ON SOME SULPHOSALT MINERALS (TETRAHEDRITE AND TENNANTITE) FROM NORTHERN JAPAN.

By

Zyunpêi HARADA and Masaharu KITAHAMA

Contribution from the Department of Geology and Mineralogy,
Faculty of Science, Hokkaido University. No. 441

During the course of studies on irregularities of crystals, the present writers collected a series of copper sulphosalt minerals.

The purpose of this paper is to present the results of crystallographic, chemical and X-ray examinations on the specimens of tetrahedrite and tennantite—copper sulphosalt mineral.

1. Localities and modes of occurrences

a. Tetrahedrite.

Tetrahedrite is wide-spread in its occurrence and varied in its association. It is commonly found in copper deposits as a primary constituent in association with chalcopyrite, sphalerite, galena, etc. It frequently becomes an important ore mineral of a peculiar metasomatic copper deposit—"Kuromono"—in northern Japan.

The following are locations of tetrahedrite, which were collected by the writers in that district:

i Kamikita mine, Kamikita County, Aomori Prefecture.
Tetrahedrite is found in cracks of massive pyrite which occurs in "Kuromono" deposit.

ii Mutu mine, Moura, East-Tugaru County, Aomori Prefecture.
Tetrahedrite crystals are discovered in sericite clay which develops around gold quartz vein.

iii Daté mine, Usu County, Iburi Province, Hokkaido.
It occurs in quartz copper pyrite impregnation deposit with some tellurium minerals.

Journ. Fac. Sci. Hokkaido Univ., Ser. IV, VIII, No. 2, 1952.

iv Bokoi, Muroran City, Iburi Province, Hokkaido.
Tetrahedrite crystals are found in small veins in propylite with zincblende and galena.

v Suehiro (formerly Kutosan) mine, near Kuttyan, Abuta County, Iburi Province, Hokkaido.
Massive or granular tetrahedrites occur in gold quartz veinlets with gold, pyrite and arsenopyrite.

vi Teiné mine, Sapporo County, Isikari Province, Hokkaido.
Tetrahedrite is found in gold quartz vein with native tellurium and barite. It usually forms minutely granular masses, rarely in crystals.

b. Tennantite.

Tennatite has the same occurrences as tetrahedrite, but is less widely distributed. Only one locality (Osarizawa mine) has been reported, here we add a new locality of tennantite in northern Japan.

i Osarizawa mine, Kazuno County, Akita Prefecture.
Tennantite occurs in granular aggregate or in fine crystals in copper veins.

ii Zenikamezawa mine, Kameda County, Osima Province, Hokkaido.
Tennantite crystals are associated with chalcopyrite, zincblende and galena in veins.

2. Crystal forms

a. Tetrahedrite

i Tetrahedrite from the Mutu mine, Moura, East-Tugaru County, Aomori Prefecture.

T. Ito and K. Sakurai (1) have described tetrahedrite crystals from the Mutu mine as follows; Tetrahedron with only *o* (111) is the most common crystal, but sometimes *n* (211) and *r* (332) are observed, rarely associated with *d* (110) and *a* (100). Triachistetrahedron chiefly with *n* (211) is commonly found, often associated with *o* (111) and *r* (332). And rarely *α* (433) appears, replacing *o* (111). Striations are observed on *n* (211), *d* (110) and *r* (332). Vicinal faces dominantly develop on *o* (111). Crystals are 3–12 mm in size. Sometimes it occurs in crystal aggregate or penetrating each other.

On crystals obtained in the course of the present work the following forms were found: o (111), n (211), r (332), d (110), a (100).

ii Tetrahedrite from the Suehiro mine, Iburi Province, Hokkaido.
It is massive or granular, crystals are rare. Observed crystal forms are: o (111), d (110), n (211).

iii Tetrahedrite from the Teiné mine, Isikari Province, Hokkaido.
Tetrahedrite is mainly fine granular aggragate, rarely single or grouped crystal. Sometimes it occurs in twin (penetration twin). Crystal forms: o (111), n (211), a (100), o_1 $(1\bar{1}1)$, d (110).

b. Tennantite.

i Tennantite from the Osarizawa mine, Kazuno County, Akita Prefecture.
The crystal forms of tennantite from the Osarizawa mine have been studied by M. Hosina (2). The faces observed on crystals are o $(1\bar{1}1)$, o_1 (111), d (110), a (100) and n (211).
Following two types of combinations are distinguished (3):
Tetrahedron type, dominantly o (111) develops.
Rhombic dodecahedron type, chiefly d (110) predominates.

iii Tennantite from the Zenikamezawa mine, Osima Province, Hokkaido.
Crystals are of the following three principal habits:
a) Simple Triachistetrahedron n (211). (Fig. 1)
b) Triachistetrahedron n (211) with d (110). (Fig. 2)
c) Triachistetrahedron n (211) with d (110) and o (111). (Fig. 3)
Observed crystal forms are as follows: n (211), d (110), o (111). Rarely large crystals (3–5 cm in diameters) were found.

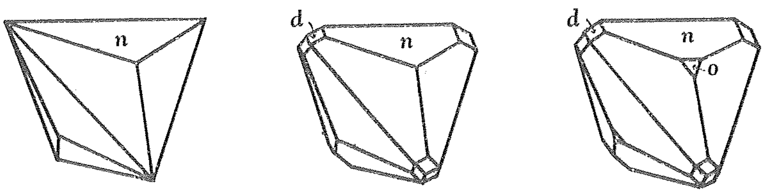

Fig. 1. Fig. 2. Fig. 3.
Tennantite crystals from the Zenikamezawa mine, Hokkaido.

3. Chemical Composition

a. Tetrahedrite.

Materials for analyses obtained consisted of broken fragments of crystals. But specimens from the two mines named in the table still possessed zincblende and quartz as admixtures.

The results of analyses are given in the following table I.

TABLE I Chemical Composition of tetrahedrite.

No.	1		2		3	4
Locality	Mutu mine		Daté mine		Muroran	Teiné mine
Analyst	M. KITAHAMA	Calculated for impurities	M. KITAHAMA	Calculated for impurities	M. KITAHAMA	M. KITAHAMA
S	27.54%	28.70%	24.72%	22.26%	30.12%	25.41%
As	5.32	5.55	0.49	1.44	8.33	4.82
Sb	20.15	21.00	8.55	25.23	12.15	22.17
Cu	38.82	40.46	12.19	35.92	38.69	41.57
Fe	4.12	4.29	5.14	15.15	5.24	1.99
Zn	tr.	—	35.01	—	2.50	2.55
Ag	tr.	—	—	—	0.70	0.27
Bi	—	—	—	—	—	0.56
Pb	tr.	—	—	—	1.30	—
SiO_2	3.51	—	13.41	—	0.83	—
Total	99.46	100.00	99.21	100.00	99.86	99.34

The obtained two results (1 and 2) with admixtures deduced and the remainder were recalculated to 100 per cent.

The analyses have been reduced to Cu (Fe), Sb (As) and S atom ratio, which are given in table II.

TABLE II Atom ratio of tetrahedrite.

No.	1	2	3	4
Locality	Mutu mine	Daté mine	Muroran	Teiné mine
Cu (Fe)	714—2.68—3	694—2.50—3	707—3.35—3	705—2.82—3
Sb (As)	247—0.93—1	226—0.81—1	211—1.00—1	250—1.00—1
S	895—3.36—3	836—3.00—3	606—2.87—3	780—3.12—3

Tetrahedrite has some of the Cu replaced by Fe and the same relation also is observed in respect to Sb and As. The atom ratios agree closely with that required for the formula: $\{Cu(Fe)\}_3Sb(As)S_3$.

b. Tennantite.

The materials used for analyses were tennantite crystals from one locality in Hokkaido.

The results of chemical analyses of the tennantite are listed in table III.

An analysis of tennantite from the Osarizawa mine which was taken in 1908 (2) is presented for comparison. Those values are given under column 2.

TABLE III Chemical Composition of tennantite.

No.	1	2
Locality	Zenikamezawa mine	Osarizawa mine
Analyst	M. KITAHAMA	Metallurgical laboratory, Osarizawa mine
S	31.61%	28.80%
As	14.75	18.07
Sb	5.11	—
Cu	42.51	46.60
Fe	5.51	4.54
Zn	tr.	0.37
Ag	tr.	—
Bi	tr.	—
Mn	—	0.35
Pb	0.17	—
Al_2O_3	—	tr.
SiO_2	—	0.43
Total	99.66	99.16

The atom ratios calculated from these analyses are given below:

TABLE IV Atom ratios of Tennantite.

No.	1	2
Locality	Zenikamezawa mine	Osarizawa mine
Cu (Fe)	768—2.67—3	805—3.00—3
As (Sb)	288—1.00—1	241—0.90—1
S	985—3.42—3	876—3.27—3

The ratios of the two analyses closely agree with the formula: $\{Cu(Fe)\}_3As(Sb)S_3$.

4. X-ray studies

Tetrahedrite and tennantite belong to gray copper ore. There is a complete series from the Sb to the As compound; also Bi, Ag, Zn and Pb may be present.

Since the atomic radius of As differs slightly from that of Sb, it would be expected that the tetrahedrite structure would differ from that of tennantite by replacement of some portion of the Sb atoms with As atoms.

On the assumption that a study of the structure of those two minerals by X-ray methods might contribute some evidence as to the variation of the lattice constant, X-ray diffraction photographs were taken of two specimens each of tetrahedrite and of tennantite.

Powder diffraction patterns were made with Cu radiation, using a cassette of 30.28 mm radius. The lattice constant a_0 of these minerals was calculated in Ångstrom Units. ($\times 10^{-8}$ cm).

The patterns given by the two minerals proved to be similar, but there is slight difference in the value of the lattice constants.

The measured lattice constants on these minerals are as follows:

Tetrahedrite,	Mutu mine.	$a_0 = 10.35 \pm 0.05$ Å
"	Teiné mine.	10.38 ± 0.05
Tenantite,	Osarizawa mine.	10.21 ± 0.06
"	Zenikamezawa mine.	10.24 ± 0.06

The measured value of a_0 for tennantite is shorter than that of tetrahedrite. A variation of the lattice constant in the series is observed.

The lattice constants of tetrahedrite and tennantite have already been determined by J. PALACOIS (5), DE JONG (6) and F. MACHATSCHKI (7).

Their results were:

$a_0 = 10.39$ Å	J. PALACOIS
10.190～10.555 Å	DE JONG
10.189～10.379 Å	F. MACHATSCHKI

A comparison of the measured lattice constants by the authors with those determined by the various other investigations shows similarity in the values.

F. MACHATSCHKI (7) worked out the lattice constants of tetrahedrite and tennantite and pointed out that the lattice constant of tetrahedrite increases with increase of Zn, Fe, Ag, and Bi, while it decreases with increase of As. Also it seems that increasing lattice constant of tetrahedrite may be correlated with the value of As : Sb ratio, which is calculated from the chemical composition.

The valus of As : Sb ratio for both minerals whose lattice constants were determined by various authors, was calculated from their chemical analyses. The relation between the lattice constant and the As : Sb ratio are shown in the following table:

TABLE V

Locality	As : Sb	a_0
Redruth, Cornwall (7)	∞	10.189 Å
Osarizawa mine, Akita Pref. Japan	∞	10.21
Zenikamezawa mine, Hokkaido, Japan	2.88	10.24
Kaulsdorf, Oberfranken (7) (8)	0.678	10.265
Mutu mine, Aomori Pref. Japan	0.25	10.35
Teiné mine, Hokkaido, Japan	0.20	10.38
Schlangenberg, Altai (7) (9)	0.179	10.296
Lake City, Colorado (7) (10)	0.124	10.303
Botés, Siebenbürgen (7) (11)	0.104	10.323
Wermland (7) (12)	0	10.400

A study of this table at once reveals that increasing value of the As : Sb ratio brings about a decrease in the lattice constant a_0.

Summary

Tetrahedrite is a wide-spread mineral species in northern Japan. The atom ratios calculated from these chemical analyses closely agree with the formula of tetrahedrite and tennantite—$R^I_3R^{III}S_3$, where R^I is principally Cu (Fe or Zn) and R^{III} may be Sb and As.

The measured lattice constants of both minerals from four localities in northern Japan are as follows:

Tetrahedrite, Mutu mine, Aomori Pref.	$a_0 = 10.35 \pm 0.05$ Å
" Teiné mine, Hokkaido.	10.38 ± 0.05
Tennantite, Osarizawa mine, Akita Pref.	10.21 ± 0.06
" Zenikamezawa mine, Hokkaido.	10.24 ± 0.06

They agree well with the values obtained by various other investigations.

Data obtained by the studies of chemical compositions and X-ray diffraction patterns of the two minerals show a some intimate relationship between the lattice constant a_0 and the As : Sb ratio. The lattice constant a_0 of tetrahedrite increases with decrease in the value of the As : Sb ratio.

The writers hearty thank to Mr. M. TAKAYASU for his helps in X-ray examinations.

The work here reported was made possible in part through aid of the Grant in Aid for Fundamental Scientific Research, Ministry of Education. The writers are very grateful for this assistance.

References

(1) T. ITO and K. SAKURAI: WADA's Minerals of Japan, I, 3rd Ed. 1947, 129-130.
(2) M. HOSHINA: J. Geol. Soc. Tokyo, 15 (1908) 450.
(3) K. NAKASIMA: Ibid. 540.
(4) F. MACHATSCHKI: Z. Krist. 68 (1928) 204-222.
(5) J. PALACOIS: Anal. Soc. Esp. Fis. Quim 25 2460; Chem. Zbl. 1927, II, 2492.
(6) W. DE JONG: Proef, Schrift, Delft, 1928, 26, ff.
(7) F. MACHATSCHKI: loc. cit.
(8) F. SANDBERGER: N. Jb. Min. (1865) 592.
(9) P. PILIPENKO: Nachr. Univ. Tomsk. 62 (1925) 402.
(10) F. A. GENTH: Am. Journ. Sci. 23 (1885) 38.
(11) J. LESZKA: Z. Krist. 34 (1901) 86.
(12) L. F. NILSON: Z. Krist. 1 (1877) 421.