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TELLURIAN TENNANTITE FROM THE BESSHI-TYPE DEPOSITS IN THE SAMBAGAWA METAMORPHIC BELT, JAPAN

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ABSTRACT

Tellurian tennantite with up to 11.17 wt.% Te was found in copper-rich ores of the Besshi-type Ikadazu and Sazare deposits in the Sambagawa metamorphic belt in Japan. Electron-microprobe analyses of the tellurian tennantite reveal that Te^{4+} substitutes for $(As,Sb)^{3+}$, and electrical-charge-balance is maintained by simultaneous substitution of Te^{4+} for $(As,Sb)^{3+}$ and of Cu^{+} for $(Zn,Fe)^{2+}$. The continuous solid-solution $Cu_{10}Cu_x(Zn,Fe)_{2-x}(As,Sb)_{4-x}Te_xS_{13}$, with $x = 0$ to 2, ranges from $Cu_{10}(Zn,Fe)_2(As,Sb)_4S_{13}$ to $Cu_{12}(As,Sb)_2Te_2S_{13}$ by coupled substitution. As shown by Kalbskopf (1974) for the tellurium end-member of synthetic tetrahedrite, vacancies in the copper sites of varieties with excess tellurium maintain charge balance in this solid solution.

Keywords: tellurian tennantite, goldfieldite, Besshi-type deposits, balance of electrical charges, Japan.

SOMMAIRE

Une tennantite tenant jusqu'à 11.17% (en poids) de Te^{4+} se trouve dans les minerais de cuivre des gîtes Ikadazu et Sazare, du type Besshi, dans la ceinture métamorphique de Sambagawa, au Japon. Soumise à l'analyse par microsonde électronique, cette tennantite révèle deux substitutions simultanées: celle de Te^{4+} à $(As,Sb)^{3+}$ et celle de Cu^{+} à $(Zn,Fe)^{2+}$. La solution solide $Cu_{10}Cu_x(Zn,Fe)_{2-x}(As,Sb)_{4-x}Te_xS_{13}$, avec $x = 0$ à 2, s'étend de $Cu_{10}(Zn,Fe)_2(As,Sb)_4S_{13}$ à $Cu_{12}(As,Sb)_2Te_2S_{13}$ par double substitution. C'est Kalbskopf (1974) qui a montré, sur le pôle tellurium d'une tetraédrite synthétique, que des lacunes dans les sites de cuivre des variétés à excédent de tellure maintiennent l'équilibre des charges dans la solution solide.

(Traduit par la Rédaction)

Mots-clés: tennantite à Te^{4+}, goldfieldite, Besshi (gîtes du type), équilibre des charges électriques, Japon.

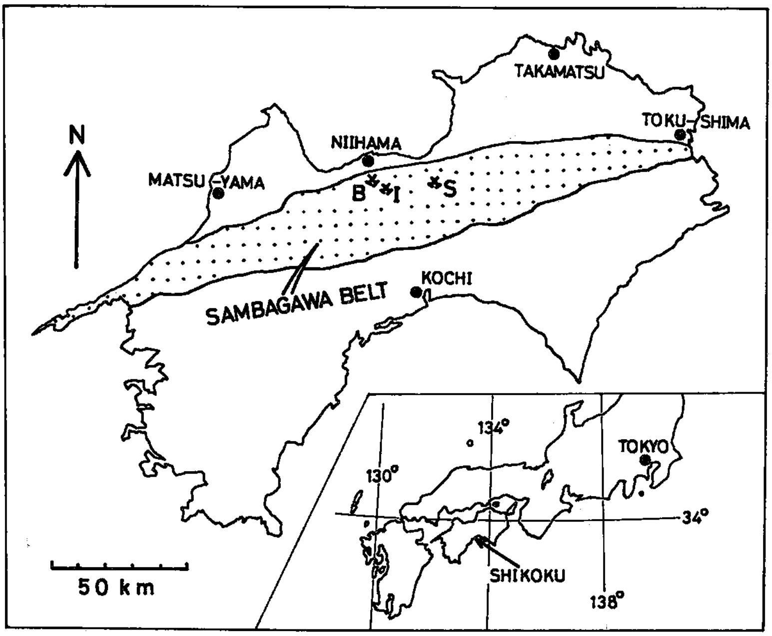

FIG. 1. Location of the Ikadazu (I), Sazare (S) and Besshi (B) deposits in the Sambagawa metamorphic belt (dotted) in Shikoku.

INTRODUCTION

The formula $(CuAg)_{10}(Cu,Fe,Zn,Hg)_2(Sb,As)_4S_{13}$ is thought to describe the chemical composition of the tetrahedrite–tennantite solid-solution (described as tetrahedrite$_{ss}$ hereafter) (Charlat & Lévy 1974). Members of the series can incorporate other elements such as Pb, Cd, Bi and Se. Considerable amounts of tellurium also enter into solid solution.

The tellurian mineral from Goldfield, Nevada, described originally as goldfieldite by Ransome (1909), was proven to be tellurian tennantite by X-ray powder diffraction (Thompson 1946). Concerning the chemistry of tellurian tetrahedrite$_{ss}$, Kato & Sakurai (1970b) concluded that tellurium substitutes for arsenic and antimony, and that the tellurium content is restricted to a maximum of 2 atoms in the chemical formula. Thus, goldfieldite was redefined by them as tetrahedrite$_{ss}$ with a larger atomic fraction of tellurium than of arsenic or antimony. On the other hand, Kalbskopf (1974) synthesized the tellurium end-member tetrahedrite and examined its crystal structure by powder diffraction. He found a formula $Cu_{12-x}Te_4S_{13}$ ($x \approx 2$), and vacancies that occur in the 3-co-ordinated Cu sites. Nevertheless, few analyses of natural tellurian tetrahedrite$_{ss}$ have been carried out. This explains why knowledge of the nature and extent of tellurium substitution has been incomplete.

In the course of mineralogical studies of the Besshi-type deposits, tennantite with variable tellurium contents was found in the Ikadazu and Sazare deposits. This paper discusses the chemistry of the tellurian tennantite with results of 37 analyses in order to clarify the nature and extent of tellurium substitution.

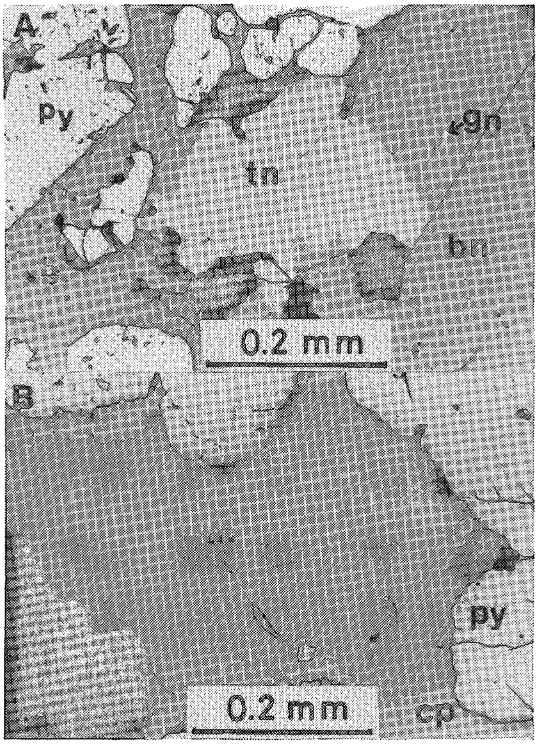

FIG. 2. Photomicrographs of tellurian tennantite (tn) from the Ikadazu and Sazare deposits. A. Tennantite in bornite (bn) with associated pyrite (py) and galena (gn). B. Tennantite, chalcopyrite (cp) and bornite (bn) in interstices of pyrite (py).

OCCURRENCE OF TELLURIAN TENNANTITE

The Besshi-type deposits are conformable massive copper–pyrite deposits in the sequences of basaltic volcanic rocks or their metamorphosed equivalents, and clastic sediments. The ores are usually composed of pyrite with subordinate chalcopyrite, sphalerite and gangue silicates. The two deposits, Ikadazu and Sazare, occur in the Sambagawa high-pressure metamorphic belt of central Shikoku (Fig. 1). They were subjected to regional metamorphism in the lower epidote–amphibolite facies, and constituent sulfides and silicates were thoroughly recrystallized.

The Ikadazu deposits, which were closed in 1973, are about 5 km southeast of the Besshi deposits. The deposits produced 2.4 million tonnes of crude ore grading 1.6 % Cu. Tellurian tennantite occurs in small amounts in the interstices of granular pyrite, with chalcopyrite, bornite, and sphalerite (Fig. 2A), and has a grain size ranging from 0.1 to 0.5 mm in diameter. Galena, which very rarely occurs in ordinary ores, is commonly observed as minute grains in ores with tennantite.

The Sazare deposits, which produced 5.6 million tonnes of crude ore with 1.5% Cu until the mine was abandoned in 1979, are about 20 km east of the Besshi deposits. Tellurian tennantite is also found in interstices of granular pyrite, with chalcopyrite, bornite and sphalerite (Fig. 2B). The ore assemblage and mode of occurrence of the tennantite are almost the same as mentioned above.

The ores with tellurian tennantite were collected near the crests of tight folds, where copper and lead are also significantly enriched. In reflected light, the tellurian tennantite is very similar to ordinary tennantite, except that it does not display a greenish tint.

Members belonging to the tetrahedrite solid-solution series have been found in several other Besshi-type deposits, such as the Okuki deposits in the Ehime prefecture, the Nago and Oba deposits of the Kune mine in the Shizuoka prefecture, and the Shirataki deposits in the Kochi prefecture (Imai

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS AND FORMULAE OF TELLURIAN TENNANTITE FROM THE SAZARE (S) AND IKADAZU (I) DEPOSITS*

No.	1(S)	2(S)	3(I)	4(I)	5(I)	6(I)	7(I)	8(I)	9(I)	10(I)
Cu	43.73	44.10	43.23	44.69	45.13	46.32	46.40	46.59	46.43	46.44
Fe	0.28	0.35	0.28	0.28	0.20	0.12	0.09	0.11	0.21	0.67
Zn	7.99	7.86	7.02	4.82	4.11	3.31	3.19	2.85	2.72	2.77
As	18.28	18.07	14.61	11.95	10.83	11.66	11.21	11.25	11.18	11.29
Sb	1.63	1.67	6.12	5.04	5.55	2.56	3.03	2.54	2.15	2.04
Te	0.42	0.71	1.84	6.70	7.98	9.90	10.21	10.65	10.99	11.17
Se	n.d.**	n.d.	0.04	0.08	0.06	0.26	0.24	0.23	0.25	0.24
S	28.11	27.78	27.10	26.64	26.64	26.55	26.07	26.25	26.00	26.38
Total	100.44	100.54	100.24	100.20	100.50	100.68	100.44	100.47	99.93	101.00
	Number of atoms per formula unit									
Cu	10.22	10.33	10.39	10.92	11.06	11.32	11.44	11.46	11.50	11.36
Fe	0.08	0.10	0.08	0.08	0.06	0.03	0.02	0.03	0.06	0.19
Zn	1.82	1.79	1.64	1.15	0.98	0.79	0.77	0.68	0.66	0.66
As	3.62	3.59	2.98	2.48	2.25	2.42	2.34	2.35	2.35	2.34
Sb	0.20	0.21	0.77	0.64	0.71	0.33	0.39	0.33	0.28	0.26
Te	0.05	0.08	0.22	0.81	0.97	1.20	1.25	1.31	1.35	1.36
Se			0.01	0.02	0.01	0.05	0.05	0.05	0.05	0.05
S	13.02	12.90	12.91	12.90	12.94	12.86	12.74	12.80	12.76	12.79

1. $(Cu,Fe,Zn)_{12.12}(As,Sb,Te)_{3.87}S_{13.02}$
2. $(Cu,Fe,Zn)_{12.22}(As,Sb,Te)_{3.88}S_{12.90}$
3. $(Cu,Fe,Zn)_{12.11}(As,Sb,Te)_{3.97}(S,Se)_{12.92}$
4. $(Cu,Fe,Zn)_{12.15}(As,Sb,Te)_{3.93}(S,Se)_{12.92}$
5. $(Cu,Fe,Zn)_{12.10}(As,Sb,Te)_{3.93}(S,Se)_{12.95}$
6. $(Cu,Fe,Zn)_{12.14}(As,Sb,Te)_{3.95}(S,Se)_{12.91}$
7. $(Cu,Fe,Zn)_{12.23}(As,Sb,Te)_{3.98}(S,Se)_{12.79}$
8. $(Cu,Fe,Zn)_{12.17}(As,Sb,Te)_{3.99}(S,Se)_{12.85}$
9. $(Cu,Fe,Zn)_{12.22}(As,Sb,Te)_{3.98}(S,Se)_{12.81}$
10. $(Cu,Fe,Zn)_{12.21}(As,Sb,Te)_{3.96}(S,Se)_{12.84}$

Results of electron-microprobe analyses quoted in wt.%. * Listed in order of increasing Te content. ** not detected. Number of atoms per formula unit calculated on the basis of 29 atoms per formula unit.

1950, Kamiyama & Yamae 1961, Yamaoka 1962). The occurrences are, however, very limited in amount. No detailed mineralogical study has been carried out on tetrahedrite from these localities.

ANALYTICAL METHOD AND RESULTS

Electron-microprobe analysis was carried out using a JEOL Model 733, operating at an accelerating voltage of 25 kV, and a specimen current was 0.02 μA on copper metal. By qualitative analysis, Cu, Fe, Zn, As, Sb, Te and S were detected in tennantite from both the Ikadazu and Sazare deposits, and Se only from the Ikadazu tennantite. Most, but not all, of the tennantite grains are chemically homogeneous. Electron-probe traverses of grains having chemical heterogeneity clearly show that Te increases as As and Zn decrease.

Quantitative analyses were done on grains that show chemical homogeneity for at least a 5-micrometre width. Standard materials used for analyses are as follows: chalcopyrite from the Kosaka mine for Cu, Fe and S, synthetic ZnS for Zn, synthetic Bi_2Se_3 for Se, and pure metals for Sb, As and Te. The measured ratios of intensities were corrected

TABLE 2. CHEMICAL COMPOSITIONS AND FORMULAE OF TELLURIAN TETRAHEDRITE$_{SS}$ AVAILABLE IN THE LITERATURE

No.	1	2	3	4
Cu	41.9	47.6	43.7	44.3
Ag			0.2	0.6
Fe			0.2	0.1
Zn	6.8		0.2	0.2
Mn			0.1	0.1
As	11.2	8.1	8.7	5.3
Sb	9.8	1.3	0.6	7.1
Te	4.2	17.0	16.0	14.5
S	26.8	26.0	28.2	27.8
Total	100.7	100.0	97.9	100.0
	Number of atoms per formula unit			
Cu	10.27	11.98	10.93	11.11
Ag			0.03	0.09
Fe			0.06	0.03
Zn	1.62		0.06	0.06
Mn			0.03	0.03
As	2.32	1.74	1.86	1.13
Sb	1.25	0.17	0.09	0.93
Te	0.52	2.15	2.00	1.80
S	13.02	12.99	13.98	13.83

1. $(Cu,Zn)_{11.9}(As,Sb,Te)_{4.1}S_{13.0}$
2. $Cu_{12.0}(As,Sb,Te)_{4.1}S_{13.0}$
3. $(Cu,Ag,Fe,Zn,Mn)_{11.1}(As,Sb,Te)_{4.0}S_{14.0}$
4. $(Cu,Ag,Fe,Zn,Mn)_{11.3}(As,Sb,Te)_{3.9}S_{13.8}$

Formula unit calculated as explained in Table 1. The results of the electron-microprobe analyses are quoted in wt.%. 1,2: Butte mine, Montana (Springer 1969), 3: Kawazu mine, Shizuoka prefecture, Japan (Kato & Sakurai 1970a), 4: Mohawk mine, Goldfield, Nevada (Kato & Sakurai 1970b).

for background and dead time, and then converted into concentrations according to the method described by Sweatman & Long (1969).

Ten representative compositions from the 37 new analyses are listed in Table 1. Some previously published compositions of tellurian tetrahedrite$_{ss}$ are shown in Table 2 for comparison.

Figures 3, 4 and 5 show the solid-solution relationships of Te and related elements. As + Sb content (N_{As+Sb}) shows a good negative linear correlation with Te (N_{Te}). The least-squares regression is $N_{As+Sb} = -0.92N_{Te} + 3.88$. The correlation coefficient is - 0.998. The slope of the equation (- 0.92) implies that most of the tellurium substitutes for arsenic and antimony. The extent of substitution of sulfur by tellurium is small or nil.

The amount of Cu (N_{Cu}) and Zn + Fe (N_{Zn+Fe}) increases or decreases linearly with increasing N_{Te}. The regression equations for these are $N_{Cu} = 0.96N_{Te} + 10.19$ and $N_{Zn+Fe} = -0.89N_{Te} + 1.92$. The correlation coefficients are 0.972 and - 0.988, respectively. Since the slopes of the three equations can be regarded as approximately 1, the substitution of (As + Sb) by Te results in a one atom increase of Cu and a one atom decrease of (Zn + Fe).

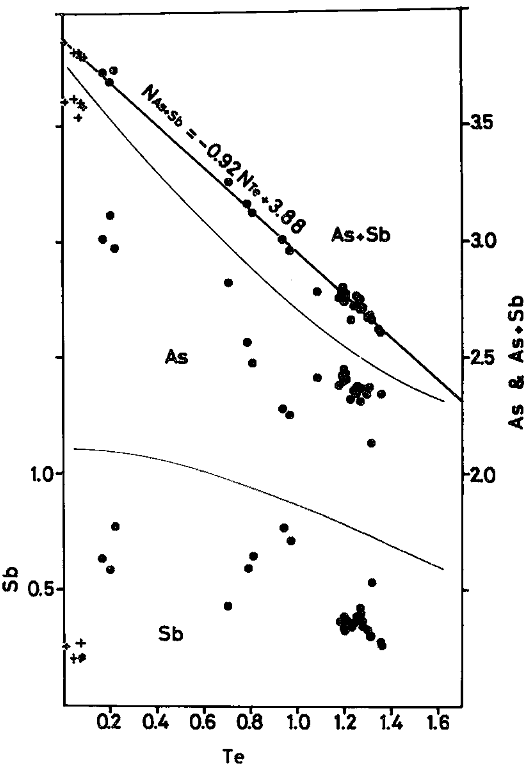

FIG. 3. Relationships between proportions of Sb, As and (As + Sb) to those of Te in tellurian tennantite, based on formulae calculated on the basis of 29 atoms per formula unit. The linear regression equation for N_{As+Sb} *versus* N_{Te} and its correlation coefficient are referred to in the text. Solid circles: Ikadazu deposits, crosses: Sazare deposits.

DISCUSSION

The observed systematic chemical changes of the constituent elements can be explained in the following manner. Arsenic and antimony have three electrons in the outer *p* orbital, and they enter as trivalent cations into the structure of tetrahedrite$_{ss}$. Tellurium has four *p* electrons, and it is usually tetravalent. The substituion of Te^{4+} for $(As,Sb)^{3+}$ is balanced by coupled substitution of Cu^{+} for $(Zn,Fe)^{2+}$.

The substitution of Cu for (Zn,Fe) was verified by Charlat & Lévy (1974) in a study of 54 tetrahedrite$_{ss}$ samples from selected localities worldwide. Nakai *et al.* (1976) studied the valence state of copper atoms by X-ray photoelectron spectroscopy in some twenty sulfide and sulfosalt minerals, including tetrahedrite. They found that all copper is monovalent. The Mössbauer spectral analysis of tetrahedrite showed that the iron is divalent

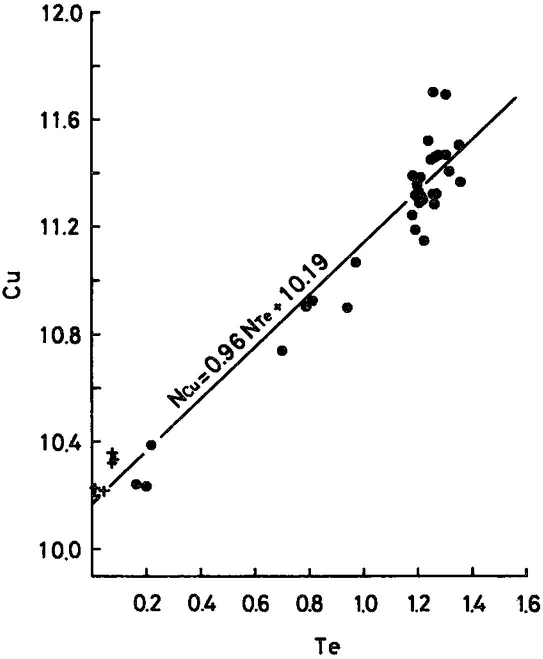

FIG. 4. Relationship between proportion of Cu and of Te in tellurian tennantite. Symbols as in Figure 3.

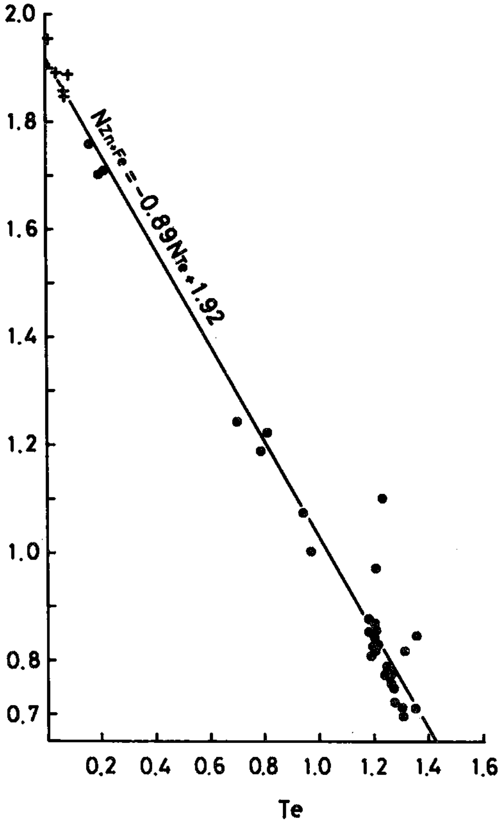

FIG. 5. Relationship betwen proportion of (Zn +Fe) and of Te in tellurian tennantite. Symbols as in Figure 3.

(Kawai *et al.* 1972). Furthermore, Takéuchi (1970) summarized the crystal chemistry of sulfide and sulfosalt minerals and concluded that members of the tetrahedrite$_{ss}$ can be regarded as normal-valence compounds where charge balance is maintained. These results support the present conclusions for tellurian tennantite.

The substitution of Te for (As,Sb) seems to be permissible up to $Cu_{12}(As,Sb)_2Te_2S_{13}$ without change of total number of constituent atoms. According to the microprobe data given by Springer (1969), tennantite from Butte, Montana, contains tellurium that slightly exceeds this limit (No. 2, Table 2). Vacancies in the sites occupied by monovalent copper may be responsible for the charge balance of such excess-tellurium varieties. However, such a statement cannot be proved on the basis of his analytical data alone. Kalbskopf (1974) clarified the presence of vacancies in 3-co-ordinated copper sites for synthetic tellurium end-member of tetrahedrite, as already stated. Johnson & Jeanloz (1983) found, using a Brillouin-zone approach, that the appropriate formula for pure tellurian tetrahedrite should be $Cu_{10}Te_4S_{13}$. Furthermore, Tatsuka & Morimoto (1977) proposed that vacancies in cation sites could explain the extensive solid-solution found in tetrahedrite. Vacancies are thus believed to occur in tetrahedrite$_{ss}$ compositions that have more than 2 atoms of tellurium in the formula, leading to continuous solid-solution from $Cu_{12}(As,Sb)_2Te_2S_{13}$ to $Cu_{10}Te_4S_{13}$. The general formula can be written $Cu_{10}Cu_x(Zn,Fe)_{2-x}(As,Sb)_{4-x}Te_xS_{13}$, with x between 0 and 2.

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