

Ferritungstite from the Nita Mine, Yaku Island Kagoshima Prefecture, Japan

By

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Abstract Average of seven microprobe analyses of ferritungstite from the Nita mine, Yaku Island, Kagoshima Prefecture, gave: CaO 0.51, Al₂O₃ 1.10, Fe₂O₃ 6.10, WO₃ 80.10, MoO₃ 0.19, total 88.00 wt%. The low total is ascribed to H₂O. The empirical formula is: Ca_{0.04}(W⁶⁺_{1.55}Mo⁶⁺_{0.01}Fe³⁺_{0.34}Al_{0.10})_{Σ2.00}(O_{4.76}(OH)_{1.24})_{Σ6.00}·2.38 H₂O (basis: (W + Mo + Fe + Al)=2). If Ca is dropped, the ideal formula is derived as W⁶⁺₃Fe³⁺O₆(OH)₃·nH₂O, where n~5. X-ray powder pattern is indexed on a cubic face-centered cell with *a*=10.288 Å, *Z*=4 [W⁶⁺₃Fe³⁺O₆(OH)₃·~5H₂O], substantiating the conclusion of ERCIT & ROBINSON (1988), who indicated ferritungstite to be a pyrochlore type compound with an A-site deficit, which is more remarkable in the present material.

Introduction

Ferritungstite was originally described from Germania mine, Washington, by SCHALLER (1911), who provided the ideal formula Fe²⁺₂WO₄(OH)₄·4H₂O. In 1957, RICHTER *et al.* described a secondary wolfram mineral from Arizona, and provided the ideal formula Ca₂Fe²⁺₂Fe³⁺₂[WO₄]₇·9H₂O, tetragonal symmetry from the morphology, and the cell parameters *a*=10.28 Å and *c*=7.28 Å, *Z*=1, despite the X-ray powder pattern indexable on a cubic face-centered cell with *a*=10.28 Å. They have also judged the material studied by SCHALLER (1911) as jarosite, although they retained the name ferritungstite. In 1961 VAN TASSEL examined materials from Ruanda and Uganda and obtained face-centered cubic cells (*a*=10.22~10.31 Å). ERCIT and ROBINSON (1988) investigated materials from Kalzas Mountain, Yukon, which have cubic cell, space group Fd3m, and a pyrochlore-type structure. One of them has *a*=10.352 Å and *Z*=8[(K_{0.20}Ca_{0.06}Na_{0.02})_{Σ0.28}(W⁶⁺_{1.46}Fe³⁺_{0.54})_{Σ2}(O_{4.70}(OH)_{1.30})_{Σ6}·1.13H₂O] with an A-site deficit. The cationic content in the A-site of the present material is lower than their material, Ca_{0.03-0.06}, using the same calculation basis. If Ca and Al are disregarded, the ideal formula is W⁶⁺₃Fe³⁺O₆(OH)₃·nH₂O, where n~5. The deficit in A-site may not be real vacancy but occupied by H₂O molecules with the expectation that the Canadian and present materials belong to the same species.

Occurrence

Yaku Island is located about 70 km south of Kyushu and has a subround outline. It is geologically composed of a coarse-grained biotite granite mass in the center of the island and metasediments belonging to Kumage Group of Paleogene rimming it as a horseshoe-shaped exposed area open to NW (Fig. 1). Along the contact are developed many pneumatolytic veins bearing wolfram, molybdenum, tin, bismuth, and gold (KINOSHITA, 1961).

The ore deposit of the Nita mine has the largest scale in the island. It consists of many parallel veins with minute branches in metasediments. The largest vein has the extension more than 100 m and the width reaches 30 cm. The ore minerals found to date are wolframite, scheelite, molybdenite, native gold, native bismuth, cassiterite, arsenopyrite, pyrite, and chalcopyrite, while the gangue minerals are quartz, tourmaline, and muscovite (KINOSHITA, 1961). The mining site is accessible but only some dumps are left, where the examined materials were collected.

Ferritungstite occurs as the aggregates of light yellow to lemon yellow powder in coarse-grained quartz veins. They are composed of septa-like minute selvages or botryoidal colonies occasionally embodying remnant scheelite or wolframite grains. Apparently, it was derived principally from scheelite and occasionally wolframite. Scheelite occurs as light cream to light brown interstitial grains in the aggregates of coarse-grained wolframite or in coarse-grained quartz after macroscopic observation,

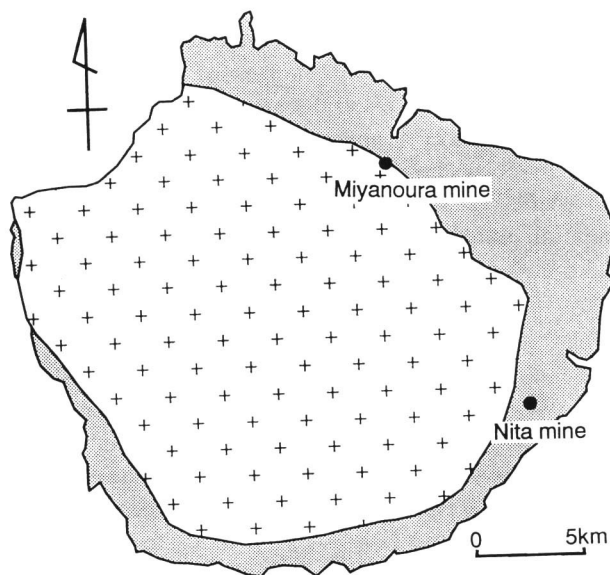


Fig. 1. Distribution of metasediments (shaded) and granite (cross marked) and the location of the Nita and the Miyanoura mines (HASHIMOTO, 1962).

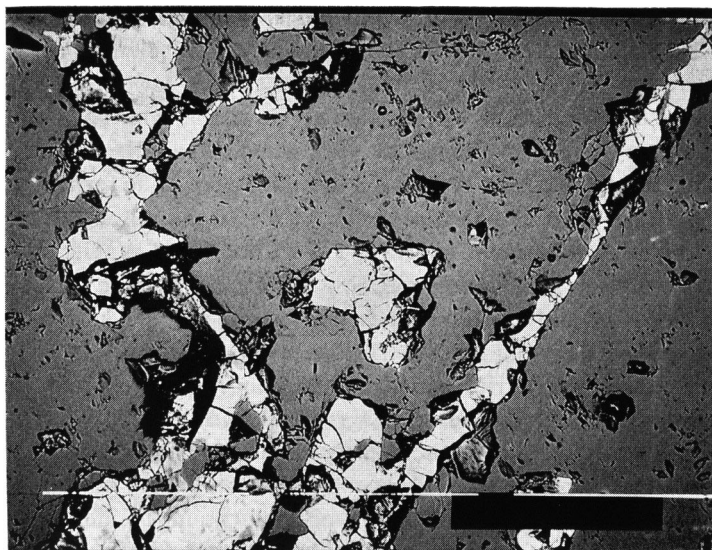


Fig. 2. Backscattered electron image of ferritungstite (grey) replacing scheelite (white) inward. A bar indicates 100 μm .

which reveals minute grains with partially developed faces embedded in quartz. There are two ways in the replacement of ferritungstite for scheelite, inward and outward replacements. The former produces rough aggregates dominated by ferritungstite and the latter does denser aggregate partially pseudomorphing scheelite idiomorphs for which the examinations were made (Fig. 2). Wolframite has two slightly different features. One forms larger thick tablets reaching a few cm long embedded in coarse-grained aggregate of quartz rather rich in voids, and the other forms millimeter-order grains with less developed faces aggregated with quartz of the similar dimension, and the wolframite-quartz aggregates are involved within coarse-grained quartz. A few pieces of coarse-grained quartz aggregates involve metallic minerals. The most common one is native bismuth forming subround grains up to a few mm across or minute inclusions in coarse-grained quartz. Also a very minute lead gray grain with a perfect cleavage along one direction was found. Although it eluded X-ray identification, it will be a member of trigonal bismuth chalcogenides.

Quartz is nearly unique gangue mineral of the vein. It occurs as rather transparent and coarse-grained aggregates. Also, less coarse grains of quartz form rather equigranular grain aggregates with wolframite, where the development of ferritungstite is less prominent. Another gangue minerals is kaolinite forming white film on walls of minute fractures cutting coarse-grained quartz.

Except for ferritungstite, goethite is the unique secondary mineral. It occurs as brown powdery aggregate filling the interstices of coarse-grained quartz, or aggregates apparently pseudomorphing wolframite in voids of coarse-grained quartz com-

posed of minute aggregated tablets grown in subparallel relation, the maximum length being a mm. It is worthy of note that ferritungstite and goethite are not in direct contact, though they co-exist within a single specimen.

The veins are developed in biotite hornfels in either single or composite form, the latter being less frequent. Composite veins accompany either aplite or greisen in the marginal portions with sharp boundaries in both cases. The former consists of the aggregate of granular quartz, orthoclase, and dravite of submillimeter order, whereas the latter is composed of granular quartz and short needles of dravite and their aggregates, the length of individual needle reaching a few mm. Aplite of similar mode of occurrence is described along wolfram-bearing veins in the Miyanoura mine located about 10 km NNW of the Nita mine (MIYAHISA, 1956).

Under the microscope, ferritungstite is light greenish yellow in color and isotropic. No individual grain is observed but the aggregates are all composed of fine powdery material with a partially developed incomplete concentric banding.

It is evident that ferritungstite was secondarily derived from scheelite. But, some aggregates of ferritungstite involve remnant wolframite grains besides scheelite. While, some wolframite grains are replaced by goethite without ferritungstite. These evidences inform that ferritungstite was derived from scheelite and scheelite plus wolframite, where both could be the source of wolfram in ferritungstite. But, in case of presence of wolframite without scheelite, wolfram component was not retained but removed therefrom to form goethite.

These evidences inform that in case of decomposition of scheelite calcium was removed and wolfram was retained, and ferric iron, aluminum and water were added, whereas that of wolframite, wolfram was in the side to be removed and the oxidation of iron and incorporation of watery component took place unless it accompanies scheelite.

Chemical Analyses of Ferritungstite, Scheelite and Wolframite

Chemical analyses of ferritungstite, scheelite and wolframite in a single specimen using Link Systems energy dispersive X-ray spectrometer are given in Table 1. The calculation using the basis of $(W+Mo+Al+Fe)=2$ after the reference to that employed ERCIT and ROBINSON (1988) on two Canadian materials yields the empirical formula $Ca_{0.04}(W^{6+}_{1.55}Mo^{6+}_{0.01}Fe^{3+}_{0.34}Al_{0.10})_{\Sigma 2}(O_{4.76}(OH)_{1.24})_{\Sigma 6} \cdot 2.38H_2O$ if all the difference is ascribed to H_2O . The content of larger cation is far lower than two Canadian materials, which are slightly low in WO_3 and high in Fe_2O_3 contents and devoid of Al_2O_3 . The authors of the Canadian materials refer to the extremely low contents of larger cations, which the materials with pyrochlore structure admit. Thus, the present analyses lead to the creation of ideal formula of ferritungstite as $W^{6+}_{1.5}Fe^{3+}_{0.5}(O_{4.5}(OH))_{1.5} \cdot nH_2O$ ($n \sim 2.5$), or $3WO_3 \cdot Fe(OH)_3 \cdot nH_2O$. The former formula is to have 2 'molecules' of vacant site, which is capable of hosting the same number of H_2O molecules. The creation of above formula requires $(W^{6+}+Mo^{6+})$:

Table 1. Chemical analyses of ferritungstite (1. range; 2. average of 7 analyses), 3. scheelite (MoO_3 highest), and 4. wolframite (average of 2 analyses).

Weight percentages:				
	1.	2.	3.	4.
FeO				18.43
MnO				5.25
CaO	0.33 ~ 0.68	0.51	19.54	
Al_2O_3	0.58 ~ 1.33	1.10		
Fe_2O_3	5.37 ~ 6.49	6.10		
WO_3	78.76 ~ 81.39	80.10	79.13	76.33
MoO_3	0.00 ~ 0.72	0.19	0.73	
	85.21 ~ 90.05	88.00	99.40	100.01
Empirical formulae:				
(bases of calculation: $(\text{W} + \text{Mo} + \text{Fe} + \text{Al}) = 2$ and the difference = H_2O for 2.; $\text{O} = 4$ for 3. and 4.)				
2. $\text{Ca}_{0.04}(\text{W}^{6+}_{1.55}\text{Mo}^{6+}_{0.01}\text{Fe}^{3+}_{0.34}\text{Al}_{0.10})_{\Sigma 2}(\text{O}_{4.76}(\text{OH})_{1.24})_{\Sigma 2} \cdot 2.38\text{H}_2\text{O}$				
3. $\text{Ca}_{1.00}(\text{W}_{0.98}\text{Mo}_{0.01})_{\Sigma 0.99}\text{O}_4$				
4. $(\text{Fe}_{0.78}\text{Mn}_{0.22})_{\Sigma 1.00}\text{WO}_4$				

$(\text{Fe}^{3+} + \text{Al}) = 3 : 1$. The fluctuations from this value are seemingly insignificant in Canadian and the present materials. It is certain that the ionic radii of W^{6+} and Fe^{3+} are so close that the dimensional relation may permit the substitution. However, the valence difference between the two seems to be so significant to impede it. MATSUBARA *et al.* (1984) has discussed the chemical formulae of anthoinite and mpororoite, both being hydrous oxides composed of W^{6+} , Al, and Fe^{3+} with mutual substitutions between W^{6+} and Al or Fe^{3+} , according to the original description. Their studies on Tasmanian materials proved that in both of them $\text{W} : (\text{Al} + \text{Fe}^{3+})$ ratio is essentially unity, leading to the fixing of stoichiometric $(\text{W}^{6+} + \text{Mo}^{6+}) : (\text{Fe}^{3+} + \text{Al})$ ratio in them rather than substitutions of Al and Fe^{3+} for W^{6+} .

The scheelite analysis is very close to theoretical composition. Minor Mo^{6+} vicarious to W^{6+} indicates the prevalence of oxidizing condition at the time of formation of primary minerals. Since minor MoO_3 is also found in ferritungstite, the behaviour of molybdenum was similar to that of wolfram from the time of formation of scheelite to that of ferritungstite through the decomposition of scheelite. Wolframite seems to have rather limited variation range of $\text{Fe}/(\text{Fe} + \text{Mn})$ ratio. Since the mole ratio of $(\text{Fe} + \text{Mn}) : \text{W}$ is very close to unity, neither iron nor manganese is in the trivalent states despite the oxidation condition yielding Mo^{6+} .

X-ray Powder Study

Since the X-ray powder diffractometer patterns of light yellow and lemon yellow materials using Cu/Ni and Co/Fe radiations are essentially identical, the pattern of best quality is demonstrated in Table 2, in which the data of RICHTER *et al.* (1957) are

Table 2. X-ray powder pattern of ferritungstite.

1.		2.			
I	d	I	d _{obs.}	d _{cal.}	hkl
100	5.94	100	5.96	5.94	111
90	3.10	80	3.10	3.102	311
100	2.966	77	2.972	2.970	222
60	2.572	25	2.573	2.572	400
30	2.361	10	2.361	2.360	331
5	2.294	2	2.300	2.300	420
10	2.101				422
50	1.979	15	1.979	1.980	333
80	1.819	32	1.819	1.819	440
50	1.738	16	1.740	1.739	531
5	1.625				620
30	1.569	5	1.569	1.569	533
50	1.550	18	1.551	1.551	622
30	1.485	6	1.485	1.485	444
40	1.441	8	1.440	1.441	711, 551
40	1.341	7	1.339	1.339	731
20	1.286	2	1.286	1.286	800
$a=10.28 \text{ \AA}$		$a=10.288 \text{ \AA}$			

1. Ferritungstite. Nevada Scheelite mine, Mineral County, Nevada. After RICHTER *et al.* (1957). Cu/Ni radiation. Camera method. A revised cubic cell is taken. See text.
2. Ferritungstite. Nita mine, Yaku Island, Kagoshima Prefecture. Cu/Ni radiation. Diffractometer method. The present study.

also tabulated to indicate the essential coincidence after the elimination of their hkl indices. The pattern corresponds well to that of pyrochlore and is indexed on a face-centered cubic cell with $a=10.288 \text{ \AA}$ and slightly smaller than that of one of the Canadian materials, $a=10.352 \text{ \AA}$ (ERCIT & ROBINSON, 1988), which has higher A-site cationic contents. The unit cell is to contain 4 molecules of $3\text{WO}_3 \cdot \text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$. Calculated density for the material with $3\text{WO}_3 \cdot (\text{Fe}, \text{Al})(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ (Fe: Al=78: 22) is 5.24 g/cm^3 using above unit cell. The obtained cell edge is very close to a of tetragonal cell of RICHTER *et al.* (1957), whose cell is accepted with difficulty due to the discrepant figure of their calculated density (4.7 g/cm^3) based on the tetragonal cell with $a=10.28 \text{ \AA}$ and $c=7.28 \text{ \AA}$, $Z=1[\text{Ca}_2\text{Fe}^{2+}_2\text{Fe}^{3+}_2(\text{WO}_4)_7 \cdot 9\text{H}_2\text{O}]$, from their measured one, 5.2 g/cm^3 , which is close to our calculated figure.

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