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Some Characteristic Features of Ferberite from the Ashio Copper Mine, Japan (Studies on Minerals from the Ashio Copper Mine, Japan II)*

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1. Introduction

Wolframite occurs as thin tabular, thin platy or slender needle crystals from the Ashio copper mine (KISHI, 1933; ITO and SAKURAI, 1947; NAKAMURA, 1951, 1954).

During the course of a study of the mineral deposits of the Ashio copper mine, the subvolcanic hydrothermal deposits with copper, zinc, lead, bismuth and tin ores, the author was able to examine the mode of occurrence and mineralogical features of this mineral. The chemical properties and X-ray studies clarified this mineral to be the ferberite with a composition near the Fe-end member of the wolframite mineral series.

In this paper, the mode of occurrence and mineralogical features of ferberite from the mine will be described and further some characteristic features of the wolframite mineral series from the subvolcanic hydrothermal deposits in Japan will be shown from the view point of ore genesis.

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2. Mineralogical properties of wolframite mineral series

The wolframite mineral series is a complete isomorphous series between $MnWO_4$ and $FeWO_4$. Species names applied to particular ranges of composition are shown in Table 1. The Fe-rich members (80 to 100% Fe) are commonly referred to as ferberites, Mn-rich members (80 to 100% Mn) as huebnerites, and all others as wolframites.

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Table 1. Wolframite mineral series.

Species name	Atomic per cent substitution		Corresponding weight percentages	
	Mn	Fe	MnO	FeO
Huebnerite	100 - 80 %	0 - 20 %	23.4 - 18.7%	0 - 4.8%
Wolframite	80 - 20 %	20 - 80 %	18.7 - 4.7%	4.8 - 18.9%
Ferberite	20 - 0 %	80 - 100%	4.7 - 0%	18.9 - 23.6%

The wolframite mineral series was mineralogically studied by BROCH (1929) to be a continuous solid solution varying from orthorhombic $FeWO_4$, $\beta=90°00'$, to monoclinic $MnWO_4$ with a β angle of 90°53'. According to him, the gradual increase of the a_0, b_0, and c_0 lattice parameters and the increase in the angle β seem to correspond with increasing of Mn content.

BERMAN and CAMPBELL (1957) studied the relationship of composition to thermal stability in the wolframite mineral series and also gave the methods for determining the MnO content by the precise measurements of (200) and (030) spacings.

TAKANO (1957) also examined the relationships between lattice parameters and chemical composition on some specimens from Japan.

Recently, SASAKI (1959) has examined the variation of unit cell parameters of this mineral series on the synthesized specimens and some chemically analysed natural specimens, and clarified that a_0, b_0, and c_0 increase almost linearly with increasing MnO content as follows: from $a_0=4.732$Å, $b_0=5.707$Å and $c_0=4.965$Å in $FeWO_4$ to $a_0=4.834$Å, $b_0=5.758$Å and $c_0=4.999$Å in $MnWO_4$. His results also showed that angle β varies gradually from 90°00' in $FeWO_4$ to 91°11' in $MnWO_4$.

3. The mode of occurrence of ferberite from the Ashio copper mine

The ore deposits of the Ashio copper mine occur both in the Ashio rhyolitic body and in the Paleozoic chert bed. The deposits consist of two types, veins and massive replacement or widely disseminated deposits. The veins occur chiefly in the Ashio rhyolitic body, but also in the Paleozoic chert bed. On the other hand, the massive replacement or widely disseminated deposits, which are called "Kajika" by miners, are especially developed in the Paleozoic chert bed and also found in the Ashio rhyolitic body.

a) Ferberite of the central Sn-W-Bi-Cu zone in the Ashio rhyolitic body

As described in the previous paper (NAKAMURA, 1954, 1961) the distribution of metals, Sn·W·Bi·Cu·Pb·Zn etc., and the mineral parageneses in the deposits show a considerable variation in the individual vein, but also in the district as a whole.

Considering the area occupied by the Ashio rhyolitic body as a whole, three hypogene mineral zones are distinguished both horizontally and vertically: (i) a central Sn-W-Bi-Cu zone, (ii) an intermediate Cu-As-Zn zone, and (iii) a marginal Zn-Pb-Cu-As zone. Ferberite occurs in the cassiterite-bearing quartz vein in the central Sn-W-Bi-Cu zone.

The central Sn-W-Bi-Cu zone is characterized by the presence of high-grade Sn-Cu ore (more than 1% Sn) and the high-temperature mineral parageneses. Tin bonanza is chiefly restricted in the higher mine-levels (above the 13th level) in the Ashio rhyolitic body. Frequently, the thin platy or slender needle ferberite, 0.3mm. to 0.5mm. long and 0.02mm. to 0.05mm. thick, occurs in close association with a colloform variety of cassiterite, "wood tin".

Sometimes, in the lower mine-levels of the central Sn-W-Bi-Cu zone, the thin tabular ferberite, 5mm. to 1cm. long and 0.5mm. to 1mm. thick, is scattered in the quartz vein with small amounts of chalcopyrite and pyrite. Under the microscope very small fibrous aggregates of cassiterite are observable in this quartz vein.

From the sequence of mineralization ferberite was formed simultaneously with or slightly later than cassiterite.

b) *Ferberite of the "Kajika" deposits in the Paleozoic chert bed*

Ferberite rarely occurs from the "Kajika" deposits in the Paleozoic chert bed. It is also closely associated with cassiterite.

4. Mineralogical properties of ferberite from the Ashio copper mine

a) *Specimen analysed*

The analysed ferberite specimen was taken from the upper sub-6th level of the 200-shaku vein in the Yokomabu-higashi-10-i cross-cut in the upper 6th level. In the 200-shaku vein, the thin tabular ferberite, 5mm. to 1cm. long and 0.5mm. to 1mm. thick, of which chemical and X-ray studies were made, is scattered in the quartz vein with small amounts of chalcopyrite and pyrite. Under the microscope, small grains of cassiterite are scattered in the quartz vein. The wall-rock suffers strong silicification and sericitization.

Ferberite-rich part picked up with pincette was crushed and sized, the minus 100-, plus 200- fraction being retained. Then, ferberite was separated by means of bromoform. It was then ready for further mineralogical investigations. The material used for chemical analysis was fairly free from impurities.

b) *Chemical composition*

The result of chemical analysis is shown in Table 2.

From the chemical analysis, the chemical formula of this mineral was expressed as $(Fe_{0.96}Mn_{0.04})\,WO_4$. This is very close to the Fe-end member of the ferberite species.

Furthermore, this mineral was examined semiquantitatively by means of the fluorescent X-ray spectrographic methods. Comparing the intensity of FeK_β $(2\theta=51.73°)$ with that of $MnK_\beta(2\theta=56.62°)$, the value of $I_{(FeK_\beta)}/I_{(MnK_\beta)}$ is approximately 14. The fluoresent X-ray spectrographic data also clarified this mineral to be the ferberite with a composition near the Fe-end member.

Table 2. Chemical composition of ferberite from the Ashio copper mine.

	Weight %	Mol. prop.	$WO_3=1$
WO_3	75.95 %	3275	1.00
FeO	22.49	3130	0.96
MnO	0.98	138	0.04
CaO	0.08	14	—
MgO	0.04	10	—
Total	99.54		

(Analyst: T. NAKAMURA)

c) X-ray diffraction data

The X-ray diffraction data obtained by Philips Norelco diffractometer are shown in Table 3. Indexing of reflections was made in terms of being orthorhombic.

Table 3. X-ray powder diffraction data of ferberite from the Ashio copper mine.

(*hkl*)	*I*	*d* obs. (Å)	*Q* obs.	*d* calc. (Å)	*Q* calc.
(100)	40	4.733	0.0446	4.733	0.0446
(011)	25	3.742	0.0714	3.747	0.0712
(110)	30	3.645	0.0753	3.645	0.0753
(111)	100	2.938	0.1159	2.939	0.1158
(020)	55	2.854	0.1228	2.854	0.1228
(002)	30	2.474	0.1634	2.484	0.1621
(021)				2.474	0.1633
(120)	5	2.445	0.1673	2.444	0.1674
(200)	15	2.367	0.1785	2.367	0.1784
(121)	20	2.193	0.2079	2.193	0.2079
(210)				2.187	0.2091
(112)	5	2.053	0.2373	2.052	0.2374
(211)	5	2.002	0.2495	2.002	0.2496
(030)	10	1.902	0.2764	1.902	0.2763
(022)	5	1.874	0.2847	1.874	0.2848
(220)	5	1.822	0.3012	1.822	0.3012
(130)	30	1.767	0.3203	1.765	0.3209
(202)	30	1.713	0.3408	1.714	0.3405
(221)				1.711	0.3417
(113)	20	1.507	0.4403	1.507	0.4401
(222)	5	1.470	0.4629	1.469	0.4633
(311)	10	1.455	0.4724	1.455	0.4726
(040)	5	1.427	0.4912	1.427	0.4912
(041)	10	1.371	0.5319	1.371	0.5319

$a_0=4.733$Å, $b_0=5.707$Å, $c_0=4.967$Å

The experimental conditions are as follows: Ni-filtered Cu radiation, 35kV, 10mA, scanning speed 1°(2θ) and 1°/4(2θ) per minute, time constant 4 seconds, receiving slit 0.006 inches, angular aperture 1°, and goniometer radius 170mm.

Unit cell parameters determined by the measurements of (030), (200), (020), (111), (110), and (011) spacings are shown as follows:

a_0=4.733Å, b_0=5.707Å, c_0=4.967Å, and β=90°00'.

Calculated density is 7.516 g/cm^3.

5. Characteristic features of the wolframite mineral series from the subvolcanic hydrothermal deposits in Japan

On the mineral features of the wolframite mineral series from various types of Bolivian deposits, AHLFELD (1936) suggested that only with high-temperature formation in pegmatitic and hypothermal phase all members of this mineral series (except those rich in Mn) are formed; further he noticed that with decreasing temperature of formation a gap in mixtures occurs, so that in the mesothermal and epithermal deposits members rich in Fe or those rich in Mn are formed.

KHASIN (1949) and LEUTWEIN (1952) suggested that the proportions of Mn to Fe in this mineral series are controlled by the temperature of formation, Mn-rich wolframite being deposited at higher temperatures.

EDWARDS and LYON (1957) clarified that analyses of wolframite sample from localities selected so as to cover the full range in depth and lateral extent of the Aberfoyle mine, Tasmania, show no simple relationship between Mn content and depth. However, according to them, the composition of the wolframite is about intermediate of the ferberite-huebnerite series at the Aberfoyle mine.

In Japan the wolframite mineral series occur both from the subvolcanic hydrothermal deposits and from the plutonic hydrothermal deposits including pegmatitic deposits. The atomic ratios of Fe/(Fe+Mn) of this mineral series from the subvolcanic and plutonic hydrothermal deposits in Japan are shown in Table 4.

Seeing from the value of Fe/(Fe+Mn), it is clear that both ferberites and huebnerites generally occur in the subvolcanic hydrothermal deposits, and that wolframites of intermediate composition chiefly occur in the plutonic hydrothermal deposits including pegmatitic deposits, although all members of the wolframite mineral series occur in the plutonic type deposits.

Seeing from the mode of occurrence, the ferberite crystal from the subvolcanic hydrothermal deposits, such as those of Akenobe, Ikuno and Ashio, shows a thin platy or slender needle habit and further it is genetically closely associated with the colloform variety of cassiterite, "wood tin". The huebnerite crystal from the subvolcanic hydrothermal deposits, such as those of Ikuno and Nishizawa, also shows a thin platy or slender needle habit. On the other hand, the wolframite from the plutonic hydrothermal deposits including pegmatitic deposits, such as those of Kaneuchi and Takatori, occurs as a large tabular crystal.

As shown above, there is a marked contrast in the mineralogical features of the wolframite mineral series between those from the subvolcanic hydrothermal deposits and those from the plutonic hydrothermal deposits. *A thin platy or slender needle ferberite or huebnerite closely associated with a colloform variety of cassiterite is a characteristic mineral of the subvolcanic hydrothermal deposits in Japan.* The mode of occurrence and mineralogical properties of the wolframite mineral series are very interesting from the view point of ore genesis.

Table 4. The value of Fe/(Fe+Mn) in the wolframite mineral series from Japan.

Species name	Locality	Fe/(Fe+Mn) (atomic ratios)	Analyst
Huebnerite	Nishizawa mine,*) Tochigi Prefecture	0.13	KAWAKITA (1908)
Wolframite	Gessei, Kaneuchi mine,**) Kyoto Prefecture	0.35	HARAMURA (1959)
Wolframite	Takatori mine, **) Ibaragi Prefecture	0.48	KOZAKI (1927)
Wolframite	Yomei, Kaneuchi mine,**) Kyoto Prefecture	0.54	HARAMURA (1959)
Wolframite	Nishizawa mine,*) Tochigi Prefecture	0.71	WATANABE (1908)
Wolframite	Funai, Kaneuchi mine,**) Kyoto Prefecture	0.73	HARAMURA (1959)
Ferberite	Akenobe mine,*) Hyogo Prefecture	0.96	KOZAKI (1927)
Ferberite	Ashio mine, *) Tochigi Prefecture	0.96	NAKAMURA (1959)
Ferberite	Otomezaka mine,**) Yamanashi Prefecture	0.96	KODERA (1915)

*) Subvolcanic hydrothermal deposits.

**) Plutonic hydrothermal deposits including pegmatitic deposits.

Besides, Huebnerite (Fe/(Fe+Mn)=0.05) was reported from the quartz vein (plutonic type) cutting through the bedded manganese deposits in the Paleozoic formation at the Hagidaira mine, Gunma Prefecture (SASAKI, 1959). Huebnerite also occurs from the manganese deposits at the Kaso mine, Tochigi Prefecture (KATO, 1959) and the Renge mine, Yamaguchi Prefecture (LEE, 1955).

The thin platy or slender needle ferberite and huebnerite also occur from the Ikuno mine, Hyogo Prefecture (ITO and SAKURAI, 1947).

References

AHLFELD, F. (1936) : The Bolivian tin belt, Econ. Geol., vol. 31, pp. 48-72.

BERMAN, J., and CAMPBELL, W.J. (1957) : Relationship of composition to thermal stability in the huebnerite-ferberite series of tungstates, U.S. Bureau of Mines, Rept. of Invest. 5300.

BROCH, N. A. (1929) : Norsk. Ak. Oslo. Math. -Nat. Kl, Skrifter 8 : PALACHE, C. BERMAN, H. FRONDEL, C. ; The system of mineralogy, vol. 2, p. 1065 (1951).

EDWARDS, A. B., and LYON, R. J. P. (1957) : Mineralization at Aberfoyle tin mine, Rossarden, Tasmania, Proc. Aus. Inst. Min. Met., No. 181, pp. 93-145.

ITO, T. and SAKURAI, K. (1947) : Wada's minerals of Japan, 3rd Ed. (in Japanese).

KATO, A. (1958) : Huebnerite from the Kaso mine, Tochigi Prefecture, Jour. Miner. Soc. Japan, vol. 3, pp. 422-423 (in Japanese).

KHASIN, R. A. (1949) : On the zonality of the isomorphous series ferberite-huebnerite in tungsten deposits, C. R. (Doklady) Acad. Sci., U.S.S.R., vol. 64, pp. 117-119.

KISHI, T. (1933) : On minerals from the Ashio copper mine, Jour. Geol. Soc. Japan, vol. 40, pp. 261-271 (in Japanese).

LEE, D. E. (1955) : Mineralogy of some japanese manganese ores, Stanford Univ. Publications, Univ. Ser., Geol. Sci., vol. 5, pp. 1-64.

LEUTWEIN, F. (1952) : Die chemische Zusammensetzung der Wolframit und ihre lagerstättenkundliche Bedeutung, Acta Geol., Akad. Sci. Hung., vol. 1, pp. 133-141 ; Miner.

Abst., vol. 12, no. 3, p. 158 (1953).

PALACHE, C., BERMAN, H. and FRONDEL, C. (1951) : The system of mineralogy, vol. 2, pp. 1064-1072.

NAKAMURA, T. (1951) : High-temperature mineral associations in a certain quartz vein at the Ashio mine, Jour. Fac. Sci. Univ. of Tokyo, Sec. 2, vol. 8, Pt. 2, pp. 89-98.

NAKAMURA, T. (1954) : Tin mineralization at the Ashio copper mine, Japan, Jour. Inst. Polytech. Osaka City Univ., Ser. G, vol. 2, pp. 35-52.

NAKAMURA, T. (1959) : Ferberite from the Ashio copper mine, Japan, Jour. Miner. Soc. Japan, vol. 4, pp. 184-191 (in Japanese).

NAKAMURA, T. (1961) : Mineralization and wall-rock alteration at the Ashio copper mine, Japan, Jour. Inst. Polytech. Osaka City Univ., Ser. G, vol. 5, pp. 53-127.

SASAKI, A. (1959) : Variation of unit cell parameters in wolframite series, Miner. Jour., vol. 2, pp. 375-396.

TAKANO, K. (1957) : The relation between lattice constants and chemical components in wolframite series, Jour. Assoc. Miner. Petr. Econ. Geol., vol. 41, pp. 32-39 (in Japanese).