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# Tapiolite, its chemistry and cell dimensions

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SUMMARY. Electron-probe analyses and cell dimensions are reported for twenty members of the tapiolite group. The minerals can be placed in ordered and disordered structural groups, the latter with a significantly larger *c* dimension. The *a* and *c* dimensions for both groups are dependent mainly on their titanium contents. The disordered set form part of a discontinuous series through strüverite/ilmenorutile to rutile. The chemical and structural data are incompatible with the existence of ferrotantalite or mossite as valid species.

TAPIOLITE, the tetragonal member of the Ta-Nb Fe-Mn-O group, is structurally related to the minerals rutile and cassiterite and also to a number of other $AB_2X_6$ compounds (Byström *et al.*, 1941). Chemically, Ta and Fe predominate in tapiolite, giving the ideal formula $FeTa_2O_6$, while ordering of Fe and Ta atoms leads to a tri-rutile type structure. The relationship to rutile is shown by direct correspondence of the *a* cell dimension but in tapiolite the *c* dimension is tripled. However, Hutton (1958) noticed that specimens of tapiolite from Skogböle, Finland, tended towards the rutile structure, with the extra tri-rutile lines from the X-ray powder pattern weak or, in some cases, missing altogether. He concluded that tapiolite can exist in either an ordered or disordered form and showed that shifts in the positions of several strong X-ray lines between samples of the two forms could be accounted for by a slightly larger *c* dimension (and hence a larger cell volume) for the disordered tapiolite. Hutton also found that heating the disordered mineral causes its structure to become ordered. Part of the present investigation was undertaken to discover the extent of order-disorder in a wide range of tapiolite specimens and to assess the over-all variation in cell parameters.

All tapiolites show some substitution of manganese for iron, and niobium for tantalum. Usually, small amounts of titanium and tin are also present. It was widely held that a series exists between tapiolite (Fe,Mn) $(Ta,Nb)_2O_6$ and mossite (Fe,Mn) $(Nb,Ta)_2O_6$ but Hutchinson (1955) has pointed out that since niobium is more abundant than tantalum in nature, mossite should be the more common mineral. In fact there are no reliable modern reports of such a mineral with Nb > Ta although Černý *et al.* (1964) have found it convenient to visualize ilmenorutile as being formed by the substitution of a mossite-type compound in rutile. Accordingly several authors have investigated the composition field for tapiolite. Moreau and Tramasure (1964, 1965), from synthetic studies, placed the solubility limit of $FeNb_2O_6$ in tetragonal $FeTa_2O_6$ at 20%. At higher concentrations intergrowths of tapiolite and orthorhombic columbite were observed. They concluded therefore that tetragonal $FeNb_2O_6$ is unlikely to occur. Beugnies and Mozafari (1968) tabulated the compositions of a number of tapiolites and found substitution limited to 36% $FeNb_2O_6$ along the $FeNb_2O_6$-$FeTa_2O_6$ join and 12·4% $MnTa_2O_6$ along the $MnTa_2O_6$-$FeTa_2O_6$ join. On the other hand synthetic studies by Turnock (1966) on the system $MnTa_2O_6$-$FeTa_2O_6$ put the boundary between the formation of tapiolite and tantalite+tapiolite near 58% $MnTa_2O_6$ at 1000 °C, increasing to 68% at 1500 °C. Schröcke (1966) gives very similar figures; in addition, along the $FeNb_2O_6$-$FeTa_2O_6$ join he shows 56% $FeNb_2O_6$ solubility at 110 °C. However, naturally occurring tapiolites with these extreme compositions have not so far been reported. Consequently the additional purpose of the present investigation was to acquire further information on the composition range of natural tapiolites through analytical studies on a wide range of samples.

*Experimental details.* The investigation was conducted on twenty specimens of tapiolite, plus one so-called mossite. Fragments from each specimen were embedded in an epoxy resin and polished for electron probe microanalysis. Pure element standards were used in the quantitative analyses, carried out in a Geoscan microanalyser, and the measured intensities were computer-corrected for the usual matrix effects. In each case the analysis spot was marked and 11·46 cm diameter X-ray powder photographs made from material removed from the relevant area. A graphical high-angle

TABLE I. *Electron-probe analyses of tapiolites, in wt. % and recalculated to* O = 12, *together with unit cell data*

| Specimen no. | $Ta_2O_5$<br>$Ta^{5+}$ | $SnO_2$<br>$Sn^{4+}$ | $Nb_2O_5$<br>$Nb^{5+}$ | FeO<br>$Fe^{2+}$ | MnO<br>$Mn^{2+}$ | $TiO_2$<br>$Ti^{4+}$ | Total | *a* Å | *c* Å | Ordered O<br>Disordered D<br>Intermediate I |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 85·21 | 0·02 | 1·32 | 9·67 | 4·17 | 0·46 | 100·85 | 4·7597 | 9·293 | D |
| | 3·876 | 0·001 | 0·100 | 1·353 | 0·590 | 0·058 | | | | |
| 2 | 83·90 | 0·36 | 2·59 | 11·51 | 1·81 | 0·54 | 100·71 | 4·7568 | 9·220 | O |
| | 3·791 | 0·024 | 0·194 | 1·599 | 0·254 | 0·068 | | | | |
| 3 | 83·37 | 0·52 | 2·71 | 11·48 | 1·98 | 0·46 | 100·52 | 4·7567 | 9·221 | O |
| | 3·772 | 0·034 | 0·204 | 1·597 | 0·280 | 0·058 | | | | |
| 4 | 82·25 | 1·66 | 2·23 | 12·31 | 1·15 | 0·38 | 99·98 | 4·7565 | 9·290 | D |
| | 3·749 | 0·111 | 0·169 | 1·725 | 0·163 | 0·048 | | | | |
| 5 | 81·86 | 1·30 | 3·31 | 12·32 | 1·53 | 0·61 | 100·93 | 4·7550 | 9·260 | I |
| | 3·662 | 0·085 | 0·246 | 1·695 | 0·213 | 0·076 | | | | |
| 6 | 81·86 | 2·00 | 2·77 | 12·19 | 1·17 | 0·53 | 100·52 | 4·7559 | 9·287 | D |
| | 3·692 | 0·132 | 0·208 | 1·691 | 0·165 | 0·066 | | | | |
| 7 | 81·65 | 1·03 | 2·59 | 11·92 | 1·18 | 0·35 | 98·72 | 4·7576 | 9·293 | D |
| | 3·766 | 0·069 | 0·199 | 1·691 | 0·169 | 0·044 | | | | |
| 8 | 81·65 | 3·85 | 2·01 | 10·26 | 2·65 | 0·43 | 100·85 | 4·7563 | 9·265 | I |
| | 3·684 | 0·254 | 0·151 | 1·424 | 0·373 | 0·054 | | | | |
| 9 | 80·15 | 0·86 | 5·56 | 13·26 | 1·06 | 0·18 | 101·07 | 4·7570 | 9·287 | D |
| | 3·547 | 0·056 | 0·411 | 1·805 | 0·146 | 0·022 | | | | |
| 10 | 80·33 | 1·61 | 4·36 | 12·33 | 0·83 | 1·31 | 100·77 | 4·7518 | 9·225 | O |
| | 3·548 | 0·105 | 0·321 | 1·681 | 0·115 | 0·161 | | | | |
| 11 | 80·13 | 0·60 | 4·86 | 11·99 | 2·13 | 0·83 | 100·54 | 4·7563 | 9·290 | D |
| | 3·557 | 0·039 | 0·358 | 1·637 | 0·294 | 0·101 | | | | |
| 12 | 79·91 | 0·91 | 4·06 | 12·05 | 1·42 | 1·31 | 99·66 | 4·7539 | 9·216 | O |
| | 3·577 | 0·060 | 0·302 | 1·659 | 0·198 | 0·162 | | | | |
| 13 | 79·61 | 0·86 | 6·14 | 12·67 | 1·16 | 1·02 | 101·46 | 4·7543 | 9·2254 | O |
| | 3·470 | 0·055 | 0·445 | 1·698 | 0·158 | 0·123 | | | | |
| 14 | 77·81 | 0·90 | 7·09 | 14·17 | 0·11 | 0·60 | 100·68 | 4·7536 | 9·210 | O |
| | 3·409 | 0·058 | 0·517 | 1·909 | 0·015 | 0·073 | | | | |
| 15 | 76·60 | 1·13 | 8·23 | 13·68 | 0·48 | 0·42 | 100·54 | 4·7554 | 9·210 | O |
| | 3·344 | 0·072 | 0·597 | 1·837 | 0·065 | 0·050 | | | | |
| 16 | 76·47 | 0·56 | 7·54 | 13·19 | 0·85 | 1·23 | 99·84 | 4·7513 | 9·214 | O |
| | 3·347 | 0·036 | 0·549 | 1·775 | 0·116 | 0·149 | | | | |
| 17 | 74·55 | 0·18 | 9·47 | 13·70 | 0·66 | 1·57 | 100·13 | 4·7508 | 9·242 | O |
| | 3·205 | 0·011 | 0·677 | 1·811 | 0·089 | 0·187 | | | | |
| 18 | 74·41 | 1·15 | 9·53 | 14·16 | 0·18 | 1·77 | 101·20 | 4·7506 | 9·255 | D |
| | 3·156 | 0·071 | 0·672 | 1·847 | 0·024 | 0·208 | | | | |
| 19 | 73·83 | 1·08 | 8·95 | 13·70 | 0·53 | 1·83 | 99·92 | 4·7516 | 9·2606 | D |
| | 3·177 | 0·068 | 0·640 | 1·813 | 0·071 | 0·217 | | | | |
| 20 | 73·61 | 1·25 | 8·96 | 13·65 | 0·67 | 2·01 | 100·15 | 4·7521 | 9·259 | D |
| | 3·154 | 0·078 | 0·638 | 1·798 | 0·089 | 0·238 | | | | |

1. B.M. 1977, 62. Maršikov, n. Moravia, Czechoslovakia.
2. B.M. 1931, 548. Greenbushes, Western Australia.
3. B.M. 86507. Greenbushes, Western Australia.
4. B.M. 1937, 1794. Skogböle, Kimito, Finland.
5. B.M. 1929, 252. Tantalite gully, Darwen, Western Australia.
6. B.M. 83043. Skogböle, Kimito, Finland.
7. B.M. 83044. Skogböle, Kimito, Finland.
8. B.M. 1954, 159. Orense, Spain.
9. B.M. 1948, 147. Rosendal, Kimito, Finland.
10. B.M. 1937, 1795. Chanteloube, Limoges, France.
11. B.M. 1928, 94. Strelley, Pilbara, Western Australia.
12. B.M. 1937, 1800. Rockford, Alabama, U.S.A.
13. B.M. 1974, 91. Rio Grande do Norte, Brazil.
14. B.M. 1958, 729. Angarf-Nord, Morocco.
15. B.M. 1968, 324. Olgiasca, Como, Italy.
16. B.M. 1970, 93. Frei Martinho, Brazil.
17. B.M. 1937, 126. Punia River, Belgian Congo [Zaïre].
18. B.M. 1947, 161. Makerwali, Rajputana, India.
19. B.M. 50031. Sukkula, Tammela, Finland.
20. B.M. 43256. Sukkula, Tammela, Finland.

extrapolation method was used to derive the cell dimensions for each tapiolite, giving figures accurate to 2–3 parts in 10 000. The analyses are given in Table I, both in wt. % and recalculated to a unit cell containing twelve oxygen atoms. They are tabulated in order of decreasing wt. % Ta and also shown are the cell dimensions and order–disorder state determined for each mineral.

*Discussion of results.* The compositions given in Table I plot in a fairly compact group at the FeTa$_2$O$_6$ corner of the FeTa$_2$O$_6$–MnTa$_2$O$_6$–MnNb$_2$O$_6$–FeNb$_2$O$_6$ system (fig. 1). All the minerals in this group proved to be tetragonal, including several previously labelled ferrotantalite, tending to confirm Turnock's (1966) suggestion that orthorhombic ferrotantalite does not exist. The boundary for the tapiolite group proposed by Moreau and Tramasure (1965), denoted by (1) in fig. 1, follows the compositions obtained here fairly closely and comfortably accommodates the tapiolite from Maršikov, Czechoslovakia, reported by Čech (1973) as the highest Mn-bearing tapiolite so far found. The sample supplied to us by Dr. Čech gives a slightly lower MnO figure (4·17 %) than that given in his paper (5·96 %) but nevertheless contains significantly more Mn and Ta than any other tapiolite examined. The composition boundary (2) of Beugnies and Mozafari (1968) does not include this specimen nor that from Orense, Spain (MnO 2·65 %). Their results may be distorted slightly by the inclusion of Permingeat's (1955) analysis of the Angarf-Nord, Morocco, tapiolite. A sample from the same locality examined here gave a much lower Nb/Ta ratio than that given by Permingeat, but very similar Fe and Mn figures, and is notable, in fact, for its low MnO concentration (0·11 %). Turnock's (1966) composition limits for the MnTa$_2$O$_6$–FeTa$_2$O$_6$ system (3) occur well outside the observed range and it is likely that the presence of niobium in naturally occurring tapiolites restricts the composition range. Reference to fig. 1 shows that the tapiolite compositions determined in the present study are contained on the Fe- and Ta-rich side of the (Fe$_{0\cdot6}$Mn$_{0\cdot4}$)Ta$_2$O$_6$ Fe(Ta$_{1\cdot5}$Nb$_{0\cdot5}$)O$_6$ join.

The X-ray determinations show that nine of the tapiolites have disordered structures, nine are ordered and two are of an intermediate nature. The general tendency apparent from the analytical data is for the *a* dimension to decrease with increasing Ti and Nb and to increase with increasing Mn, and for no obvious correlation of chemistry with the order–disorder state to be apparent. The *c* dimensions, on the other hand, are higher for the disordered group and at first glance this appears to obscure any chemical correlation. Figs. 2 and 3 show the *a* and *c*

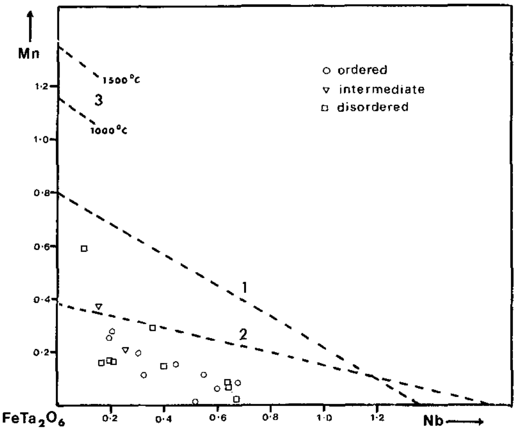

FIG. 1. Tapiolite compositions plotted in a portion of the FeTa$_2$O$_6$–MnTa$_2$O$_6$–MnNb$_2$O$_6$–FeNb$_2$O$_6$ system. The scales are in atomic units taken from Table I.

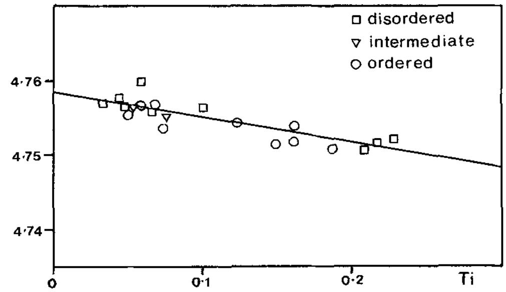

FIG. 2. The *a* cell dimension in tapiolite plotted against the titanium content (in atomic units taken from Table I).

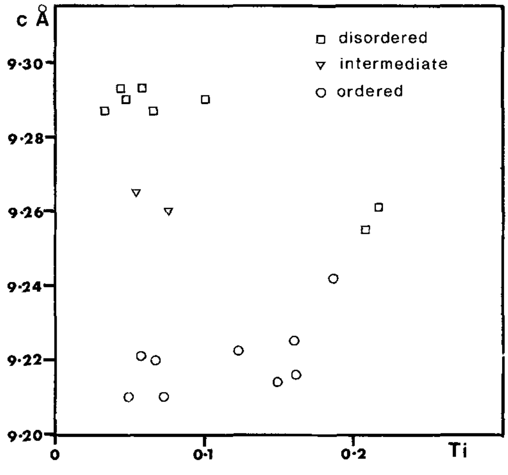

FIG. 3. The *c* cell dimension in tapiolite plotted against the titanium content (in atomic units taken from Table I).

dimensions respectively plotted against the Ti content of the tapiolites. The line in fig. 2 was calculated from a linear regression.

*Multivariate analysis.* The chemical data and cell dimensions were processed by the multiple correlation method (Hey, 1969). Errors of 1% were assumed to be present in each of the elements determined, and in the case of the cell dimensions, 0·0004 Å for *a* and 0·002 Å for *c*. As expected, arising from the changes in *c* between the ordered and disordered tapiolites, the data can be conveniently divided into two sets, setting aside the two specimens with intermediate structures. Correlation matrices were formed, leading to sets of latent roots and latent vectors, and finally equations for *a* and *c* in terms of the chemical variables.

For the disordered tapiolites only the Ti concentration plays an obviously significant role in determining the cell dimensions. However, the best fit for *a* was found to be given by:

$$a = 4{\cdot}7611 - 0{\cdot}0309\ (\mathrm{Ti}+\mathrm{Sn}) - 0{\cdot}0023\ \mathrm{Nb}$$

but *c* is dependent solely on Ti:

$$c = 9{\cdot}299 - 0{\cdot}178\ \mathrm{Ti}$$

One unexpected fact to emerge from the disordered data is a marked correlation between Nb and Ti although this could well be the result of the presence in the set of two Sukkula specimens (B.M. 50031 and 43256).

For the ordered data set the best fit is:

$$a = 4{\cdot}7563 - 0{\cdot}356\ \mathrm{Ti} + 0{\cdot}0128\ \mathrm{Mn}$$
$$\text{and } c = 9{\cdot}213 + 0{\cdot}0437\ \mathrm{Ti}$$

The Punia River specimen (B.M. 1937, 126) was omitted from the group as its high *c* value puts it close to the intermediate structures. In the ordered group Ti and Mn have opposite effects on *a* and *c* respectively when compared with the disordered set.

*Conclusions.* The ordering in the tapiolite structure is apparently not governed by its chemistry, but is more likely to be related to the mineral's temperature of formation and crystallization history. Significantly, the Finnish samples, from three distinct localities, are all disordered. The tapiolite type locality (Sukkula, Tammela, Finland), therefore, furnishes samples which, in their natural state, do not conform to the tri-rutile structure required in the definition of the mineral. Nevertheless, we believe this is preferable to the introduction of nomenclature changes designed to distinguish between ordered and disordered minerals.

The specimen labelled mossite (B.M. 1914, 1378 from Iveland, Nedenäs, Norway) proved to be ilmenorutile. Following Hutton's (1959) re-examination of 'manganomossite', found to be columbite, there can now be little doubt that mossite does not exist as a valid species. Also, that there is no direct tapiolite–tantalite inversion with increasing Mn and Nb concentrations, but instead a transition to an intergrowth of tapiolite + tantalite indicates the presence of a miscibility gap in the system. Several iron-rich tantalites examined during the course of this study have shown exsolution of tapiolite and the extent of the tantalite–tapiolite field is currently under investigation. From the work reported here, however, it can be concluded that there is little likelihood of a tetragonal $FeNb_2O_6$ phase or an orthorhombic $FeTa_2O_6$ phase occurring.

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