The Secondary Tungsten Minerals, a Review

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INTRODUCTION
The secondary tungsten minerals form a group of species with no crystallographic interrelationship. The species have crystallized mostly, if not always, at the expense of primary tungsten minerals such as scheelite. They are usually not considered products of atmospheric weathering but rather of hydrothermal or supergene alteration. The minerals occur as fine-grained to powdery masses with a white or yellowish color. Crystals suitable for micromounting are rare. The small grain size makes most of these species mineralogically difficult to characterize. This paper presents a review of the following species: anthoinite, morororoite, ferritungstite, alumotungstite, hydrotungstite, tungstite, yttrotungstite and cerotungstite.

THE CENTRAL AFRICAN TUNGSTEN PROVINCE
This remarkable province with its numerous deposits extends from southwestern Uganda (Kigezi district) and Rwanda to eastern Zaire (Maniema and Kivu districts). The Fe-rich members of the ferberite-huebnerite series constitute virtually the sole economic source of tungsten (Pargeter, 1956; Varlamoff, 1958; de Magnée and Aderca, 1960; Corin and Snel, 1962). According to local miners’ usage, two minerals of this series can be distinguished in the field. Wolframite, simply called wolfram, occurs in black crystals of uniform orientation recognizable by their large, shiny cleavage planes. The crystals are fresh, without traces of alteration. On the other hand, ferberite forms fine-grained masses of a dull-black color without visible cleavage. These two species simply reflect different generations.

The dull-black ferberite is an example of reinite. The name reinite applies to a variety of polycrystalline ferberite which is pseudomorph after scheelite, the Ca of scheelite replaced by Fe. Such reinite masses, known from a number of localities throughout the world, commonly display the tetragonal crystal form of scheelite. In central Africa, tetragonally shaped reinite pseudomorphs (Fig. 1) are common and range up to 15 or 20 cm in length. On breaking a reinite crystal the inside is seen to consist largely of a yellow to white, fine-grained to cryptocrystalline mass referred to here by the mineralogically ill-definable name tungstic ocher (Fig. 2). The ocher material is enclosed in a margin of black ferberite which also penetrates the core in thin veinlets. In some pseudomorphs the ocher has been leached away leaving behind a porous honeycomb network of ferberite.

The tungstic ocher is mineralogically complex and consists of a number of secondary tungsten minerals. The occurrence of these minerals in a cavity, as is commonly found under the microscope (polished section, reflected light), is schematically illustrated in Fig. 3. The equidimensional grains of the ferberite mosaic (F) become elongated in the vicinity of the cavity with the long axis perpendicular to the cavity wall. The ferberite crystals which grew on the wall against the tungstic ocher are beautifully euhedral with somewhat varying habit. An example is illustrated in Fig. 4. The

Figure 1. Crystal habit of central African ferberite (reinite), pseudomorphic after scheelite.

Figure 2. Broken reinite pseudomorph showing black ferberite and yellow tungstic ocher. Nyamulilo mine, Kigezi, Uganda. Specimen size: 2.5 cm.
ferberite wall of the cavity is lined with ferritungstite-alumotungstite (K in Fig. 3) and radiating groups of cerotungstite (H). The cavity core consists of anthoinite (A), typically with some scattered ferritungstite-alumotungstite octahedra.

The reinite with its tungsten ocher occurs in central Africa in graphite-bearing, fine-grained schists (phyllites) and in the quartz veins contained in them. From the general geochemistry of tungsten it is known that the element favors late magmatic crystallization, pegmatic or hydrothermal. The geochemical cycle of the element is still not among the better explored chapters of geochemistry. Parry (1956) presented an interpretation which, at that time, was courageously unorthodox for tungsten geochemistry. He suggested that the tungsten of the central African ferberite deposits is of a syngenic origin. Since then, his interpretation has been adopted by several Belgian and British geologists and is supported by the mode of origin of tungsten in the metasedimentary host rocks of the ferberite deposits (Jedwab, 1958; Van Wambke, 1976). This hypothesis was reviewed by Reedman (1973). Briefly told, the story of the secondary tungsten minerals in central Africa is this: tungsten was largely adsorbed in the depositing clayey sediments through the action of organic matter (now graphite) and iron hydroxide (Jeffery, 1959) and, in the initial stages of metamorphism, was mobilized and crystallized in the form of scheelite. Later, the scheelite was transformed into ferberite and tungstic ocher (Barnes and Parry, 1953).

The hypothesis of a syngenic origin of tungsten in the central African ferberite deposits was recently rejected by Frisch (1975). Based on extended regional studies, especially around the Gifurwe mine in Rwanda, he considered the tungsten to be epigenetic in origin, derived from granite cupolas supposed to exist beneath the schists.

Regardless of the origin of tungsten the fact remains that the central African reinite offers an outstanding opportunity to study the mineralogy of many of the important secondary tungsten minerals. It is the reason for presenting here the above short description of this tungsten province.

ANTHOCIRITE

This mineral was originally discovered and described from the eluvium of the Mt. Misobo tungsten mine (Maniema, Zaire) by Varlamoff (1947). It is now known to be a quite common constituent of tungstic ocher throughout the central African ferberite occurrences. Beautifully euhedral anthoinite pseudomorphs after scheelite are occasionally found which measure up to 10 cm in length. The mineral is powdery and white in color when free from iron. The crystals are platy with grain sizes too small (a few microns) for single-crystal X-ray study or optical microscopic characterization. According to the choice of the crystallographic axes suggested below, the crystals are platy parallel to (010).

The X-ray powder pattern and the two-dimensional electron diffraction pattern of the platy crystals were studied by Niggli and Jäger (1957) and by Sahama et al. (1970a). A reinterpretation of the powder data presented by these authors and an interchange of the crystallographic axes to conform with the rule b > a > c yields the following unit cell parameters: a = 9.21 Å, b = 11.36 Å, c = 8.26 Å, α = 94°45', β = 90°, γ = 92°35', volume = 860 Å³. The d-values of the powder lines from these cell parameters agree with those measured for anthoinite. However, such a cell does not necessarily represent the true cell of the mineral. Anthoinite is most probably triclinic with fairly large cell edges. The calculation of the X-ray powder pattern of such a mineral is unequivocal only if based on single crystal data. The above parameters are presented merely for illustrating the relationship between anthoinite and mpotorite.

The few existing chemical analyses (Varlamoff, 1947; Sahama et al., 1970a) indicate a formula (W,Al)₁₆(O,OH)₄₈ or (W,Al)(O,OH)₃ with a small amount of excess non-stoichiometric water. Whether or not W and Al occupy equivalent sites in the structure cannot, at present, be determined.

The most reliable values for the density of anthoinite are 4.78 (anthoinite from Gifurwe; Frisch, 1975) and 4.87 (Kikagati, Uganda; unpublished), both measured on unanalyzed specimens. The density calculable for the analyzed specimen from Bugarama (Sahama et al., 1970a) amounts to 4.84. The higher value for this specimen given by these authors, viz. 5.06, is apparently erroneous.

The occurrence of anthoinite outside central Africa has not been demonstrated in the literature. As a mineral species, anthoinite is readily identified by its characteristic X-ray powder pattern with numerous sharp lines, but its X-ray crystallography remains unsolved.
**MPOROROITE**

This mineral is known only from the Mpororo tungsten mine (Kigézi, Uganda) which is unique among the central African deposits in containing abundant scheelite at all stages of replacement by ferberite (von Knorring et al., 1972). The greenish yellow powdery mpororoite is indistinguishable from an iron-contaminated anthothinite in hand specimen. Under the electron microscope it is platy like anthothinite. Its X-ray powder pattern is different from that of anthothinite and indicates that mpororoite represents a distinct species, supposedly monoclinc. Some lines are, however, analogous to those of anthothinite. In addition, the two-dimensional electron diffraction patterns of the two minerals are markedly similar except for the intensities of the diffraction spots. Therefore, the powder pattern of mpororoite was recalculated in a way analogous to that of anthothinite, assuming triclinic symmetry. The following unit cell parameters were obtained: \(a = 9.40 \, \text{Å}, \, b = 11.46 \, \text{Å}, \, c = 8.20 \, \text{Å}, \, \alpha = 94^\circ 20', \, \beta = 89^\circ 45', \, \gamma = 95^\circ 10', \) volume = \(877 \, \text{Å}^3\). Like those of anthothinite, these values are only tentative and should be tested on the basis of single crystal data.

The only existing chemical analysis of mpororoite yields the formula \((\text{W,Al,Fe})_2(\text{O,OH})_2\cdot 9.85\text{H}_2\text{O}\) or \((\text{W,Al,Fe})(\text{O,OH})\cdot \ldots \cdot \text{H}_2\text{O}\). The mineral may be considered a hydrated analogue of anthothinite formed at a beginning stage in the scheelite alteration. Mpororoite and anthothinite have not been found in the same deposit.

**FERRITUNGSTITE AND ALUMOTUNGSTITE**

Ferritungstite was described by Schaller (1911) as a new mineral from the Germania tungsten mine, Washington. Kerr (1946) reexamined the material and found it to be sulfur-bearing. Richter et al. (1957) concluded that the material on which Schaller based his description was actually a mixture of ferritungstite and jarosite. These authors studied ferritungstite from another locality, the Nevada scheelite mine, Mineral County, Nevada. They presented a chemical analysis and an X-ray powder pattern of the Nevada mineral, suggesting it to be tetragonal.

Van Tassel (1961) published a very detailed study of ferritungstite, mainly from central Africa where the mineral occurs in larger crystals (exceptionally up to 250 microns) than in the American localities. Two morphological habits of identical X-ray crystallography were described with illustrative drawings: strictly octahedral with penetration twinning according to the spinel law, and platy parallel to an octahedron face in six-sided cyclic twins according to the same spinel law. Crystals of both habits are weakly birefringent. Van Tassel remarked that the X-ray powder pattern of the Nevada ferritungstite could be indexed on the basis of a cubic cell and that the powder pattern of ferritungstite is closely similar to that of microlite. Single crystal X-ray rotation photographs about all three crystallographic axes of an octahedron from Nyakabingu, Rwanda, yielded identical patterns indicating that the mineral is cubic with an F-lattice.

Burnol et al. (1964) presented an X-ray powder pattern and two analyses of ferritungstite from La Bertrande, Haute-Vienne, France. The first analysis on hand picked material was made by wet chemical methods and the second one by microprobe on one homogeneous octahedron. The first analysis showed a remarkable content of alumina \((\text{Fe}_2\text{O}_4)/\text{Al}_2\text{O}_3 = 2\) with no ferrous iron and the second one indicated absence of alumina.

Machin and Süße (1975) presented an abstract of their crystal structure determination of ferritungstite from the Bjórdal (= Namulilo) mine in Uganda. They drew attention to the similarity in X-ray powder patterns between ferritungstite and the pyrochlore group. Ferritungstite was found to be cubic with the space group \(Fd\bar{3}m\) and structurally analogous to koppite. Tungsten and iron were considered to occupy equivalent sites in the crystal structure.

Jedwab and Preat (1980) studied ferritungstite from Gifurwe, Rwanda, by scanning electron microscopy. They found that, besides W and Fe, the mineral contains Pb. The X-ray spectra also show the presence of Al.

Ferritungstite is abundant in some parts of the Borrolha tungsten mine (Minho, northern Portugal) which produces both wolframite (roughly two-thirds of the production) and scheelite (one-third). An excellent ferritungstite-bearing specimen was available for this review (Fig. 5). Wherever pseudomorphic crystal faces or outlines could be traced in the ferritungstite masses of this specimen, they were found to reflect the crystal form of scheelite. Some few tiny inclusions of scheelite, on the order of 1 micron in size, could be identified by microprobe between the ferritungstite octahedra (this paper). The margins of the former scheelite crystals consist now of a layer of the platy ferritungstite variety known in central Africa from the description by Van Tassel (1961). Figure 6 gives an idea of the platy ferritungstite from Borrolha, each plate representing a cyclic twin (sixling). Sometimes the plates form a complicated

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*Figure 5. Ferritungstite (yellow) and wolframite (black). Borrolha mine, Minho, Portugal. Specimen size: 7 cm.*

*Figure 6. Platy ferritungstite. Borrolha mine, Minho, Portugal. Area of figure: 110 by 130 microns. Scanning electron micrograph.*
Figure 7. Complicated rosette of ferritungstite. Borralha mine, Minho, Portugal. Diameter of rosette: 70 microns. Scanning electron micrograph.

Towards the core of the former scheelite crystal, now usually hollow, the habit of ferritungstite changes over to octahedral (Fig. 8). Both platy and octahedral crystals exhibit weak birefringence. Microprobe tests of the Borralha ferritungstite did not reveal any Al or Pb.

Figure 8. Single ferritungstite octahedron. Borralha mine, Minho, Portugal. Crystal diameter: 40 microns. Scanning electron micrograph.

Alumotungstite was first mentioned in the literature as the aluminum analogue of ferritungstite by Davis and Smith (1971, p. 262). The mineral was discovered in yttriumtungstite specimens from the Kramat Pulai mine, Kinta, Perak, Malaysia. Later, the same mineral was mentioned from central Africa by Sahama et al. (1971). Alumotungstite is included in the list of minerals compiled by Fleischer (1980). To the knowledge of the author, no detailed description of the mineral has been published.

Figure 9. Alumotungstite octahedra. Gifurwe mine, Rwanda. Average size of single octahedra: 250 microns. Scanning electron micrograph.

The central African alumotungstite is distinguishable from ferritungstite only through its chemistry and/or through its unit cell parameter. Both minerals occur together and may be found even in the same specimen. Like those of ferritungstite, the alumotungstite crystals are octahedral, usually less than 100 microns in size. Figure 9 shows a ferberite cavity with exceptionally large octahedra. The crystals are largely arranged in rounded groups (Fig. 10) and the single octahedra typically exhibit penetration twins according to the spinel law (Fig. 11). The crystals commonly show a thin skin visible in Figure 11 or contain an outer margin easily detached from the core (Fig. 12). Such crystals appear zoned with rather loose zone boundaries. The crystals are invariably weakly birefringent.

Figure 10. Group of octahedral alumotungstite crystals. Nyamulili mine, Uganda. Size of the group: 30 microns. Scanning electron micrograph.
The chemical formulas to be assigned to ferritungstite and alunotungstite are not well established. The similarity in crystal morphology and in X-ray crystallography between the two minerals suggest analogous formulas.

The available analytical data, admittedly rather scarce, make it apparent that the atomic ratio of W to (Al + Fe) is not stoichiometric but variable. This circumstance, along with the crystal structure proposed by Machin and Süss (1975), could indicate that W, Al and Fe occupy equivalent sites in the structure.

The Nyakabinga (Van Tassel, 1961) and Borralha (this paper) ferritungstites are reported to be free of Pb. The X-ray spectra of the Gifurwe ferritungstite (Jedwab and Preat, 1980) show quite appreciable Pb lines. A few provisional microprobe tests on alunotungstite from the Kirwa mine, Uganda, made for this review (not reproduced here) indicate variable contents of PbO, up to 10 wt. percent. It is concluded that Pb is not essential but just accessory for ferritungstite-alunotungstite.

Aluminum-free ferritungstite is known to exist (La Bertrande, Borralha, by microprobe tests). Some alunotungstite crystals from the Kirwa mine (microprobe tests for this review) are only slightly Fe-bearing. These few data seem to indicate that solid solution between ferritungstite and alunotungstite is very limited.

Taking the above data into account, the following formulas are proposed: for ferritungstite (W,Fe)$_2$(O,OH)$_3$, or (W,Fe)(O,OH)$_2$, and for alunotungstite (W,Al)$_2$(O,OH)$_2$, or (W,Al)(O,OH)$_2$, both with non-stoichiometric amounts of Pb, Ca and excess water. These formulas are merely tentative and should be revised when more data become available. It is worth noting that the ideal formulas suggested for anthohinte and alunotungstite are similar to each other, the only difference being in the ratio between W and Al.

X-ray data for ferritungstite and alunotungstite are conformable with a cubic symmetry of the space group $Fd\bar{3}m$. However, the invariably observable weak birefringence points to the possibility that these minerals are only pseudocubic and that the true symmetry is lower. Fleischer (1980) mentions that alunotungstite is trigonal. A tetragonal symmetry proposed for ferritungstite by Richter et al. (1957) is most probably erroneous. Numerical data for the parameter of the cubic or pseudocubic cell presented in the literature or calculable from X-ray powder patterns vary from $a = 10.20$ Å to $a = 10.31$ Å. The values have not always been obtained on materials of known composition but seem in some instances to apply to mixtures between ferritungstite and alunotungstite. If the powder pattern is recorded with a photographic camera of 57.3 mm diameter, then the measurement may just yield a weighted average of the parameters of these component phases. Summing up the information it seems that the cell parameter for pure ferritungstite is $a = 10.33$ Å, measured for the Al-Pb-free Borralha ferritungstite, and for pure alunotungstite $a = 10.20$ Å.

The few data for the density of ferritungstite found in the literature vary between 4.4 (Van Tassel, 1961) and 5.2 (Richter et al., 1957). A value of D = 5.02 was measured for the octahedral crystals of the Borralha ferritungstite (Berman balance). No data for alunotungstite have been published. It seems that the variation in the ratios between W, Fe, Al and Pb affect the density to a considerable extent.

The species ferritungstite and alunotungstite are readily identified by their crystal morphology, especially if studied under the scanning electron microscope, and by their X-ray powder pattern. Attention should, however, be paid to the possibility that the material under study may consist of a mixture of the two species. The range of variation in chemical composition and in physical properties needs refinement.

HYDROTUNGSTITE

This hydrous tungstic oxide was discovered as a natural mineral from Calacalani, Oruro, Bolivia, by Kerr and Young (1944). At that locality it occurs as an initial alteration product of ferberite. Hydrotungstite is said to be dark green when freshly broken, but the museum specimens which have been exposed to air are yellow green. The crystals are platy and occur intergrown as crystal groups (Fig. 13). Under the binocular microscope such groups are not easily distinguished from other secondary tungsten minerals of a bladed or platy habit. Polysynthetic twinning is common. The only existing chemical analysis of the mineral was presented by Kerr and Young and corresponds to the formula $H_2WO_6\cdot H_2O$. The $d$-values of the more intense X-ray powder lines were listed.

Mitchell (1963) reported the complete X-ray powder pattern of hydrotungstite and noticed that it is remarkably similar to that of synthetic molybdic acid ($H_2MoO_6\cdot H_2O$). As no single crystal X-ray data were available for hydrotungstite, its powder pattern was indexed on the basis of the data for molybdic acid and the unit cell parameters were calculated. The mineral was tentatively considered monoclinic with the possible space group $P2_1/m$. 

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Sahama and Lehtinen (1971) refined the X-ray powder data for hydrotungsite on the basis of data from the original specimen (Smithsonian #104901) used by Mitchell. These authors were able to select a single crystal for X-ray precession work. They found the following data: \(a = 7.379 \, \text{Å}, \quad b = 6.901 \, \text{Å}, \quad c = 3.748 \, \text{Å}, \quad \beta = 90^\circ 22',\) monoclinic space group \(P2_1/m\) (\(P2, \ Pm\)).

The crystal structure of natural hydrotungsite has not been determined. It is most probably similar to that of the molybdic acid.

Hydrotungsite has been reported from some central African ferberite deposits, but the data are incomplete.

TUNGSTITE

The mineral name tungsite has been widely used in the literature to denote yellow, powdery tungstic ocher not subjected to valid mineral characterization. It seems likely that some specimens labeled tungsite in the collections are actually fine powdery ferri-tungsite (alumotungsite), hydrotungsite, etc. It is recommended that the name tungsite not be used unless the mineral has been shown to represent this species by X-ray or other means.

Natural tungsite was chemically analyzed using impure material from Salmo, British Columbia, by Walker (1908) who found it to correspond to the formula \(\text{WO}_4\cdot\text{H}_2\text{O}\). Kerr and Young (1944) presented a review of the early literature dealing with tungsite and studied specimens from Calacalani, Oruro, Bolivia, where it occurs in the same deposit as hydrotungsite. The chemical analysis reported by these authors confirms the formula suggested by Walker.

The yellow tungsite varies in color and occurs as earthy incrustations. The crystals are prisms which appear to be orthorhombic, terminated by the basal pinacoid or cleavage plane \([001]\). The length of the crystals ranges up to 75 microns in the Calacalani deposit. The mineral is generally considered to be orthorhombic on the basis of its optical properties. The X-ray powder patterns tabulated in the literature contain a large number of lines and are difficult to interpret without the aid of single crystal data. Therefore, the question of the true symmetry of the mineral must be left open.

The characterization of the mineral is hampered by the fact that tungsite is difficult to obtain free from hydrotungsite or other admixture.

In central Africa, tungsite has been reported from Nzombe, South Kivu, Zaire, by Bourguignon (1953).

As a mineral species tungsite is still inadequately described and needs to be studied with modern laboratory techniques.

REMARKS ON MEYMACITE

In 1874 Carnot described a yellow tungstic ocher from Meymac, Corrèze, France, considered it to be a distinct species and named it meymacite. Since then it has been included in the mineral nomenclature as a doubtful species. Van Tassel (1961) presented a detailed review of meymacite and studied it from the original French locality, also using similar central African material. He found these materials to be chemically identical with hydrotungsite. Later, Pierrot and Van Tassel (1965) were able to examine the original specimen used by Carnot. They found that Carnot's meymacite is actually identical with finely crystalline ferritungs; they redefined the name meymacite to apply to X-ray-amorphous \(\text{WO}_4\cdot\text{H}_2\text{O}\), the counterpart of crystalline hydrotungsite. This redefinition was approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association.

YTROTUNGSTITE

Ytrotungsite is known from the Kramat Pulai mine and from Tapah, Kinta, Perak, Malaysia. Its history has been reviewed by Davis and Smith (1971) who made a very detailed study of it including a complete crystal structure analysis. Ytrotungsite occurs as earthy, yellow material and, in small open vugs, as lath-shaped, elongated, twinned crystals, arranged in radiating groups. X-ray powder patterns and/or chemical analyses, including ratios between the rare earth elements, have been presented by Butler (1957), Bradford (1961), Semenov et al. (1965), Sahama et al. (1970b) and Davis and Smith. Following these last named authors, ytrotungsite is characterized as monoclinic with the space group \(P2_1/m\), \(a = 6.95 \, \text{Å}, \quad b = 8.64 \, \text{Å}, \quad c = 5.77 \, \text{Å}, \quad \beta = 104^\circ 56',\) simplified chemical formula \(\text{YW}_4\text{O}_{12}\text{(OH)}\cdot\text{H}_2\text{O}\). In this formula Y represents strongly predominating yttrium among the rare earth elements.

Ytrotungsite has not been reported from localities outside Malaysia.

Among all secondary tungsten minerals reviewed in this paper, the mineralogy of ytrotungsite has been explored most completely.

CEROTUNGSTITE

From the tungsten ocher of the central African ferberite deposits a mineral is known which has been named cerotungsite (Sahama et al., 1970b). This mineral occurs characteristically in radiating groups and represents a cerian analogue of the Malaysian ytrotungsite. Under the binocular microscope the habit and color of cerotungsite (Fig. 14) are similar to ytrotungsite. The mineral is


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monoclinic with the space group $P2_1/m$, $a = 7.07 \text{ Å}$, $b = 8.70 \text{ Å}$, $c = 5.87 \text{ Å}$, $\beta = 105^\circ 27'$ ($a$ and $b$ interchanged to correspond to those of yttrotungstite). The simplified chemical formula may be written CeWO$_4$(OH)$_2$.H$_2$O, where Ce indicates a strong predominance of cerium and neodymium among the rare earth elements.

Cerotungstite has not been reported from outside central Africa.

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