SYNTHETIC WODGINITE, TAPIOLITE AND TANTALITE

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ABSTRACT

Solid phases in the systems MnTa$_2$O$_7$-FeTa$_2$O$_7$-O and MnTa$_2$O$_7$-FeTaO$_4$ have been synthesized at various temperatures and partial pressures of oxygen.

In the binary system MnTa$_2$O$_7$-FeTa$_2$O$_7$, the two solid phases produced were: (i) orthorhombic Mn$_{1-x}$Fe$_x$Ta$_2$O$_6$ (tantalite), and (ii) tetragonal Fe$_{1-x}$Mn$_x$Ta$_2$O$_4$ (tapiolite). The maximum amounts of substitution at 1200 °C were $x = 0.18$, $y = 0.62$.

The oxidation of these tantalites and tapiolites (the system MnTa$_2$O$_7$-FeTa$_2$O$_7$-O) produced solid phases with compositions that are on the join MnTa$_2$O$_7$-FeTaO$_4$, plus exsolved Ta$_2$O$_5$.

In the system MnTa$_2$O$_7$-FeTaO$_4$, the three solid phases produced were: (i) orthorhombic MnTa$_2$O$_4$ (tantalite), (ii) monoclinic Mn$_{0.08}$Fe$_{0.29}$Ta$_{1.04}$O$_{12}$ with $0 < x < 0.29$ at 1200 °C (wodginite), and (iii) tetragonal Fe$_{0.57}$Mn$_{0.43}$Ta$_{2.17}$O$_{12}$ with $0 < z < 0.57$ at 1200 °C (a compound with a rutile-type structure).

It has been shown that in wodginite (i) the iron is trivalent and the manganese divalent, and that (ii) tin is not an essential component.

Wodginite was discovered by E. H. Nickel in pegmatite from Bernic Lake, Manitoba, and further study led to a definition of this mineral (Nickel, Rowland & McAdam, 1963a). It was found to be chemically and structurally related to columbite-tantalite.

Chemically, both wodginite and columbite-tantalite are complex oxides of Fe, Mn, Ta and Nb, with minor substitutions by Ti and by Sn, with cations:anions = 1:2. Columbite-tantalites have the formula (Mn, Fe)$_4$(Nb, Ta)$_8$O$_{24}$ (or $4 \times AB_2O_6$). Nickel et al. found wodginite to be $A_{10}O_{22}$, where $A$ represents chiefly Ta, Mn and Sn. It is demonstrated in the present paper that tin is not an essential element for the formation of wodginite, that it may contain ferric but not ferrous iron, and that it is a solid solution between the $AB_2O_6$ and $ABO_4$ types.

The similarity of the crystal structures of wodginite and columbite-tantalite was deduced by Nickel, Rowland & McAdam (1963a), who found the unit cells to be related by: $a_w = 2/3b_C$, $b_w = 2a_C$, and $c_w = c_C$ (subscripts W and C for wodginite and columbite-tantalite, respectively). Wodginite is monoclinic ($\beta = 91^\circ18'$), whereas columbite-tantalite is orthorhombic; this difference involves only a slight distortion without destroying the structural similarity.

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The structural similarity of columbite to wolframite was noted by Schröcke (1961), and detailed by Laves, Bayer & Panagos (1963). Broch (1929) originally discussed as the "wolframite-group" some $ABO_4$ compounds that had similar structures; Laves et al. (1963) and also Roth & Waring (1964) have expanded and formulated this family relationship. The group contains both orthorhombic and monoclinic members, structurally related by a slight distortion; this behaviour is exemplified by the wolframite series in which the angle $\beta$ changes from 90.00° in FeWO$_4$ to 91.17° in MnWO$_4$ (Sasaki, 1959). The unit cell of columbite may be described as a supercell formed by triple repetition of an orthorhombic wolframite subcell along one axis (the $a$ of wolframite in its usual setting, with $a = 4.78$, $b = 5.73$, $c = 4.98$), caused by ordering of the cations. The unit cell of wodginite, which must be added to this group, may be described as a supercell of a monoclinic wolframite subcell, with double repetition along the $a$ and $b$ axes.

**Experimental Procedure**

Crystalline materials were synthesized from reagent-grade chemicals, by firing in a quench furnace under controlled conditions of temperature and partial pressure of oxygen. The total pressure was one atmosphere for all experiments. The partial pressure of oxygen was varied in steps from $10^{-12}$ to 1 atm., by controlling the composition of the gas or gas mixture that passed through the furnace from bottom to top. Air, oxygen, and mixtures of CO$_2$ and CO were used.

It was found that mixtures of the chemicals MnC$_2$O$_4$.2H$_2$O and Ta$_2$O$_5$, plus either Fe$_2$O$_3$ or FeC$_2$O$_4$.2H$_2$O, reacted together quickly when fired at temperatures higher than 1,000° C to produce the complex oxides. For example, at 1,200° C these reactions appeared to be completed after 4 hours. The products of the first firing were further mixed by grinding, and fired at least two more times. Oxidation and reduction reactions, which were studied by firing the synthetic solids under different conditions of $P_{O_2}$, took times up to 2 days at 1,200° C to go to completion.

At the end of the firing time, the charge was lowered to the cool end of the furnace, where it cooled to room temperature in the stream of gas entering the furnace tube in about half a minute. Powder x-ray diffraction identified the phases present.

The compositions which were studied are shown in Fig. 1. This diagram emphasizes two triangular joins. The join MnTa$_2$O$_6$-FeTa$_2$O$_6$-Z, which is a portion of the larger join MnTa$_2$O$_6$-FeTa$_2$O$_6$-O, is lightly stippled in order to emphasize its position in space.
in front of the join MnTa$_2$O$_6$-FeTa$_2$O$_6$-FeTaO$_4$. In this diagram subsolidus tie-lines are omitted, except for some of those on the join MnTa$_2$O$_6$-FeTa$_2$O$_6$-FeTaO$_4$.

**Fig. 1.** Solid phases in the system MnO-FeO-Ta$_2$O$_5$-O. The hatched lines on the join MnTa$_2$O$_6$-FeTa$_2$O$_6$-FeTaO$_4$, which is behind the lightly stippled triangle, represent the extent of solid solution. Point Z represents Fe$_5$Ta$_4$O$_{13}$.

**The System MnTa$_2$O$_6$-FeTa$_2$O$_6$**

In order to keep both the manganese and iron in the divalent state, as required in this system, the partial pressure of oxygen ($f_{O_2}$) in the furnace was controlled at a low value i.e., the univariant $f_{O_2}$ of the iron-wüstite
equilibrium, by using mixed gases with CO:CO₂ in the appropriate ratios as determined by Darken & Gurry (1945).

The products of synthesis were either one or both of the following phases: (i) orthorhombic Mn₁₋₂FeₓTa₂O₆, here referred to by its mineral name tantalite, and (ii) tetragonal Fe₁₋₂MnₓTa₂O₆, here referred to as tapiolite. Their distribution is shown in Fig. 2. The firing times to produce one phase (in a one-phase region) from the oxalate and oxide starting materials was 2 hours at 1,200°C, 7 days at 1,000°C. The tapiolite solvus was determined by exsolution as well as solution experiments, i.e. tapiolite with 40 mol. % MnTa₂O₆ in solid solution will exsolve tantalite after firing for 10 days at 1,040°C.

Tantalite can take up to 18 mol. % FeTa₂O₆ into solid solution, and this limit appears to be insensitive to temperature variation. By contrast, the maximum amount of solid solution of MnTa₂O₆ in tapiolite decreases significantly with decreasing temperature; at 1,200°C (point C in Fig. 2) the extent of substitution is 62 mol. % MnTa₂O₆.

The MnO content of natural tapiolites and the FeO content of natural tantalites, as shown in compilations of analyses (Palache, Berman &
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Frondel, 1944, pp. 776 and 783), are mostly within the limits shown in Fig. 2. The comparison is not exact because of the presence of additional components, especially Nb₂O₅, in the natural materials. However, some of these samples include coexisting tapiolite and tantalite; in these cases, failure to achieve complete separation would tend to cause the analysis to plot in the two-phase region.

The analysis of ferroan tantalites (*ibid* p. 783) are of material that was not positively distinguished from tapiolite. Figure 2 suggests that the iron content of tantalites is so limited that "ferroan tantalites" cannot exist. The substitution of niobium for tantalum increases the limit of iron content, but experimental work by Schröcke (1965) suggests that the limit reaches 50 mol. % (Fe:Mn = 1) only at Nb:Ta = 1 (1,100°C). Therefore, the essential end-member of the tantalite series is MnTa₃O₆, and the prefix "mangano" is redundant.

The effect of the Fe-Mn substitution on cell size can be seen in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
<th>V (Å³)</th>
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<tr>
<td>MnTa₂O₆</td>
<td>5.768</td>
<td>14.454</td>
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<td>Mn₂₅Fe₀₇Ta₂Ta₅O₆</td>
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<td>14.430</td>
<td>5.093</td>
<td>423.7</td>
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<td>FeO₁₃Mn₀₇Ta₂Ta₅O₆</td>
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<td>9.276</td>
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<td>FeTaO₄</td>
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<td>Mn₁₃₇Fe₀₉Ta₅Ta₅O₁₂</td>
<td>9.479</td>
<td>11.441</td>
<td>5.096</td>
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<tr>
<td>Mn₁₉Fe₀₁₃Ta₅Ta₅O₁₂</td>
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<td>11.416</td>
<td>5.091</td>
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<td>540.5</td>
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<td>Rutile-type compounds:</td>
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<td>Fe₁₅Mn₁₉Ta₅Ta₅O₁₂</td>
<td>4.713</td>
<td>3.079</td>
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<td>Fe₁₅Mn₀₇Ta₅Ta₅O₁₂</td>
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<tr>
<td>FeTaO₄</td>
<td>4.678</td>
<td>3.047</td>
<td></td>
<td>66.74</td>
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Materials synthesized at 1200°C, 1 atm. total pressure. X-ray diffractometer measurements on powder made at room temperature, cobalt radiation Kα₁λ = 1.7889 Å. Internal standard used was Si, with 2θ (220) = 55.532°. Errors are estimated to be ±0.08% on cell edges.

The System MnTa₂O₆-FeTaO₄

The formulae for the end-members may be multiplied by 2 and 3, respectively, to equate the numbers of cations and anions. The results of syntheses in air (furnace atmosphere), heating times $\frac{1}{2}$ to 2 days at 1,200°C, of compositions at 5 mol.% intervals along this join were: (i) orthorhombic MnTa₂O₆ (tantalite) which takes less than 2 mol. %
Fe$_3$Ta$_2$O$_{12}$ into solid solution; (ii) monoclinic Mn$^{+3}_{1-2w}$Fe$^{+2}_w$Ta$_4$O$_{12}$ ($w =$ mol. fraction Fe$_5$Ta$_5$O$_{12}$) which has a range $0.08 < w < 0.29$ at 1,200$^\circ$C. The powder x-ray diffraction pattern of this material is similar to that of natural wodginite (Nickel et al. 1963a); (iii) a rutile-type compound Fe$^{+3}_{8-2z}$Mn$^{+2}_{2z}$Ta$_4$O$_{12}$ ($z =$ mol. fraction of Mn$_3$Ta$_4$O$_{12}$) which has a range $0 < z < 0.57$ at 1,200$^\circ$C. These ranges of composition are plotted on the left-hand side of the triangle in Fig. 3.

Cell dimensions of these compounds are listed in Table 1.

This synthetic wodginite is a compound of MnO, Fe$_2$O$_3$ and Ta$_2$O$_5$; therefore other elements found in natural wodginites, such as tin, are not essential for its formation but indicate extensive solid solution.

**The System MnTa$_2$O$_5$-FeTa$_2$O$_5$-FeTaO$_4$**

A preliminary isothermal section of this system, Fig. 3, was constructed from the following data. The extent of solid solutions along two sides of

![Fig. 3. The system Mn$_2$Ta$_2$O$_{12}$-Fe$_2$Ta$_2$O$_{12}$-Fe$_3$Ta$_3$O$_{12}$ at 1200 $^\circ$C, total pressure 1 atm.](image-url)
the triangle, MnTa₂O₆-FeTa₂O₆ and MnTa₂O₆-FeTaO₄, have been described above. The relations between composition and fₒ₂ along the remaining side of the triangle, FeTa₂O₆-FeTaO₄, were reported previously (Turnock, 1965). The approximate positions of lines within the ternary, i.e., the boundaries of the compositional fields of tapiolite and the rutile-type ferri-tantalate and the fₒ₂ isobars, are known by projection of these lines from the join MnTa₂O₆-FeTa₂O₆-O (see below, and relate Fig. 4b and Fig. 1).

**The Join MnTa₂O₆-FeTa₂O₆-O**

The oxidation of tantalites and tapiolites of the system MnTa₂O₆-FeTa₂O₆ was studied at various partial pressures of oxygen, at 1,200°C. Results are shown in Fig. 4. The base of these diagrams is the 1,200°C isotherm from Fig. 2, and points marked A, B, C and D are the boundaries of the fields of tantalite and tapiolite.

End-member tantalite, MnTa₂O₆, remains stable under the most oxidizing condition of the experiments, which was 1 atm. pₒ₂. In contrast, the iron bearing compounds are less stable, and are subject to oxidation of the iron component, at conditions of fₒ₂ according to their Fe:Mn composition, by the reaction:

\[
2\text{Fe}^{+2}\text{Ta}_2\text{O}_6 + \frac{3}{2}\text{O}_2 \rightleftharpoons 2\text{Fe}^{+3}\text{TaO}_4 + \text{Ta}_2\text{O}_5 \quad \text{(Eq. 1)}
\]

For end-member tapiolite, FeTa₃O₈, this oxidation reaction has already been described (Turnock, 1965). Ta₂O₅ is exsolved, but the FeTaO₄ may remain in solid solution by the substitution:

\[
\text{Fe}_2\text{Ta}_4\text{O}_{12} \leftrightarrow \text{Fe}_3\text{Ta}_3\text{O}_{12} \quad \text{(Eq. 2)}
\]

Tapiolite solid solutions, which are stable at relatively low oxygen pressures, were found to take up to 22 mol. % Fe₂Ta₃O₁₂ into solid solution according to Eq. 2, at 1,200°C. The rutile-type compound A₂O₄, containing 30 to 100 mol. % Fe₃Ta₃O₁₂, formed at higher oxygen pressures.

The presence of manganese in solid solution changes the stability of tapiolites, making them more resistant to oxidation; this is illustrated in in Fig. 4(a) by the manner in which the oxygen isobars radiate out from the MnTa₂O₆ corner. The oxidation of manganian tapiolites is also described by equations 1 and 2, because the MnTa₂O₆ component remains stable. At low and intermediate oxygen partial pressures, (Fig. 4a), the ferric iron produced (Eq. 1) remains in solid solution (Eq. 2), with small amounts of Ta₂O₅ being exsolved, so that tapiolite has a field of ternary solid solution as shown in projection in Fig. 4(b). At higher oxygen pressures, tapiolite is not stable, and it is oxidized to form either one or
both of wodginite and a rutile-type compound, plus Ta$_2$O$_5$ (see Fig. 4b).

The tantalites also react by the oxidation of the FeTa$_2$O$_6$ component according to equation 1, but they are stable to higher oxygen pressures as shown in Fig. 4(a). Tantalite, however, did not incorporate any ferric iron into solid solution; wodginite and Ta$_2$O$_5$ were produced and the composition of the tantalite changed towards the MnTa$_2$O$_6$ end-member as this oxidation proceeded (Fig. 4a).

The bulk compositions of the oxidation products of all (Mn$^{+2}$, Fe$^{+2}$)Ta$_2$O$_6$ materials that were heated in air or oxygen atmospheres plotted along the join MnTa$_2$O$_6$-[2/3FeTaO$_4$ + 1/3Ta$_2$O$_5$] (Fig. 4(a),

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**Fig. 4.** The join MnTa$_2$O$_6$-FeTa$_2$O$_6$-O at 1200 °C, total pressure = 1 atm. (a) Plot of bulk compositions of solid phases at various oxygen pressures ($f_{O_2}$), giving isobaric tie-lines. (b) Stability fields of the solid phases. Hatched lines indicate solid solution along a line. Three-solid phase fields are lined, four-solid phase fields are triangles.
see also Fig. 1). The weight gain involved in this oxidation corresponds to the oxidation of the iron content, indicating that the wodginite and the rutile-type products contained iron in the trivalent state and manganese in the divalent state. It was known that the end-member of the rutile-type compound is FeTaO₄ (Turnock, 1965). The occurrence of exsolved Ta₂O₅ in the oxidation products with wodginite and with the rutile-type compound suggests that both of these compounds have compositions on or close to the join MnTa₂O₅-FeTa₂O₅-FeTaO₄.

The join MnTa₂O₅-FeTa₂O₅-O is therefore a plane in the system MnO-FeO-Ta₂O₅-O (see Fig. 1) which intersects tie-lines connecting Ta₂O₅ with the solid phases that lie in the join MnTa₂O₅-FeTa₂O₅-FeTaO₄. The tie-lines in Fig. 4(b) are intersections of 3-solid-phase triangles, and the triangles are intersections of 4-solid-phase tetrahedrons.

All the oxidation reactions were reversed by variation of $p_{O_2}$. The reaction rates of these oxidation and reduction reactions are relatively fast, going to completion within 12 hours under the most oxidizing and reducing conditions, and within 50 hours under intermediate ($f_{O_2} = 10^{−2.5}$) conditions (at $1,200^\circ$ C).

**Mineralogical Applications**

In nature, wodginite, tapiolite and tantalite are found in certain granitic pegmatites. Such pegmatites are greatly enriched in Ta, and some are also enriched in one or more of the elements Nb, Sn, Fe and Mn. Where this chemical enrichment has been achieved in a pegmatite magma, the partial pressure of oxygen will control which mineral or minerals will form and the Fe⁺²/Fe⁺³ ratio therein, in accord with the tie-lines and $f_{O_2}$ isobars as shown in Figs. 2, 3 and 4.

Tapiolite is relatively the most common of the tantalates considered here; Palache et al. (1944, p. 777) mention about a dozen localities. In general, its presence indicates genetic conditions of relatively low oxygen pressures. The stability range in terms of $f_{O_2}$ for the end-member (FeTa₂O₅) at $1,200^\circ$ C has been reported (Turnock, 1965), it will vary with temperature, Mn content and Fe⁺³ content.

The analyses of tantalites listed in Palache et al. (1944, p. 783) include only three (ibid, numbers 11, 12 and 14) which are low in iron. Those with high iron contents (ibid, numbers 13 and 15) are suspected, by comparison with Fig. 2, of being tapiolites erroneously identified as ferrotantalites. As shown in Figs. 3 and 4, tantalite is stable over a relatively large range of oxygen pressures, so its rarity is probably a reflection of the limit of manganese content in pegmatites.

Wodginite is known from three localities (Nickel et al., 1963(a), Bourguignon & Mélon, 1965). Its occurrence, either without other
tantalates or with tantalite, indicates genetic conditions of relatively high oxygen pressure. In the Bernic Lake pegmatite, wodginite and tapiolite are in close association (Nickel et al., 1963(a)); this assemblage is at least bivariant, and could have formed either in equilibrium with an intermediate partial pressure of oxygen, or by an incomplete oxidation of manganian tapiolite, or, conversely, by an incomplete reduction of ferrian wodginite.

The rutile-type ferri-tantalate, which has the largest range of \( \text{Fe}^{+8}/\text{Fe}^{+2} \) of all the compounds mentioned in Fig. 3, is not known as a mineral but its occurrence is predicted. It is possibly represented by ixiolite (Nickel et al., 1963b), which could have a polymorphic relationship to the rutile structure such as that described by Schröcke (1962) for the system \( \text{FeNbO}_4-\text{FeTaO}_4 \), and by Laves et al. (1963) and by Roth & Waring (1964) for \( \text{FeNbO}_4 \).

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**References**


——— (1965): Personal communication.


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