SYNTHETIC WODGINITE, TAPIOLITE AND TANTALITE

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ABSTRACT

Solid phases in the systems $MnTa_2O_6$-$FeTa_2O_6$-O and $MnTa_2O_6$-$FeTaO_4$ have been synthesized at various temperatures and partial pressures of oxygen.

In the binary system $MnTa_2O_6$-$FeTa_2O_6$, the two solid phases produced were: (i) orthorhombic $Mn_{1-x}Fe_xTa_2O_6$ (tantalite), and (ii) tetragonal $Fe_{1-y}Mn_yTa_2O_6$ (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 $MnTa_2O_6$-$FeTa_2O_6$-O) produced solid phases with compositions that are on the join $MnTa_2O_6$-$FeTaO_4$, plus exsolved Ta_2O_5.

In the system $MnTa_2O_6$-$FeTaO_4$, the three solid phases produced were : (i) orthorhombic $MnTa_2O_6$ (tantalite), (ii) monoclinic $Mn_{2-2w}^{+2}Fe_{3w}^{+3}Ta_{4-w}O_{12}$ with $0.08 < w < 0.29$ at 1200 °C (wodginite), and (iii) tetragonal $Fe_{3-3z}^{+3}Mn_{2z}^{+2}Ta_{3+z}O_{12}$ with $0 \leqslant z < 0.57$ 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 $(Mn, Fe)_4(Nb, Ta)_8O_{24}$ (or $4 \times AB_2O_6$). Nickel *et al.* found wodginite to be $A_{16}O_{32}$, 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: $a_W \equiv 2/3\, b_C$, $b_W \equiv 2a_C$, and $c_W \equiv c_C$ (subscripts W and C for wodginite and columbite-tantalite, respectively). Wodginite is monoclinic ($\beta = 91°18'$), 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 β 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 $MnC_2O_4 . 2H_2O$ and Ta_2O_5, plus either Fe_2O_3 or $FeC_2O_4 . 2H_2O$, 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 plot in the joins $MnTa_2O_6$-$FeTa_2O_6$-O and $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$. Their chemical relationships are shown in Fig. 1. This diagram emphasizes two triangular joins. The join $MnTa_2O_6$-$FeTa_2O_6$-Z, which is a portion of the larger join $MnTa_2O_6$-$FeTa_2O_6$-O, is lightly stippled in order to emphasize its position in space

in front of the join $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$. In this diagram subsolidus tie-lines are omitted, except for some of those on the join $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$.
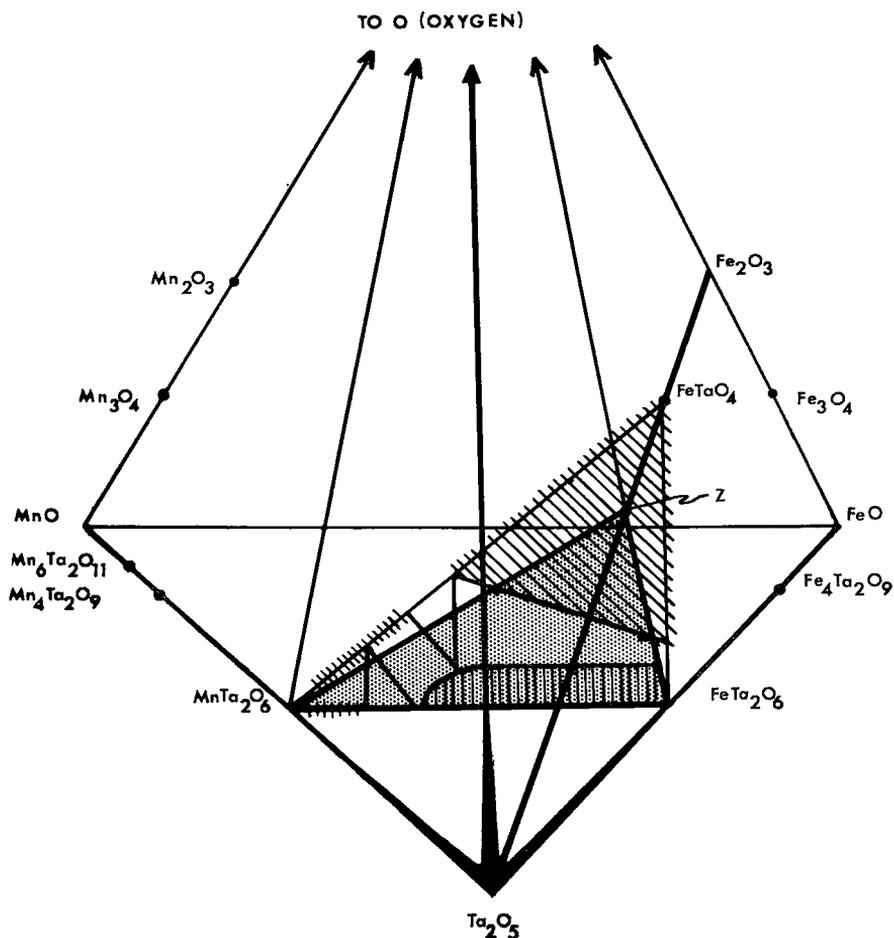
FIG. 1. Solid phases in the system MnO-FeO-Ta_2O_5-O. The hatched lines on the join $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$, which is behind the lightly stippled triangle, represent the extent of solid solution. Point Z represents $Fe_2Ta_4O_{13}$.

THE SYSTEM $MnTa_2O_6$-$FeTa_2O_6$

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 $CO:CO_2$ 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 $Mn_{1-x}Fe_xTa_2O_6$, here referred to by its mineral name tantalite, and (ii) tetragonal $Fe_{1-y}Mn_yTa_2O_6$, 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. % $MnTa_2O_6$ in solid solution will exsolve tantalite after firing for 10 days at 1,040° C.

Tantalite can take up to 18 mol. % $FeTa_2O_6$ into solid solution, and this limit appears to be insensitive to temperature variation. By contrast, the maximum amount of solid solution of $MnTa_2O_6$ in tapiolite decreases significantly with decreasing temperature; at 1,200° C (point C in Fig. 2) the extent of substitution is 62 mol. % $MnTa_2O_6$.

The MnO content of natural tapiolites and the FeO content of natural tantalites, as shown in compilations of analyses (Palache, Berman &
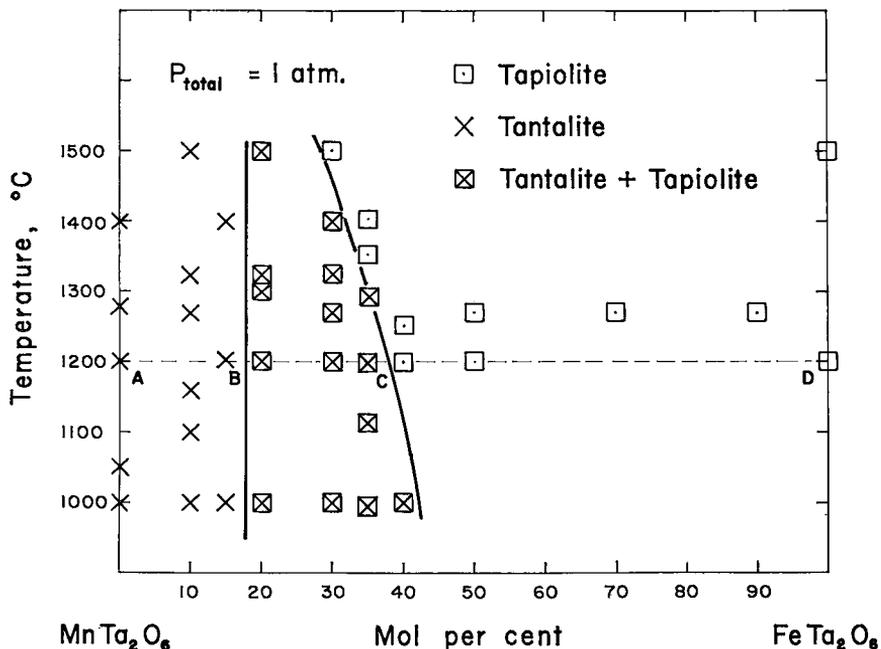
FIG. 2. The system $MnTa_2O_6$-$FeTa_2O_6$. The data points present the results of synthesis for various lengths of time, plus reversals of the equilibrium along the tapiolite field boundary.

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 Nb_2O_5, 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 $MnTa_2O_6$, and the prefix "mangano" is redundant.

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

TABLE 1. CELL DIMENSIONS OF SYNTHETIC IRON/MANGANESE TANTALATES

Material	a (Å)	b (Å)	c (Å)	β	V (Å³)
Tantalites:					
$MnTa_2O_6$	5.768	14.454	5.097		424.9
$Mn_{0.9}Fe_{0.1}Ta_2O_6$	5.763	14.436	5.094		423.8
$Mn_{0.85}Fe_{0.15}Ta_2O_6$	5.765	14.430	5.093		423.7
Tapiolites:					
$Fe_{0.4}Mn_{0.6}Ta_2O_6$	4.765		9.276		210.6
$Fe_{0.5}Mn_{0.5}Ta_2O_6$	4.762		9.264		210.1
$Fe_{0.7}Mn_{0.3}Ta_2O_6$	4.761		9.221		209.2
$Fe_{0.9}Mn_{0.1}Ta_2O_6$	4.758		9.207		208.3
$FeTa_2O_6$	4.756		9.198		208.0
Wodginites:					
$Mn_{1.3}Fe_{0.3}Ta_{3.9}O_{12}$	9.479	11.441	5.096	91°08′	552.5
$Mn_{1.6}Fe_{0.6}Ta_{3.8}O_{12}$	9.456	11.416	5.091	91°01′	549.5
Rutile-type compounds:					
$Fe_{1.5}Mn_{1.0}Ta_{3.5}O_{12}$	4.713		3.079		68.37
$Fe_{1.8}Mn_{0.8}Ta_{3.4}O_{12}$	4.704		3.069		67.89
$FeTaO_4$	4.678		3.047		66.74

Materials synthesized at 1200° C, 1 atm. total pressure. X-ray diffractometer measurements on powder made at room temperature, cobalt radiation $\bar{K}a_1 \lambda = 1.7889$ A. Internal standard used was Si, with 2θ (220) = 55.532°. Errors are estimated to be ±0.08% on cell edges.

THE SYSTEM $MnTa_2O_6$-$FeTaO_4$

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 $MnTa_2O_6$ (tantalite) which takes less than 2 mol. %

$Fe_3Ta_3O_{12}$ into solid solution; (ii) monoclinic $Mn^{+2}_{2-2w}Fe^{+3}_{3w}Ta_{4-w}O_{12}$ (w = mol. fraction $Fe_3Ta_3O_{12}$) which has a range $0.08 < w < 0.29$ at 1,200° 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 $Fe^{+3}_{3-3z}Mn^{+2}_{2z}Ta_{3+z}O_{12}$ (z = mol. fraction of $Mn_2Ta_4O_{12}$) which has a range $0 \leqslant z < 0.57$ at 1,200° 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_2O_3 and Ta_2O_5; therefore other elements found in natural wodginites, such as tin, are not essential for its formation but indicate extensive solid solution.

THE SYSTEM $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$

A preliminary isothermal section of this system, Fig. 3, was constructed from the following data. The extent of solid solutions along two sides of
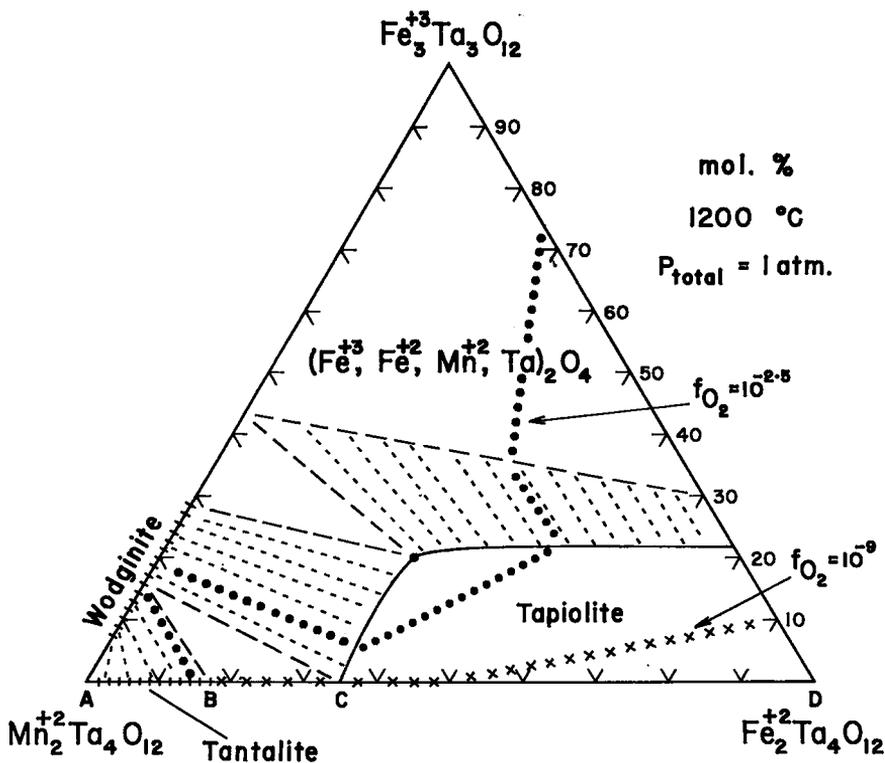
FIG. 3. The system $Mn_2Ta_4O_{12}$-$Fe_2Ta_4O_{12}$-$Fe_3Ta_3O_{12}$ at 1200 °C, total pressure 1 atm.

the triangle, $MnTa_2O_6$-$FeTa_2O_6$ and $MnTa_2O_6$-$FeTaO_4$, have been described above. The relations between composition and f_{O_2} along the remaining side of the triangle, $FeTa_2O_6$-$FeTaO_4$, 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 f_{O_2} isobars, are known by projection of these lines from the join $MnTa_2O_6$-$FeTa_2O_6$-O (see below, and relate Fig. 4b and Fig. 1).

The Join $MnTa_2O_6$-$FeTa_2O_6$-O

The oxidation of tantalites and tapiolites of the system $MnTa_2O_6$-$FeTa_2O_6$ 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° 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, $MnTa_2O_6$, remains stable under the most oxidizing condition of the experiments, which was 1 atm. p_{O_2}. In contrast, the iron bearing compounds are less stable, and are subject to oxidation of the iron component, at conditions of f_{O_2} according to their Fe:Mn composition, by the reaction:

$$2Fe^{+2}Ta_2O_6 + \tfrac{1}{2}O_2 \rightleftharpoons 2Fe^{+3}TaO_4 + Ta_2O_5 \qquad \text{(Eq. 1)}$$
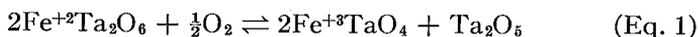
For end-member tapiolite, $FeTa_2O_6$, this oxidation reaction has already been described (Turnock, 1965). Ta_2O_5 is exsolved, but the $FeTaO_4$ may remain in solid solution by the substitution:

$$Fe_2Ta_4O_{12} \leftrightarrow Fe_3Ta_3O_{12} \qquad \text{(Eq. 2)}$$
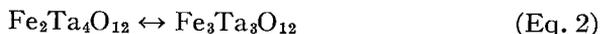
Tapiolite solid solutions, which are stable at relatively low oxygen pressures, were found to take up to 22 mol. % $Fe_3Ta_3O_{12}$ into solid solution according to Eq. 2, at 1,200° C. The rutile-type compound A_2O_4, containing 30 to 100 mol. % $Fe_3Ta_3O_{12}$, formed at higher oxygen pressures.

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 $MnTa_2O_6$ corner. The oxidation of manganian tapiolites is also described by equations 1 and 2, because the $MnTa_2O_6$ 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 Ta_2O_5 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
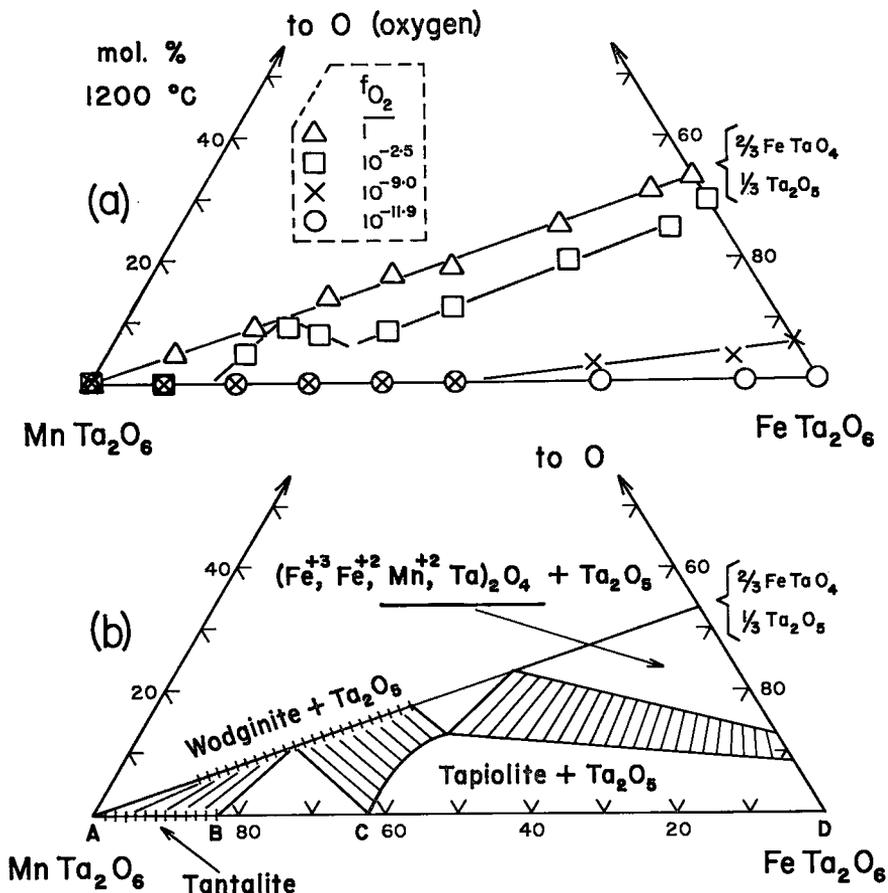
FIG. 4. The join MnTa$_2$O$_6$-FeTa$_2$O$_6$-O at 1200 °C, total pressure = 1 atm. (a) Plot of bulk compositions of solid phases at various oxygen pressures (f_{O2}), giving isobaric tie-lines. (b) Stability fields of the solid phases. Hatched lines indicate solid solution along a line. Three-solid phase fields are lined, four-solid phase fields are triangles.

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),

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 $FeTaO_4$ (Turnock, 1965). The occurrence of exsolved Ta_2O_5 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 $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$.

The join $MnTa_2O_6$-$FeTa_2O_6$-O is therefore a plane in the system MnO-FeO-Ta_2O_5-O (see Fig. 1) which intersects tie-lines connecting Ta_2O_5 with the solid phases that lie in the join $MnTa_2O_6$-$FeTa_2O_6$-$FeTaO_4$. 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° 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 ($FeTa_2O_6$) at 1,200° 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 Fe^{+3}/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 $FeNbO_4$-$FeTaO_4$, and by Laves *et al.* (1963) and by Roth & Waring (1964) for $FeNbO_4$.

ACKNOWLEDGMENTS

REFERENCES

BOURGUIGNON, P. & MÉLON, J. (1965): Wodginite du Rwanda, *Ann. Soc. Géologique de Belgique*, **88**, no. 6, B 291–300.

BROCH, E. K. (1929): Untersuchungen über Kristallstrukturen des Wolframittypus und des Scheelittypus, *Skrifter Norske Vid.-Akad. Oslo, I, Mat.-Nat.Klasse*, **3**, No. 8.

DARKEN, L. S. & GURRY, R. W. (1945): The System Fe-O. I. The wüstite field and related equilibria, *J. Am. Chem. Soc.*, **67**, (II) 1398–1412.

LAVES, F., BAYER, G. & PANAGOS, A. (1963): Strukturelle Beziehungen zwischen den Typen der α-PbO_2, $FeWO_4$ (Wolframit) und $FeNb_2O_6$ (Columbit), und über die Polymorphie des $FeNbO_4$, *Schweiz. Min. Petrogr. Mitt.*, **43**, 217–34.

NICKEL, E. H., ROWLAND, J. F. & MCADAM, R. C. (1963*a*): Wodginite—a new tin-manganese tantalate from Wodgina, Australia, and Bernic Lake, Manitoba, *Can. Mineral*, **7**, 390–402.

NICKEL, E. H., ROWLAND, J. F. & MCADAM, R. C. (1963*b*): Ixiolite-a columbite sub-structure, *Am. Min.*, **48**, 961–79.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1944): *Dana's System of Mineralogy*, seventh ed., **1**. Wiley & Sons, N.Y.

ROTH, R. S. & WARING, J. L. (1964): Ixiolite and other polymorphic types of $FeNbO_4$, *Am. Min.*, **49**, 242–46.

SASAKI, A. (1959): Variation of unit cell parameters in wolframite Series, *Min. J. (Japan)*, **2**, 375–96.

SCHRÖCKE, H. (1961): Heterotype Mischbarkeit zwischen Wolframit-und Columbit-gruppe, *Beitr. Min. Petrog.*, **8**, 92–110.

——— (1962): Heterotype Mischbarkeit zwischen Wolframit-und Rutil-gruppe, *Beitr. Min. Petrog.*, **8**, 339–48.

——— (1965): Personal communication.

TURNOCK, A. C. (1965): Fe-Ta Oxides: Phase relations at 1200 °C, *J. Am. Ceramic. Soc.*, **48**, 258–261.