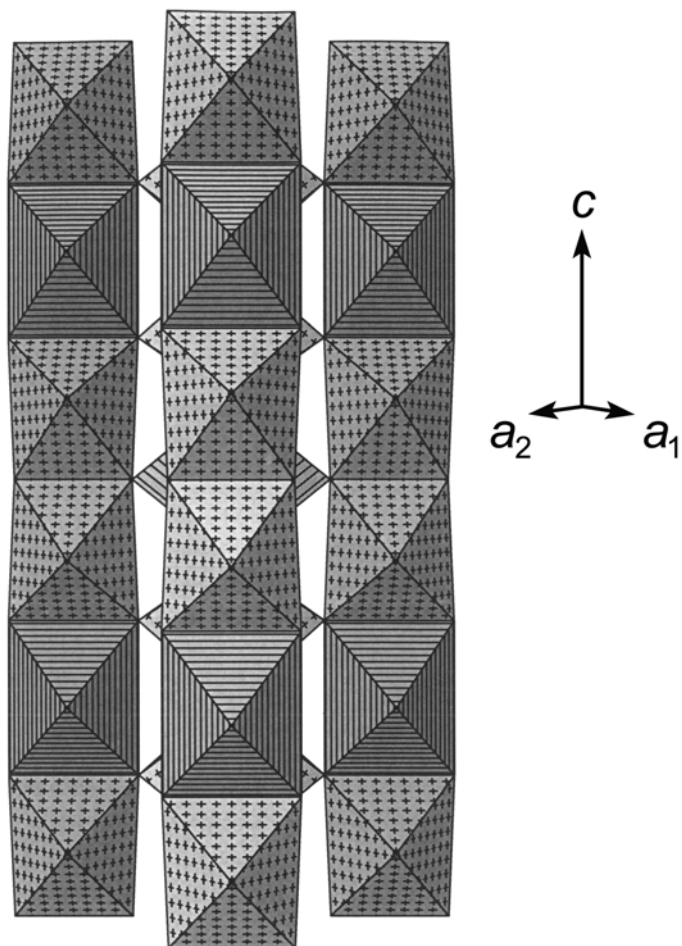


FIG. 1. A [110] perspective projection of the crystal structure of tapiolite.  $\text{FeO}_6$  polyhedra are ruled,  $\text{TaO}_6$  polyhedra are textured with crosses.

### Maximally ordered and partially ordered phases

The term 'maximally ordered' is used here instead of 'fully ordered' to terminologically accommodate solid solutions between fully cation-ordered tapiolite-structured  $\text{FeTa}_2\text{O}_6$  and  $\text{MnTa}_2\text{O}_6$  and cation-disordered rutile-structured  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $(\text{FeTa})\text{O}_4$ . Solid solution involving such rutile-structured phases necessarily has a disordering effect. For example, (1) solid solution between  $\text{TiO}_2$  and fully ordered  $\text{FeTa}_2\text{O}_6$  distributes Ti between the *A* and *B* positions of the tapiolite formula in a 1:2 ratio; a hypothetical 50:50 solid solution has the structural formula  $(\text{Fe}_{0.5}^{2+}\text{Ti}_{0.5})_{\Sigma 1}(\text{Ta}_{1.0}\text{Ti}_{1.0})_{\Sigma 2}\text{O}_6$ ; (2) solid solution

between  $(\text{FeTa})\text{O}_4$  and fully ordered  $\text{FeTa}_2\text{O}_6$  necessarily distributes  $\text{Fe}^{3+}$  between the *A* and *B* positions in a 2:1 ratio; a hypothetical 50:50 solid solution has the structural formula  $0.5 [\text{Fe}_{1.5}^{3+}\text{Ta}_{1.5}\text{O}_6] + 0.5 [\text{Fe}^{2+}\text{Ta}_2\text{O}_6] = (\text{Fe}_{0.5}^{2+}\text{Fe}_{0.5}^{3+})_{\Sigma 1}(\text{Ta}_{1.75}\text{Fe}_{0.25}^{3+})_{\Sigma 2}\text{O}_6$ . Neither composition can show greater degrees of cation order, yet both have disordered arrangements of some cations (Ti and  $\text{Fe}^{3+}$ ), hence the terminology, 'maximally ordered'. However, both compositions can show lesser degrees of cation order should the  $\text{FeTa}_2\text{O}_6$  component be less than fully ordered. For example, remembering that fully cation-disordered  $\text{FeTa}_2\text{O}_6$  has the structural formula  $(\text{Fe}_{0.33}^{2+}\text{Ta}_{0.67})_{\Sigma 1}(\text{Ta}_{1.33}\text{Fe}_{0.67}^{2+})_{\Sigma 2}\text{O}_6$ , a

hypothetical 50:50 solid solution between  $\text{TiO}_2$  and 50% ordered  $\text{FeTa}_2\text{O}_6$  results in a structural formula of  $0.5 [\text{Ti}_3\text{O}_6] + 0.5 [(\text{Fe}_{0.67}^{2+}\text{Ta}_{0.33})(\text{Ta}_{1.67}\text{Fe}_{0.33}^{2+})_{\Sigma 2}\text{O}_6] = (\text{Ti}_{0.5}\text{Fe}_{0.33}^{2+}\text{Ta}_{0.17})_{\Sigma 1} (\text{Ti}_{1.0}\text{Ta}_{0.83}\text{Fe}_{0.17}^{2+})_{\Sigma 2}\text{O}_6$ . Such compositions are best designated 'partially ordered'. Although this discussion might be considered rudimentary, the compositions assigned to ferric tapiolite by Wise and Černý (1996) are evidence to the contrary: the 8:92 and 20:80 solid solutions of  $(\text{FeTa})\text{O}_4$  and cation-ordered  $\text{FeTa}_2\text{O}_6$  should actually have the formulae  $(\text{Fe}_{0.92}^{2+}\text{Fe}_{0.08}^{3+})_{\Sigma 1}(\text{Ta}_{1.96}\text{Fe}_{0.04}^{3+})_{\Sigma 2}\text{O}_6$  and  $(\text{Fe}_{0.80}^{2+}\text{Fe}_{0.20}^{3+})_{\Sigma 1}(\text{Ta}_{1.90}\text{Fe}_{0.10}^{3+})_{\Sigma 2}\text{O}_6$ , respectively, and not those reported (cf. Turnock, 1965, 1968).

### Solid solutions involving maximally ordered tapiolite

Turnock (1968), Wise *et al.* (1988) and Wise and Černý (1996) outlined solid solution involving most common components of natural tapiolite-group minerals, namely tapiolite-structured  $\text{FeTa}_2\text{O}_6$  and  $\text{MnTa}_2\text{O}_6$  and rutile-structured  $(\text{FeTa})\text{O}_4$  and  $\text{TiO}_2$ , and the effects of all permutations of cation substitutions on unit-cell parameters involving these components. The results are summarized and analysed below.

Solid solution between  $\text{FeTa}_2\text{O}_6$  and hypothetical tapiolite-structured  $\text{MnTa}_2\text{O}_6$  obeys Vegard's law to at least 65% substitution of  $\text{Fe}^{2+}$  by Mn (Fig. 2, upper), with no loss of cation order. Solid solution between  $\text{FeTa}_2\text{O}_6$  and hypothetical tapiolite-structured  $\text{FeNb}_2\text{O}_6$  has yet to be investigated, but given the extreme similarity of  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ , solid solution is expected to be Vegardian, at least within the limited range of Nb substitution displayed by natural samples of tapiolite.

As is to be expected, solid solution between  $\text{FeTa}_2\text{O}_6$  vs.  $\text{TiO}_2$  or  $(\text{FeTa})\text{O}_4$  is non-linear (Fig. 2 middle, bottom). In addition, Wise and Černý (1996) indicate that  $\text{FeTa}_2\text{O}_6$ – $\text{TiO}_2$  solid solution retains maximal cation order to 5 mol.%  $\text{TiO}_2$ ; however, for more Ti-enriched compositions, the structure destabilizes to completely cation disordered. Turnock (1965) and Wise and Černý (1996) indicate that solid solution between  $(\text{FeTa})\text{O}_4$  and  $\text{FeTa}_2\text{O}_6$  is maximally ordered to at least 20 mol.%  $(\text{FeTa})\text{O}_4$ ; the region of destabilization to partially ordered and disordered structures lies between this point and 34 mol.%  $(\text{FeTa})\text{O}_4$ , after which only fully disordered rutile-structured  $(\text{FeTa})\text{O}_4$ – $\text{FeTa}_2\text{O}_6$  solid solution exists.

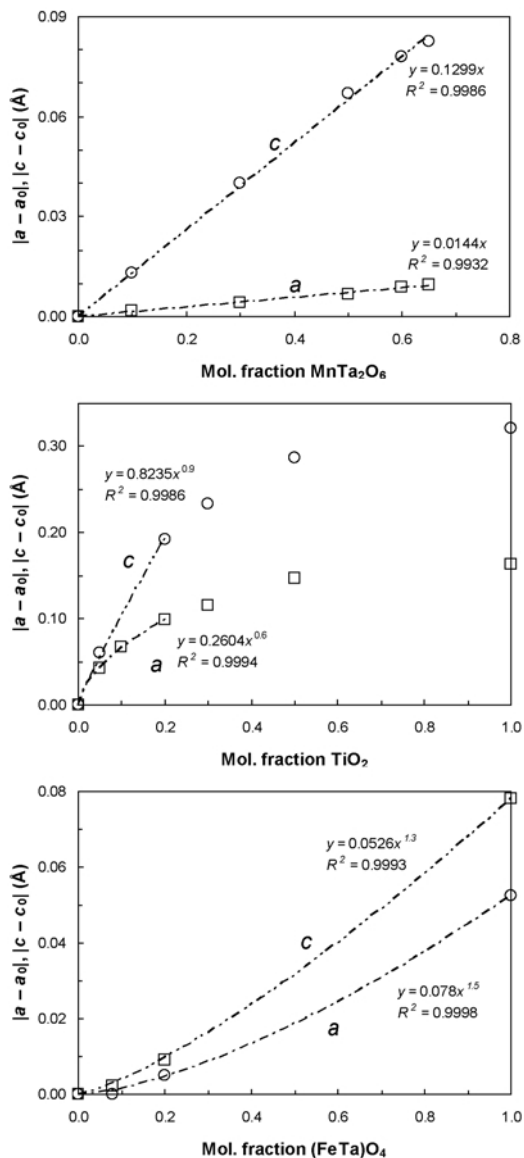


FIG. 2. Effect of solid solution between maximally ordered  $\text{FeTa}_2\text{O}_6$  vs. maximally ordered  $\text{MnTa}_2\text{O}_6$  (top), disordered  $\text{TiO}_2$  (middle), and disordered  $(\text{FeTa})\text{O}_4$  (bottom) upon the unit-cell parameters of synthetic tapiolite. Regression data for the middle plot correspond to compositions between 0 and 20 mol.%  $\text{TiO}_2$ . The parameters  $a_0$  and  $c_0$  are the unit-cell edges for end-member  $\text{FeTa}_2\text{O}_6$  ( $a_0 = 4.7570(4)$ ,  $c_0 = 9.1992(9)$  Å). All measured unit-cell parameters are from Wise and Černý (1996).

Solid solution between  $\text{FeTa}_2\text{O}_6$  and  $\text{SnO}_2$  has yet to be investigated, in part due to the high degree of reactivity between Sn and high-temperature crucible materials (e.g. Pt). Based on the work of Groat *et al.* (1994), solid solution between  $\text{FeTa}_2\text{O}_6$  and  $\text{SnO}_2$  may be extensive at higher temperatures but undergoes multi-stage spinodal decomposition under crystallization and cooling conditions typical of granitic pegmatites. Based on  $\text{FeTa}_2\text{O}_6$ – $\text{TiO}_2$  solid solution, at high temperature  $\text{FeTa}_2\text{O}_6$ – $\text{SnO}_2$  solid solution should be distinctly non-Vegardian. Maximally ordered compositions are expected to destabilize to disordered equivalents at low mol. percentages of  $\text{SnO}_2$ , and cell parameters should progress generally toward those of  $\text{SnO}_2$  with increasing Sn substitution.

Linear regression of the data presented in Fig. 2 results in the following:

$$a = 4.757 + 0.014 \text{ Mn} - 0.078 \left(\frac{2}{3} \text{ Fe}^{3+}\right)^{1.3} - 0.26 (\text{Ti}/3)^{0.6} - 0.019 (\text{Sn}/3)^{0.7} \quad (1)$$

$$c = 9.1992 + 0.13 \text{ Mn} - 0.053 \left(\frac{2}{3} \text{ Fe}^{3+}\right)^{1.5} - 0.82 (\text{Ti}/3)^{0.9} + 0.36 (\text{Sn}/3)^{0.7} \quad (2)$$

where Mn,  $\text{Fe}^{3+}$ , Ti and Sn denote cation contents per formula unit (basis of 6 oxygen atoms). Quantities contained within parentheses represent

the conversion of mole fractions to cations per formula unit (e.g. the mole fraction of Ti in tapiolite is equal to the total number of Ti atoms per 6-oxygen-based formula unit divided by 3). In the absence of synthesis data, Sn was anticipated to behave similarly to Ti; hence the exponents for Sn are the average of those for Ti. The equations reliably predict the effect of cation substitutions on the unit-cell parameters for maximally ordered tapiolite to points that fall beyond the solid-solution limits displayed by natural samples of tapiolite-group minerals (cf. Wise and Černý, 1996).

A summary of all described solid-solution relationships is presented in Fig. 3.

### Structural investigations of partially ordered tapiolite

Few structural investigations have been done on tapiolite samples with less than maximal degrees of cation order. Hutchison (1955) was the first to encounter cation-disordered tapiolite from Ross Lake, Yellowknife area, Northwest Territories, Canada. Hutton (1958) also encountered cation-disordered tapiolite-(Fe) from Skogböle, Finland, and showed that heating at temperatures in excess of 450°C for prolonged periods of time could

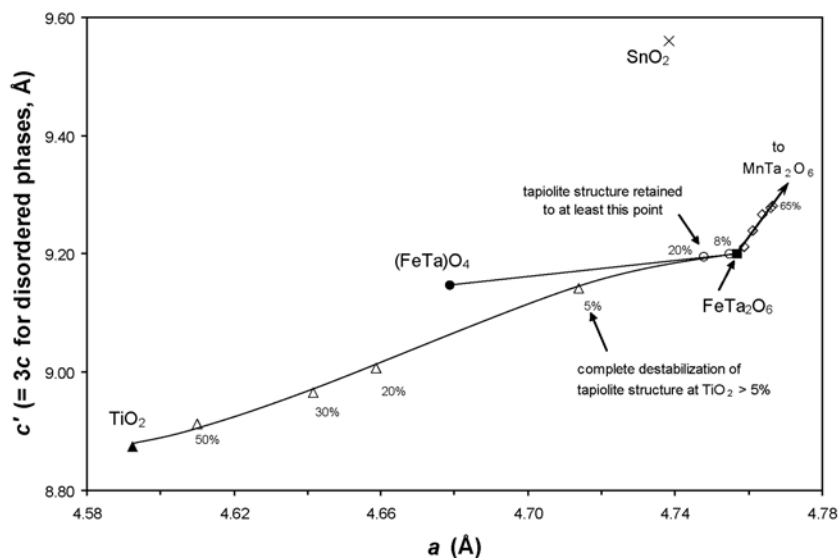


FIG. 3. Summary of solid-solution relationships between maximally ordered, tapiolite-structured  $\text{FeTa}_2\text{O}_6$  and  $\text{MnTa}_2\text{O}_6$  and between the same  $\text{FeTa}_2\text{O}_6$  and cation disordered, rutile-structured  $\text{TiO}_2$  and  $(\text{FeTa})\text{O}_4$ , as plotted on the  $a$ – $c$  plane. The position of rutile-structured  $\text{SnO}_2$  is shown for reference. Unit-cell parameters are from Wise and Černý (1996).

induce cation order in these samples. Schröcke (1966) was able to synthesize rutile-structured  $\text{FeNb}_2\text{O}_6$  at temperatures in excess of 1250°C, the lower-temperature stable form of which was columbite structured, not tapiolite structured. Von Heidenstam (1968) was the first to refine the crystal structure of a sample of partially ordered tapiolite-(Fe) (*non loc.*), which he found to be 50% ordered. Komkov and Dubik (1974) synthesized rutile-structured  $\text{FeNb}_2\text{O}_6$ ,  $\text{FeTa}_2\text{O}_6$  and  $\text{MnTa}_2\text{O}_6$  under geologically realistic conditions (200°C,  $P[\text{H}_2\text{O}] = 1.96$  kbar), as well as variably cation-ordered  $\text{FeTa}_2\text{O}_6$  (350 to 650°C,  $P[\text{H}_2\text{O}] = 1.96$  kbar). Clark and Fejer (1978) showed that variable cation order is a widespread phenomenon in tapiolite. Wise (1987) refined the crystal structure of a sample of partially ordered tapiolite-(Fe) from Prosperous Lake, Yellowknife area, Northwest Territories, Canada, which he found to be 74(3)% ordered. Wise and Černý (1996) described attempts to induce cation order by heating natural samples from Yellowknife in air at temperatures of 1000°C. Kinast *et al.* (2002) studied the Mössbauer spectra and refined the crystal structures of intergrown tapiolite- and rutile-structured phases in a sample from the Borborema pegmatite province, Paraíba, Brazil, finding that the tapiolite component shows 44% cation order (note, however, that tapiolite-columbite phase relations [e.g. Černý *et al.*, 1992] show that the assigned microprobe composition of  $\text{Fe}_{0.57}\text{Mn}_{0.37}\text{Ti}_{0.10}\text{Ta}_{1.27}\text{Nb}_{0.67}\text{O}_6$  must correspond to associated tantalite-(Fe), not the tapiolite-(Fe) used in the X-ray diffraction (XRD) study). Most recently, Zema *et al.* (2006) performed a set of *ex situ* heating experiments on seven samples of highly cation-disordered tapiolite-(Fe) from Kemiö Island, Finland (which includes, and may actually be, Skogböle, one of only two pegmatites on the island that are tapiolite-bearing; Pehrman, 1945), at variable temperatures for variable durations to induce a range of ordering states (15 to 98% order), and refined the crystal structures of 26 (mostly heated) fractions.

### Heating experiments vs. synthesis studies

Equations 1 and 2, above, provide an opportunity to examine the results of heating experiments to see whether prolonged heating under suitable conditions actually restores maximal cation order in tapiolite. If heating experiments have restored maximal order, then the equations should

adequately predict the outcome. Figure 4a shows the results of heating experiments from Wise (1987) with respect to reference curves for solid solution between maximally ordered compositions. Each vector in Fig. 4a depicts the position of the original unheated sample (start of vector) and that of its heated equivalent (tip of arrow). Given that the ends of the vectors scatter close to the maximally ordered reference curves, it is safe to say that heating under the conditions described by Wise (1987) and Wise and Černý (1996) does induce maximal cation order.

Figure 4b shows the results of equations 1 and 2 used with the data of Wise (1987). The start of each vector is as in Fig. 4a, but the end point (head) of each vector denotes the calculated position of maximal order based on each sample's composition. Ideally these calculated positions should coincide with the results of the heating experiments, but they do not. In particular, (1) the calculated points are displaced much farther along the  $\text{TiO}_2$ - $\text{FeTa}_2\text{O}_6$  join than their heated equivalents, and (2) to a lesser degree the calculated points are displaced above the reference curves for maximal order ( $\text{Fe}^{3+}$ -free systems). In an attempt to understand the greater degree of displacement along the  $\text{TiO}_2$ - $\text{FeTa}_2\text{O}_6$  join, equations 1 and 2 were recast with Ti as the dependent variable and solved for Ti. The predicted values of Ti are on the whole much smaller than observed, constrained by a maximal value of  $\text{Ti} \approx 0.03$  a.p.f.u. which corresponds to 1 mol.%  $\text{TiO}_2$  in solid solution. The possibility exists that the heating conditions used by Wise (1987) and Wise and Černý (1996) have resulted in exsolution of rutile from tapiolite for compositions with mol. fraction  $\text{TiO}_2 > 1\%$ , or that the unheated samples studied by Wise (1987) already contained submicroscopic exsolved rutile within a tapiolite-(Fe) host, much like the situation for "staringite" (Groat *et al.*, 1994). As there is currently no way to evaluate the effect of Ti upon the cell parameters of partially ordered samples of tapiolite-(Fe), unless such rutile makes up both a significant volume percentage of the total sample and occurs in large enough domains to result in characteristic X-ray scattering, it might even go undetected in powder diffraction experiments.

The study of Kinast *et al.* (2002) offers further insights on the hypothesis of exsolved rutile. Although the composition reported by those authors cannot be used with confidence in equations 1 and 2 (see above), Kinast *et al.* (2002) do report the results of heating experiments upon their sample of intergrown tapiolite + rutile.

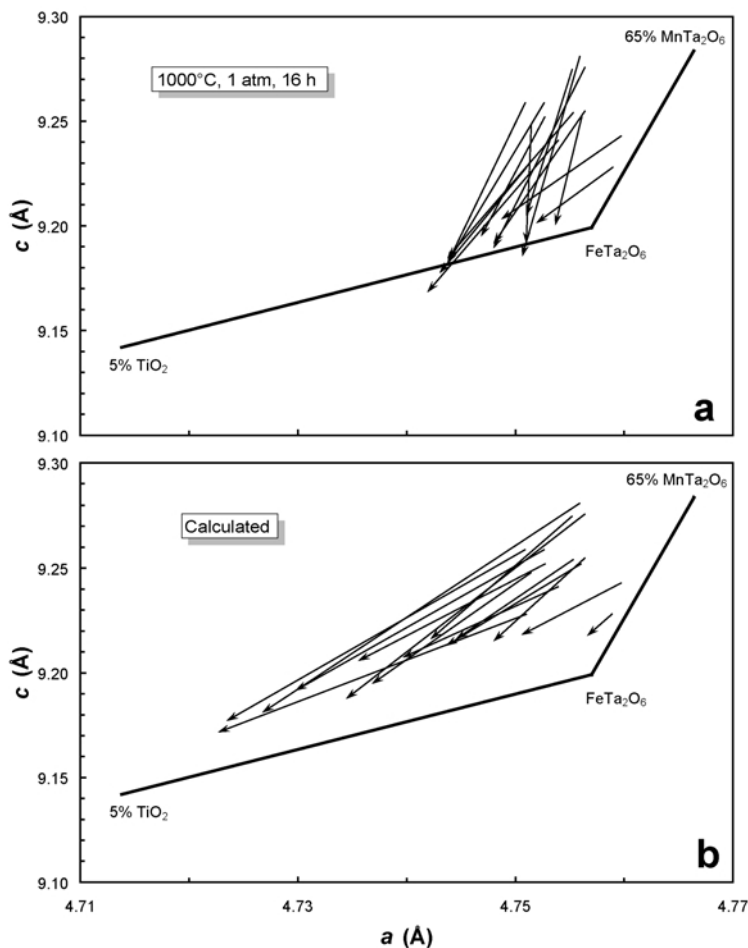


FIG. 4. Measured (a) and calculated (b) heating vectors for tapiolite samples from Wise (1987). The initial point of each vector corresponds to the unit-cell parameters of the original, unheated sample, whereas the end point of each vector corresponds to the unit-cell parameters of the equivalent heated in air. Reference lines in bold rule correspond to solid solutions involving maximally ordered phases.

They found that when heated in an oxidizing environment (air) at 1047°C, the sample transformed to a mixture of  $(\text{Fe}, \text{Mn}, \text{Ta}, \text{Nb})\text{O}_4$  and  $(\text{Ta}, \text{Nb})_2\text{O}_5$ , in agreement with the results of Wise and Černý (1996) under similar conditions. However, when heated in vacuum at the same temperature, the originally mixed diffraction pattern of partially ordered tapiolite and rutile could now be indexed as a single phase: maximally ordered tapiolite. The intergrown tapiolite + rutile reacted to form single-phase tapiolite, perhaps reversing exsolution effects that may have originally produced the intergrowth. Unlike the experiments of Wise (1987), the *in vacuo*

experiment of Kinast *et al.* (2002) results in displacement of the maximally ordered phase parallel to the  $\text{TiO}_2$ – $\text{FeTa}_2\text{O}_6$  join (Figure 5), in the vicinity of the 1 mol.%  $\text{TiO}_2$  limit displayed by the samples of Wise (1987). Figure 5 also shows the calculated position for the heated sample of Kinast *et al.* (2002) corresponding to two potential compositions: (1) that originally assigned by Kinast *et al.* (2002) (= tantalite-(Fe)), and (2) that hypothetically in equilibrium with this original tantalite composition, i.e.  $\sim\text{Fe}_{0.82}^{2+}\text{Mn}_{0.15}\text{Ti}_{0.10}\text{Ta}_{1.64}\text{Nb}_{0.29}\text{O}_6$  (conservatively assuming Ti to be partitioned equally between co-existing rutile and tantalite; cf. table 2 of Černý *et al.*, 1992). Because

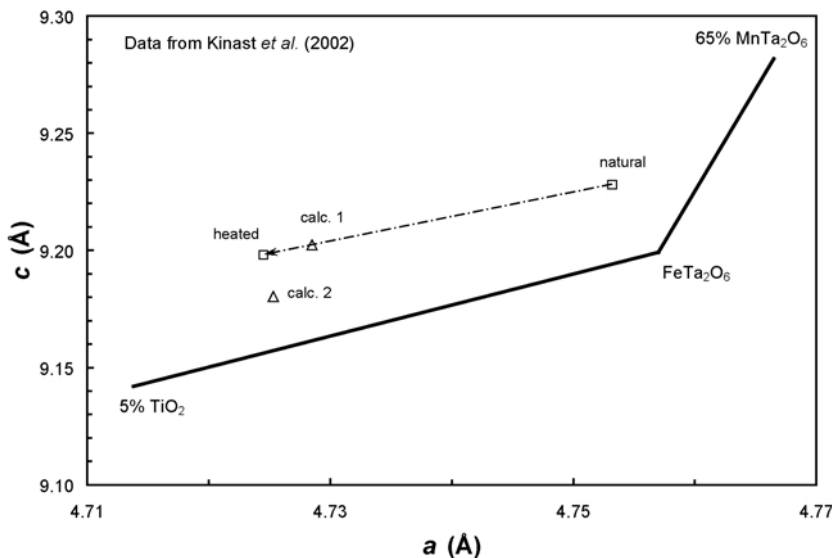


FIG. 5. Results of the *in vacuo* heating experiment of Kinast *et al.* (2002). “Calc. 1” – calculated position for the heated sample, assuming that it has the composition originally assigned by Kinast *et al.* (2002); “calc. 2” is similar, except that the composition is assumed to be  $\text{Fe}_{0.82}^{2+}\text{Mn}_{0.15}\text{Ti}_{0.10}\text{Ta}_{1.64}\text{Nb}_{0.29}\text{O}_6$ . Reference lines (bold) are as in Fig. 4.

of the predominant effect of Ti upon the *a* cell edge, the cell parameters corresponding to both scenarios give good matches to the heating experiment, certainly when compared to Fig. 4.

The displacement of the calculated positions depicted in Fig. 4b away from the reference curves of maximal order for reduced systems can only be explained as artefacts of incorrect assignment of  $\text{Fe}^{3+}$  and Sn. If the  $\text{Fe}^{2+}:\text{Fe}^{3+}$  calculations of Wise (1987) consistently erred in generating too much  $\text{Fe}^{3+}$  relative to  $\text{Fe}^{2+}$ , then the calculated data points would also generally plot where they do in Fig. 4b. However, this could only come about if all of the electron microprobe analyses of Wise (1987) resulted in systematic overestimation of total Fe or underestimation of Ta. This is unlikely as analyses of other Fe-bearing (Nb,Ta)-oxides in Wise (1987) show no evidence of overestimation of Fe or underestimation of Ta, and as the author’s own analyses of tapiolite obtained from the same laboratory, under the same conditions, using the same standards show no evidence of overestimation of Fe (Ercit, 1986). The more likely explanation of Fig. 4b is that either or both of the natural and heated samples of Wise (1987) have undetected exsolved rutile that accommodates much of the  $\text{Fe}^{3+}$  and Sn, the latter of which is to be expected, based upon the study of “staringite”

(Groat *et al.*, 1994). If each of the microprobe analyses of Wise is really a bulk analysis of submicroscopically intergrown tapiolite-(Fe) plus rutile, application of equations 1 and 2 should result in displacement of the calculated positions of maximal order both further along the  $\text{TiO}_2\text{--FeTa}_2\text{O}_6$  join (due to overestimation of  $\text{TiO}_2$  in solid solution in the tapiolite component), and upward from the join (due to overestimation of the amounts of  $\text{SnO}_2$  and  $(\text{FeTa})\text{O}_4$  in solid solution in the tapiolite component).

At this point the question is not why the samples of Wise (1987) are significantly affected by exsolution, but rather why the samples of Zema *et al.* (2006) do not seem to be affected similarly. In part this may be due to the lower titanium and certainly ferric iron contents of the samples of Zema *et al.* (2006) as compared to Wise (1987), but equal significance must be attached to the heating conditions of Zema *et al.* (2006) as compared to Wise (1987); *in vacuo* as compared to in air. As Kinast *et al.* (2002) showed, heating *in vacuo* does not promote exsolution of rutile-structured phases, whereas heating in air at high temperature promotes growth of rutile-structured phases.

In addition, the data of Wise (1987) were re-examined to see whether Nb = Ta substitution had

a significant effect upon the unit-cell parameters of maximally ordered tapiolite. Multiple regression analyses were performed with Mn, Fe<sup>3+</sup>, Ti, Sn and Nb as independent variables and the *a* and *c* cell parameters as dependent variables. Independent variable selection was done via backward elimination, with a criterion of  $\alpha = 0.15$  for removal of any variable from the model. The only variable eliminated from the model for *a* was Nb, with  $P = 0.77$ . However, both Fe<sup>3+</sup> ( $P = 0.56$ ) and then Nb ( $P = 0.23$ ) were eliminated from the model for *c*. In conclusion, for the quality of these data, Nb = Ta substitution was not seen to have a significant effect on either *a* or *c* in plots as in Fig. 3.

### Evaluation of cation order

To date, various methods have been prescribed for the estimation of cation order in tapiolite samples. Of these, only crystal-structure analysis (von Heidenstam, 1968; Wise, 1987; Zema *et al.*, 2006) can give an exact measure of long-range cation order in tapiolite; however, the non-routine and time-consuming nature of structure analysis precludes its widespread application to studies of cation order in natural samples of tapiolite. Consequently, more convenient approximations have been sought; these include heating experiments (Hutton, 1958; Wise and Černý, 1996; Kinast *et al.*, 2002; Zema *et al.*, 2006), scrutiny of supercell–subcell intensity ratios (Komkov, 1974), unspecified XRD methods (Clark and Fejer, 1978) and Mössbauer analysis (Kinast *et al.*, 2002). Of these, only the work by Zema *et al.* (2006) has been able to quantify their results and is worthy of further discussion.

The degree of cation order  $Q$  for ideal tapiolite, Fe<sup>2+</sup>Ta<sub>2</sub>O<sub>6</sub>, is defined as  $Q = |X_{\text{Fe}}^A - X_{\text{Fe}}^B| = |X_{\text{Ta}}^B - X_{\text{Ta}}^A|$ , where  $X_{\text{Fe}}^A$  is the proportion of Fe at the *A* site, etc. (Zema *et al.*, 2006). Zema *et al.* (2006) found  $Q$  values for their samples, average composition<sup>1</sup> Fe<sub>0.88</sub>Mn<sub>0.11</sub>Ti<sub>0.03</sub>Sc<sub>0.02</sub>Sn<sub>0.03</sub>Ta<sub>1.83</sub>Nb<sub>0.12</sub>O<sub>6</sub>, to vary linearly with respect to *c* and *a/c*, but to show no significant variation with respect to the *a*

cell edge. In terms of bulk variation of *a*, this statement would seem correct; however, when examined in detail for each of the seven samples Zema *et al.* (2006) used in heating experiments, this does not hold up (Fig. 6, upper). Three of the samples of Zema *et al.* (2006) were heated for suitable durations given the temperatures of their corresponding runs to show that upon annealing at temperatures ranging from 600 to 750°C, the *a* cell edge initially contracts and then later expands as a function of  $Q$ . The magnitude of the initial contraction is equivalent to that of the later expansion, which is part of the reason why, when examined in bulk, the *a* cell edge did not seem to vary systematically with  $Q$ . When examined in detail, variation of *c* as a function of  $Q$  is also non-linear (Fig. 6 middle). Figure 6 (lower) shows a plot of *c* vs. *a*, with values of  $Q$  superimposed upon the plot. The contraction of *a* with respect to *c* is isotropic in the first part of each heating curve, but the second part of the curve is distinctly anisotropic: *a* expands whereas *c* contracts with a variance three times that of *a*. Furthermore, the values of  $Q$  change only very slightly in the first part of each curve; most evolution in  $Q$  occurs during the period denoted by the second part of each curve. The exact origin of the trend denoting the first part of each curve is unknown at present; it could merely reflect the expulsion of crystal defects from the various domains making up each crystal (i.e. annealing proper), or perhaps be an indication of the effects of short-range order within domains, i.e. over scales too small to show up as a significant change in the long-range ordering parameter  $Q$ .

Figure 7 is a comparison of various data for the heating behaviour of tapiolite. Several points become apparent. First, based on the data of Zema *et al.* (2006), linear heating vectors are merely the starting point–end point approximations of the actual non-linear ordering trends of tapiolite samples. Secondly, the slopes of heating vectors vary considerably from near-vertical (sample Peg-88-2 of Wise, 1987 and the linear approximation to the data of Zema *et al.*, 2006) to a slope of 1.0 (Kinast *et al.*, 2002). Given this broad range in the slope of ordering vectors, and the variable effects of cation substitution upon unit-cell parameters, the equations of Zema *et al.* (2006) relating unit-cell parameters to  $Q$  can only serve as an accurate measure of the degree of cation order for compositions that match their sample. This is illustrated in Table 1, which compares observed measures of cation order to

<sup>1</sup> Corrected composition. Zema *et al.* (2006) give a different composition which neither corresponds to the average analysis reported in table 1 of their paper, nor does it, in having a sum of 3.041(9) cations per six oxygen atoms, pass their own rejection criterion of cation content = 3.00±0.01, apparently used in calculating the average.



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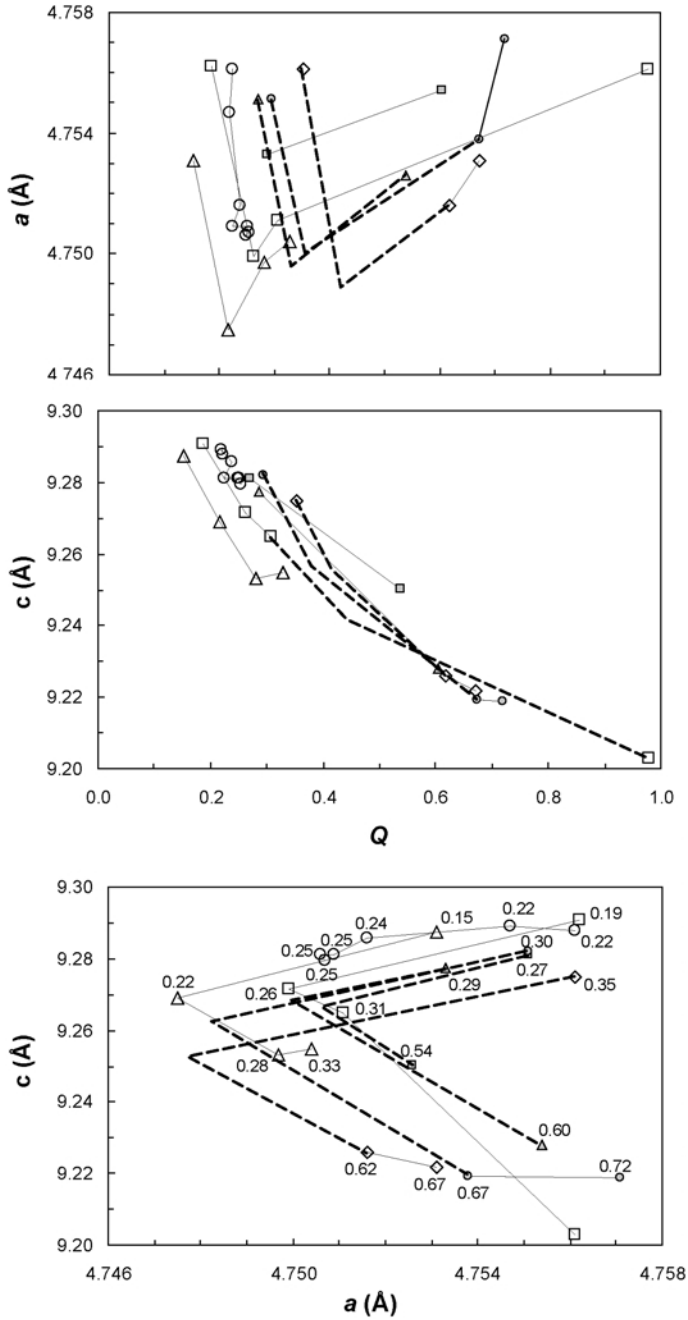


FIG. 6. Plots of unit-cell parameters vs. the cation order parameter  $Q$  (top and middle), and of  $c$  vs.  $a$  (bottom) for samples from Zema *et al.* (2006). Solid lines connect points corresponding to individual samples, with each point representing a different duration of heating. The broken rule denotes interpolated trends for samples with broad differences in the duration of heating. In the lowermost plot, the superimposed numbers correspond to values of  $Q$ .

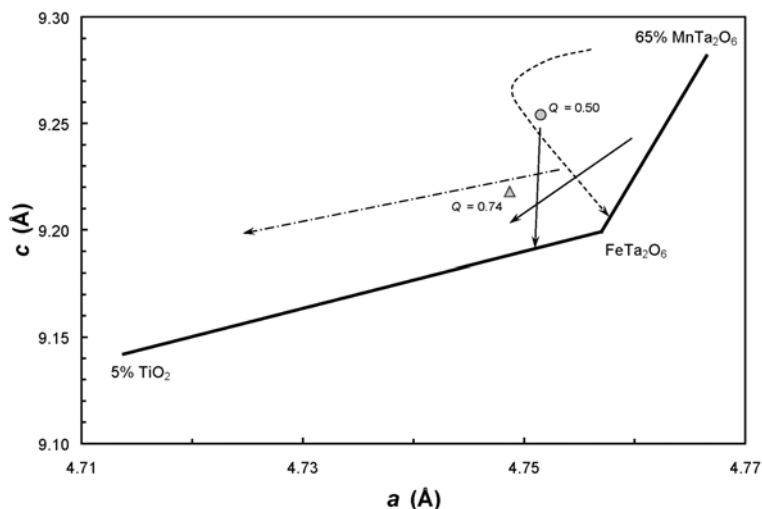


FIG. 7. Summary of cation ordering experiments for tapiolite. The average heating vector corresponding to data from Zema *et al.* (2006) is given by the broken rule; the heating vector corresponding to Kinast *et al.* (2002) is given by dot-dash rule; the minimum-slope and maximum-slope heating vectors from Wise and Černý (1996) are indicated by the solid rule; and the results of crystal-structure analyses are plotted as points (von Heidenstam, 1968, circle; Wise, 1987, triangle). Reference lines (bold) are as in Fig. 4.

those calculated in the manner prescribed by Zema *et al.* (2006):  $a/c = 0.5105(1) + 0.0072(3) Q$  (note that the sign of the coefficient in this function has been corrected from that given in Zema *et al.*, 2006). It can be seen that the equation of Zema *et al.* (2006) fails for compositions that are rich in Mn (Wise and Černý, 1996; Lahti *et al.*, 1983) and  $\text{Fe}^{3+}$  and Ti (Kinast *et al.*, 2002). This is shown spectacularly by the sample of Kinast *et al.* (2002) in which the fully ordered heated sample is calculated to have a degree of order which is 23% less than its natural, partially ordered equivalent.

And so, due to oxidation-reduction reactions, exsolution effects and intergrowths, non-linear ordering trends, and the strong effect of composition upon evolution of cell parameters during induced ordering, the use of unit-cell parameters as a quantitative measure of the degree of cation order is not and probably never will be practical.

The sole remaining approach for rapid estimation of the degree of long-range cation order in tapiolite is via the monitoring of supercell vs. subcell reflection intensities. Komkov (1974) was the first to propose the use of supercell–subcell intensity ratios as a measure of cation order in

TABLE 1. Observed values of  $Q$  vs. values calculated after Zema *et al.* (2006).

Composition/ sample	$a$ (Å)	$c$ (Å)	$Q$ (obs.)	$Q$ (calc.)	Source
$\text{FeTa}_2\text{O}_6$	4.7570	9.1992	1	0.92	Wise and Černý (1996)
$\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Ta}_2\text{O}_6$	4.7587	9.2122	1	0.84	Wise and Černý (1996)
$\text{Fe}_{0.35}\text{Mn}_{0.65}\text{Ta}_2\text{O}_6$	4.7665	9.2817	1	0.42	Wise and Černý (1996)
$\text{Fe}_{0.8}\text{Fe}_{0.3}^{3+}\text{Ta}_{1.9}\text{O}_6$	4.7478	9.1943	1	0.82	Wise and Černý (1996)
Type tapiolite-(Mn)	4.762	9.272	1	0.43	Lahti <i>et al.</i> (1983)
Tapiolite, Finland	4.7515	9.254	0.50	0.41	von Heidenstam (1968)
Tapiolite, Brazil (natural)	4.7532	9.228	0.44	0.64	Kinast <i>et al.</i> (2002)
Tapiolite, Brazil (heated)	4.7245	9.198	1	0.44	Kinast <i>et al.</i> (2002)
Tapiolite, Canada	4.7487	9.218	0.74	0.65	Wise (1987)

tapiolite, an approach later monitored by Zema *et al.* (2006). However, Komkov (1974) preferred the use of cell parameters instead of reflection intensities as it “eliminates the need for highly labour-intensive experiments regarding measurement of reflection intensities”. This statement was made at a time in which intensity data was primarily collected photographically, estimated visually and was potentially onerous. With CCD devices or chart recorders in most XRD laboratories today, intensity measurement can actually be more rapid than unit-cell refinement.

Komkov (1974) advocated the use of the intensity ratio  $I_{011}/I_{020}$  for semi-quantitative estimation of the degree of cation order in tapiolite. Unfortunately, Komkov (1974) did not explain his choice, and one is left to infer. As an aid to making these inferences, the program *PowderCell* 2.4 (Kraus and Nolze, 1996) was used to calculate reflection intensities. As the most intense supercell reflection in powder XRD patterns of tapiolite, (011) is the single best representative of the supercell reflections, yielding the most precise measure of supercell reflection intensity, and disappearing into the background at lower values of  $Q$  than other reflections. As a representative of subcell reflections, (020) is of moderate intensity, and shows less sensitivity to compositional variation than other intense subcell reflections similar in  $d$  spacing to (011), e.g. (110) (Table 2). However,

in many ways (110) is a better choice as the normalizing reflection than (020): (1) it is the most intense reflection in the pattern, four to five times more so than (020); (2) it is the closest subcell reflection to (011) in terms of interplanar spacing, thus the  $I_{011}/I_{020}$  ratio is less prone to differential instrumental effects (e.g. use of variable divergence slit vs. fixed slits and monochromators vs. filters in diffractometry); (3) it is already used as a normalizing reflection in published tabulations of diffraction data for tapiolite; published values of  $I_{011}$  are actually values normalized to  $I_{110} = 100\%$  or 10; and (4) if compositional variations are modelled rather than ignored, it is no less suitable than (020) as regards potential compositional variations.

As is to be expected for the simple linear mixing model that is  $A-B$  cation disorder in tapiolite, for any composition of tapiolite,  $Q$  varies linearly with respect to the structure-factor ratio  $F_{011}/F_{110}$ , or, correspondingly, with the square root of  $I_{011}$  (Fig. 8, Table 2). From the data used to construct Fig. 8,  $Q$  can be expressed as a linear function of the various compositional curves (expressed here as deviations from ideal  $\text{FeTa}_2\text{O}_6$ ):

$$Q = \frac{F_{011}/F_{110}}{0.288 + 0.008\text{Mn} - 0.022\text{Fe}^{3+} - 0.035\text{Ti} - 0.046\text{Nb}} \quad (3)$$

TABLE 2. Calculated intensity data for tapiolite of varying composition and structural state.

Composition	$Q$	Supercell reflections			Intensity ratios	
		$I_{011}$	$I_{112}$	$I_{002}$	$I_{011}/I_{020}$	$I_{011}/I_{110}$
$\text{FeTa}_2\text{O}_6$	1	26.9	10.1	10.8	1.114	0.269
$\text{Mn}_{0.65}\text{Fe}_{0.35}\text{Ta}_2\text{O}_6$	1	28.1	10.6	11.4	1.165	0.281
$\text{Fe}_{0.8}^{2+}\text{Fe}_{0.3}^{3+}\text{Ta}_{1.9}\text{O}_6$	1	25.8	9.7	10.5	1.086	0.258
$\text{Fe}_{0.95}\text{Ti}_{0.15}\text{Ta}_{1.9}\text{O}_6$	1	26.1	9.7	10.6	1.103	0.261
$\text{FeTa}_{1.6}\text{Nb}_{0.4}\text{O}_6$	1	23.7	8.8	9.7	1.033	0.237
Mean		26.1	9.8	10.6	1.100	0.261
Std dev. (%)		6.2	6.7	5.8	4.4	6.2
$\text{FeTa}_2\text{O}_6$	0.8	17.3	6.4	6.9	0.717	0.173
$\text{FeTa}_2\text{O}_6$	0.6	9.8	3.6	3.9	0.407	0.098
$\text{FeTa}_2\text{O}_6$	0.4	4.4	1.6	1.7	0.185	0.045
$\text{FeTa}_2\text{O}_6$	0.2	1.1	0.4	0.4	0.049	0.012
$\text{FeTa}_2\text{O}_6$	0.0	0.0	0.0	0.0	0.000	0.000

The selected compositions are the approximate maximal limits of solid solution for natural tapiolite (Wise and Černý, 1996).

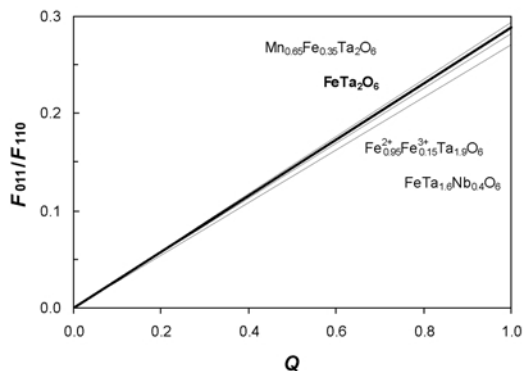


FIG. 8. Variation in  $F_{011}/F_{110}$  with respect to  $Q$ , as calculated for tapiolite compositions  $\text{FeTa}_2\text{O}_6$  (bold),  $\text{Mn}_{0.65}\text{Fe}_{0.35}\text{Ta}_2\text{O}_6$  (long dashes)  $\text{Fe}_{0.95}\text{Fe}_{0.15}\text{Ta}_{1.9}\text{O}_6$  (short dashes) and  $\text{FeTa}_{1.6}\text{Nb}_{0.4}\text{O}_6$  (dots and dashes). Individual points are not shown for each curve as the correlation coefficient in each case is equal to 1.

where element symbols represent formula contents per 6 oxygen atoms. Given the minor effects of most substituents (except Nb; Fig. 8), in the absence of compositional information equation (3) can be approximated as:

$$Q = 3.47 F_{011}/F_{110} \quad (4)$$

The equivalents of equations 3 and 4 expressed as a functions of intensity (Cu-K $\alpha$ ) are:

$$Q = \frac{\sqrt{I_{011}}}{5.2 + 0.15\text{Mn} - 0.40\text{Fe}^{3+} - 0.61\text{Ti} - 0.83\text{Nb}} \quad (5)$$

and

$$Q = 0.192\sqrt{I_{011}} \quad (6)$$

where  $I_{011}$  is the intensity of (011) with  $I_{110}$  normalized to 100%, as is conventionally done in reporting powder XRD data for tapiolite.

For X-ray sources other than Cu,  $I_{011}$  in the expressions above should be replaced by  $I'_{011}$  where

$$I'_{011} = I_{011}/(0.959 + 0.028 \lambda) \quad (7)$$

is a reasonable approximation (error of estimation = 0.2%) to the quadratic variation of  $I_{011}$  with wavelength,  $\lambda$ , over the range  $0.559 \leq \lambda \leq 1.936 \text{ \AA}$  (Ag to Fe).

For equations 4 and 6, ignorance of sample composition has its cost. Although elevated Mn,  $\text{Fe}^{3+}$  and Ti contents can result in systematic errors up to 2% in  $Q$ , elevated Nb can result in

systematic errors up to 6%. Moreover, as the coefficients for  $\text{Fe}^{3+}$ , Ti and Nb in 3 and 5 all have the same sign, for compositions simultaneously enriched in these elements, the cumulative effect of ignoring  $\text{Fe}^{3+}$ , Ti and Nb can result in systematic underestimation of  $Q$  by 10%. Such compositions are favoured during the early stages of crystallization of moderately to highly fractionated granitic pegmatite melts and during the later stages of crystallization of poorly fractionated granitic pegmatite melts (Černý and Ercit, 1985; Ercit, 2005); those studying tapiolite from such environments should strive to obtain compositional data for their samples before estimating  $Q$ .

One of the unsatisfactory aspects of using supercell-subcell intensity ratios as a measure of cation order is the large error in estimation of  $Q$  at low degrees of order. For example, a  $\pm 2\%$  absolute error in  $I$  (typical of older forms of powder diffractometry) translates into a  $\pm 4\%$  relative error in  $Q$  at full cation order and into a  $\pm 10\%$  rel. error in  $Q$  at 50% cation order. Similarly, a  $\pm 10\%$  absolute error in  $I$  (typical of, e.g. powder film methods with  $I$  estimated visually) translates into a  $\pm 18\%$  rel. error in  $Q$  at full cation order, and a  $\pm 52\%$  rel. error in  $Q$  at 50% cation order. Consequently, anyone using the above equations necessarily must make efforts to collect highly precise integrated intensities in order to obtain a reasonable degree of precision in estimating  $Q$ .

Table 3 illustrates the application of equations 3 to 6 on previously published data for tapiolite samples. The examples represent various experimental approaches (single-crystal structure refinement, Rietveld structure refinement, visual estimation of film data, interpretation of chart recordings) and various compositions. Where measured values of  $Q$  were available, agreement between the measured and calculated values is generally good; however, some cases deserve further comment. The structural states of type tapiolite-(Mn) (Lahti *et al.*, 1983) and the manganian tapiolite-(Fe) of Čech (1973) were not measured; however, as highly Mn-enriched compositions, both samples formed late in the crystallization history of their highly evolved granitic pegmatites and should similarly be expected to be highly to maximally ordered (see above). Indeed the results suggest maximal cation order for both. A series of calculations is presented in Table 3 for the tapiolite sample of Kinast *et al.* (2002) to account for uncertainty in

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 TABLE 3. Calculated values of  $Q$  for published data on tapiolite.

Composition	Description	Source	$Q$ (meas.)	$Q$ (calc.)	Equation
$\text{Fe}_{0.83}^{2+}\text{Mn}_{0.10}\text{Fe}_{0.10}^{3+}\text{Ti}_{0.01}\text{Sn}_{0.02}\text{Ta}_{1.82}\text{Nb}_{0.13}\text{O}_6$	Tapiolite-(Fe), Yellowknife area, Canada	Wise (1987)	0.74(3)	0.87(10)	3
$\text{Fe}^{2+}\text{Ta}_2\text{O}_6$	Synthetic	Komkov and Dubik (1974)		0.47(8)	6
Unknown	Tapiolite-(Fe), Otorokua Point, New Zealand	Hutton (1958)		0.33(18)	6
$\text{Mn}_{0.59}\text{Fe}_{0.32}^{2+}\text{Ca}_{0.03}\text{Ta}_{1.72}\text{Nb}_{0.27}\text{Sn}_{0.04}\text{O}_6$	Type tapiolite-(Mn), Finland	Lahti <i>et al.</i> (1983)		1.20(18)	5
$\text{Fe}_{0.65}^{2+}\text{Mn}_{0.43}\text{Ta}_{1.90}\text{Nb}_{0.07}\text{O}_6$	Manganian tapiolite-(Fe), Maršikov, Czech Republic	Čech (1973)		1.08(5)	5
$\text{Fe}^{2+}\text{Nb}_2\text{O}_6$	Synthetic; predominantly disordered	Aruga <i>et al.</i> (1985)	0.15	0.09(13)	3
$\text{Fe}_{0.57}^{2+}\text{Mn}_{0.37}\text{Ti}_{0.10}\text{Ta}_{1.27}\text{Nb}_{0.67}\text{O}_6$ ?	Partially ordered tapiolite-(Fe), Borborema, Brazil	Kinast <i>et al.</i> (2002)*	0.44	0.63(2)	3
Same	Partially ordered tapiolite-(Fe), Borborema, Brazil	Kinast <i>et al.</i> (2002)*	0.44	0.56(2)	4
Same	same, but heated <i>in vacuo</i>	Kinast <i>et al.</i> (2002)*	1.00	1.02(2)	3
Same	same, but heated <i>in vacuo</i>	Kinast <i>et al.</i> (2002)*	1.00	0.91(2)	4

\* values of  $I_{011}$  and  $I_{110}$  from C.A. dos Santos (pers. comm.)

sample composition (see above) and for the effects of heating experiments. For the natural sample, Kinast *et al.* (2002) estimated  $Q$  (meas.) at 0.44 based on the results of Mössbauer experiments; use of the assigned composition in equation 3 results in a gross overestimate of  $Q$ , but use of equation 4 results in a better match. For the heated equivalent, Kinast *et al.* (2002) estimated that full cation order was restored, and regardless of whether equation 3 or 4 is used, the values of  $Q$  (calc.) agree with this conclusion.

## Conclusions

(1) The terms ‘maximally ordered’ and ‘partially ordered’ are recommended for qualitative description of the degree of cation order of tapiolite samples.

The cell parameters of maximally ordered equivalents of natural tapiolite samples can be predicted from the following equations:  $a = 4.757 + 0.014 \text{ Mn} - 0.078 (2/3 \text{ Fe}^{3+})^{1.3} - 0.26 (\text{Ti}/3)^{0.6} - 0.019 (\text{Sn}/3)^{0.7}$  and  $c = 9.1992 + 0.13 \text{ Mn} -$

$0.053 (2/3 \text{ Fe}^{3+})^{1.5} - 0.82 (\text{Ti}/3)^{0.9} + 0.36 (\text{Sn}/3)^{0.7}$ , where element symbols represent formula contents per 6 oxygen atoms. Based on currently available data, Nb = Ta substitution does not have a significant effect on either  $a$  or  $c$ . The unit-cell parameters of samples of tapiolite that are heated so as to induce maximal cation order often do not match these calculated values, in part due to exsolution of rutile both prior to and during heating or conversely due to reaction with rutile under certain heating conditions at elevated temperature. Consequently, heating experiments should not be assumed to generate the maximally ordered equivalents to the cell parameters of natural partially ordered samples. As with tapiolite and cassiterite (Groat *et al.*, 1994), solid solution between tapiolite and rutile is anticipated to be quite limited, to <1 mol.%  $\text{TiO}_2$  under conditions typical of the later stages of crystallization of rare-element granitic pegmatites.

(2) In detail, the heating paths for single-phase tapiolite samples are not linear. In particular, the  $a$  cell edge undergoes initial contraction and later

expansion upon heating at temperatures sufficient to induce cation order, whereas the *c* cell edge undergoes differential rates of ordering.

(3) It is not (currently) practical to use variations in unit-cell parameters as quantitative measures of the degree of long-range cation order, *Q*. The published expressions of Zema *et al.* (2006) are accurate only for a restricted range of compositions (poor in Mn, Ti and Fe<sup>3+</sup>).

(4) The degree of cation order can be estimated using the intensity ratio  $I_{011}/I_{110}$  ( $= I_{011}$  under typical powder XRD conditions, i.e. when  $I_{110}$  is normalized to 100%) or from  $F_{011}/F_{110}$  for single-crystal data. For intensity data,  $Q = (I_{011})^{0.5}/(5.20 + 0.15\text{Mn} - 0.40\text{Fe}^{3+} - 0.61\text{Ti} - 0.83\text{Nb})$ , where the element symbols represent formula contents per 6 oxygen atoms. In the absence of compositional data, the expression  $Q = 0.192 (I_{011})^{0.5}$  can be used, with reservation.

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