

## STANNOIDITE-BEARING TIN ORE: MINERALOGY, TEXTURE AND PHYSICOCHEMICAL ENVIRONMENT OF FORMATION

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### ABSTRACT

Stannoidite-bearing tin ores from Japanese vein-type tin deposits have been studied. The stannoidite commonly coexists with chalcopyrite, bornite and sphalerite; the atomic Fe/Zn ratio of the sphalerite is low, in the range 0.002 – 0.015. Based on iron content of sphalerite and the mineral assemblage, the probable range in sulfur fugacity and temperature for the stannoidite-bearing tin ore is estimated to be  $10^{-6}$  –  $10^{-16}$  atm. and 200 – 300°C. This estimated range is different from that for the stannite-bearing tin ore estimated by Shimizu & Shikazono (1985). Tungsten-free tin ore deposits seem to have formed at a higher fugacity of sulfur or lower temperature than tungsten-bearing deposits of tin.

**Keywords:** stannoidite, sphalerite, tennantite, tetrahedrite, stannite, Japan, vein-type tin deposits, Fe–Zn partitioning, sulfur fugacity, temperature.

### SOMMAIRE

On a étudié le minerai d'étain à stannoidite des gisements d'étain en veines du Japon. La stannoidite coexiste couramment avec chalcopyrite, bornite et sphalérite. Le rapport atomique Fe/Zn de la sphalérite est bas, entre 0.002 et 0.015. Vu la teneur en fer de la sphalérite et l'association des minéraux, on propose une fugacité de soufre pour ce minerai entre  $10^{-6}$  et  $10^{-16}$  atmosphères et une température de formation entre 200 et 300°C. Ces valeurs diffèrent des résultats obtenus par Shimizu et Shikazono (1985) pour le minerai d'étain à stannite. Les gisements d'étain dans lesquels le tungstène est absent indiqueraient une fugacité de soufre plus élevée ou une température plus basse que les gisements d'étain à tungstène.

(Traduit par la Rédaction)

**Mots-clés:** stannoidite, sphalérite, tennantite, tétraédrite, stannite, Japon, gisements d'étain en veines, répartition de Fe et de Zn, fugacité de soufre, température.

### INTRODUCTION

Stannoidite is a common tin-bearing mineral in Japanese tin ore deposits, and was first described from the Konjo deposit by Kato (1969). The mineral

had been called hexastannite (Ramdohr 1944, 1960) and yellow stannite (Lévy 1967). The chemical formula  $Cu_5(Fe,Zn)_2SnS_8$  had been originally assigned (Kato 1969); however, the formula  $Cu_8(Fe,Zn)_3Sn_2S_{12}$  was later proposed (Springer 1972, Boorman & Abbott 1967, Petruk 1973). Mössbauer, chemical analysis and crystal-structure studies confirm the chemical formula as  $Cu_8^+Fe_2^{3+}(Fe^{2+}, Zn^{2+})Sn_2^{4+}S_{12}$  (Yamanaka & Kato 1976, Kudoh & Takeuchi 1976). Some analytical data on stannoidite have been obtained (*e.g.*, Petruk 1973, Kissin & Owens 1979), but details of the natural occurrence of the mineral and its physicochemical environment of formation have not been clarified.

In this paper, the compositional relations of coexisting stannoidite, sphalerite and tennantite-tetrahedrite-series minerals are reported. Based on these data, the sulfur fugacity of stannoidite-bearing tin ore is estimated. Considering the complementary work on stannite-bearing tin ores from Japanese ore deposits (Shimizu & Shikazono 1985), a comparison between environmental conditions of these two types of tin sulfides is made.

### SAMPLE PREPARATION AND ANALYTICAL PROCEDURE

The samples used for this study belong to the University Museum of the University of Tokyo; some were collected by the present authors. Locations of the samples studied are shown in Figure 1.

The chemical composition of coexisting stannoidite, sphalerite and tennantite-tetrahedrite-series minerals was determined using a JEOL 733 electron-microprobe analyzer at the Ocean Research Institute of the University of Tokyo. The accelerating voltage used was 25 kV, and the following standards were used for analysis: natural chalcopyrite (Cu), synthetic  $Zn_{0.6}Fe_{0.4}S$  (Zn, Fe, S), synthetic CdS (Cd), synthetic MnS (Mn), synthetic SnS (Sn), synthetic  $Ag_3AsS_3$  (Ag, As) and synthetic  $Cu_{10}Fe_{1.8}Zn_{0.2}Sb_4S_{13}$  (Sb). The characteristic X-ray intensities for each point were measured twice for a fixed interval of five seconds. The averaged values were corrected for dead time and background. Quantitative correc-

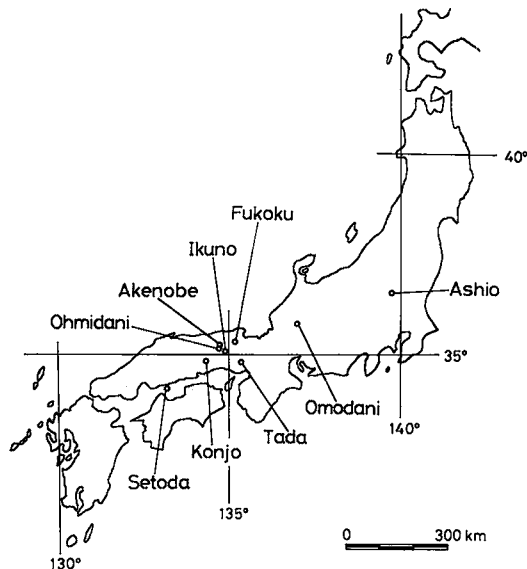
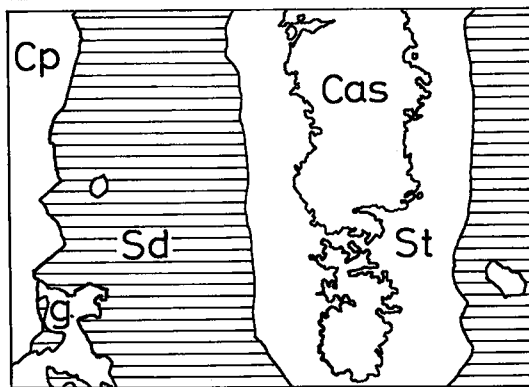
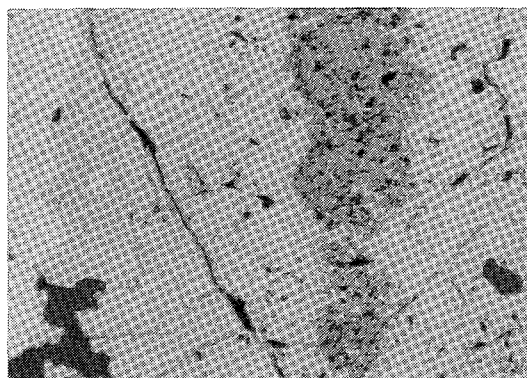


FIG. 1. Map of Japan, showing sample locations.



0 100  $\mu\text{m}$

FIG. 2. Photomicrograph of stannoidite-stannite-cassiterite-bearing sample from the Konjo ore deposit, Okayama Prefecture, Japan (Sd stannoidite, St stannite, Cp chalcopyrite, Cas cassiterite).

tions for atomic number, absorption and fluorescence effects were also performed based on the method proposed by Sweatman & Long (1969).

#### TEXTURES AND MINERAL ASSEMBLAGES OF STANNOIDITE-BEARING TIN ORES

Two characteristic textures of stannoidite-bearing ores are observed under the microscope (Figs. 2, 3). Where relict cassiterite remains, such as observed in the ores from the Konjo and Ashio deposits, stannoidite usually includes stannite, and stannite in turn includes aggregates of cassiterite grains (Fig. 2). This texture, which was pointed out by Kato (1969), suggests the following sequence of precipitation of these tin minerals: cassiterite (early)  $\rightarrow$  stannite  $\rightarrow$  stannoidite (late).

On the other hand, where mawsonite occurs at the margin of some stannoidite grains, such as observed in the samples from the Tada, Ohmidani, Omodani and Fukoku deposits, mawsonite shows a replacement or reaction texture (Fig. 3), as mentioned by Lee *et al.* (1974). In this case, stannite is invariably absent. This texture suggests the following sequence of precipitation: stannoidite  $\rightarrow$  mawsonite.

The sequence of precipitation of tin minerals inferred from the two types of textures mentioned above is considered to be cassiterite  $\rightarrow$  stannite  $\rightarrow$  stannoidite  $\rightarrow$  mawsonite. This implies a trend of increasing of metal/sulfur,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and Cu/Sn ratios in the tin sulfides.

The mineral assemblages studied are presented in Table 1. The common opaque minerals that coexist with stannoidite are chalcopyrite, bornite, sphalerite, tennantite-tetrahedrite-series minerals and roquesite. This assemblage generally does not include stannite. Stannoidite is rarely associated with galena, wittichenite, arsenopyrite and loellingite. It is noteworthy that stannoidite does not coexist with pyrite, except in the tin ores from the Ashio deposit. These ores contain stannite together with stannoidite. On the other hand, stannite usually coexists with pyrite. From the textures observed, stannoidite, bornite, chalcopyrite, sphalerite and tennantite-tetrahedrite-series minerals seem to have formed nearly contemporaneously.

#### CHEMICAL COMPOSITION OF COEXISTING STANNOIDITE, SPHALERITE AND TENNANTITE-TETRAHEDRITE-SERIES MINERALS

Scanning patterns and many analytical data obtained by electron-microprobe analyzer reveal that most stannoidite grains are compositionally homogeneous. Representative chemical compositions and atomic proportions of the mineral coexisting with sphalerite and tennantite-tetrahedrite-series

minerals are given in Table 2. It seems clear from the analytical data on stannoidite that this mineral is represented by the stoichiometry  $\text{Cu}_8\text{Fe}_2^+(\text{Fe}^{2+}, \text{Zn})\text{Sn}_2\text{S}_{12}$ , which is in agreement with the results by Yamanaka & Kato (1976) and Kudoh & Takeuchi (1976).

There is a wide range in extent of Fe and Zn substitution in stannoidite ( $\Sigma\text{Fe}/\text{Zn}$  between 2.03 and 14.4), as summarized in Table 3. The stannoidite from the Tada deposit is the richest in Zn (5.24 wt. % Zn, 9.09 wt. % Fe) and has the approximate formula  $\text{Cu}_8\text{Fe}_2\text{ZnSn}_2\text{S}_{12}$ ; that from the Konjo deposit is the richest in Fe (11.90 wt. % Fe, 1.69 wt. % Zn) and has the formula  $\text{Cu}_8\text{Fe}_2(\text{Fe}_{0.77}\text{Zn}_{0.19})\text{Sn}_2\text{S}_{12}$ . From the  $\text{Fe}^{2+}/\text{Zn}^{2+}$  ratio of stannoidite, a continuous solid-solution is inferred to exist between  $\text{Cu}_8\text{Fe}_2\text{ZnSn}_2\text{S}_{12}$  and  $\text{Cu}_8\text{Fe}_2\text{FeSn}_2\text{S}_{12}$ , as already pointed out by Petruk (1973).

Iron and manganese contents of sphalerite coexisting with stannoidite are in the range from 0.17 to 1.93 wt. %, and from 0.02 to 0.16 wt. %, respectively (Table 2). The cadmium content of sphalerite, from 0.17 to 0.25 wt. %, is generally higher than iron and manganese. The Fe/Zn ratio of sphalerite coexisting with stannite or stannoidite is listed in Table 4. Note that the iron content of sphalerite is very low, compared with that of sphalerite coexisting with stannite (Shimizu & Shikazono 1985).

Chemical analytical data on tennantite-tetrahedrite-series minerals indicate that the As content is generally higher than the Sb content; thus they can be called tennantite, but some are rich in Sb and Ag, and can be called Ag-bearing tetrahedrite.

Representative chemical compositions of coexisting stannoidite and sphalerite (Table 2) and ranges in the atomic  $\text{Fe}^{2+}/\text{Zn}^{2+}$  ratio of coexisting stannoidite, sphalerite and tennantite-tetrahedrite-series minerals from Japanese vein-type tin deposits are summarized in Table 5 and Figure 4. The atomic  $\text{Fe}^{2+}/\text{Zn}^{2+}$  ratio of stannoidite was calculated from the  $\Sigma\text{Fe}/\text{Zn}$  ratio obtained by electron-microprobe analyzer and is based on the relationship:  $(\text{Fe}^{2+}/\text{Zn}^{2+})_{\text{stannoidite}} = \frac{1}{2}\{(\Sigma\text{Fe}/\text{Zn})-2\}$ . The  $\text{Fe}^{2+}/\text{Zn}^{2+}$  ratio of stannoidite is positively correlated with that of sphalerite and tennantite-tetrahedrite-series minerals (Fig. 4).

## DISCUSSION

As described above, stannoidite commonly coexists with sphalerite (sp), chalcopyrite and bornite. Therefore, the following chemical reaction can be used to estimate the fugacity of sulfur [ $f(\text{S}_2)$ ] of formation of the mineral assemblage.

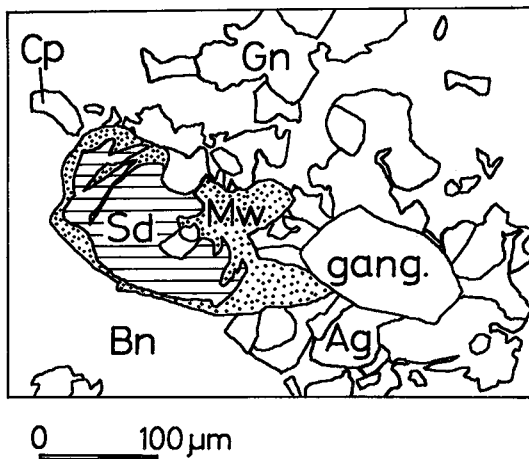
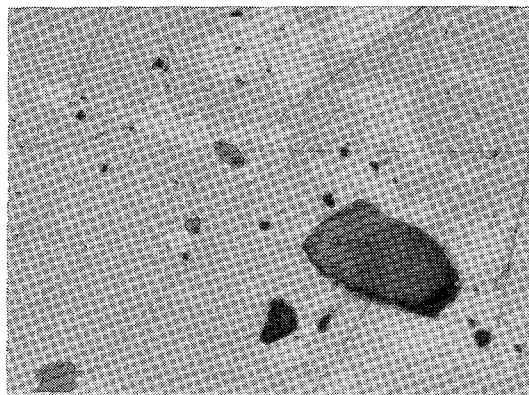
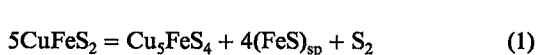


FIG. 3. Photomicrograph of stannoidite-mawsonite-bornite-bearing sample from the Tada ore deposit, Hyogo Prefecture, Japan (Sd stannoidite, Mw mawsonite, Bn bornite, Cp chalcopyrite, Gn galena, Ag Ag-mineral, gang. gangue mineral).

in which  $(\text{FeS})_{\text{sp}}$  denotes the FeS component in sphalerite. The equilibrium constant for reaction (1) is expressed as

$$K = a_{\text{FeS}}^{\text{sp}} \cdot f(\text{S}_2) \quad (2)$$

The free energy of reaction (1) is expressed as

$$\Delta\text{Gr} = -RT \ln K = -RT \ln [a_{\text{FeS}}^{\text{sp}} \cdot f(\text{S}_2)] \quad (3)$$

Therefore, sulfur fugacity (in logarithmic units) is expressed as

$$\log f(\text{S}_2) = -\frac{\Delta\text{Gr}}{4.575T} - \log a_{\text{FeS}}^{\text{sp}} \quad (4)$$

TABLE 1. LOCATIONS AND REPRESENTATIVE MINERAL ASSEMBLAGES OF SAMPLES STUDIED

Ore Dep.	Cp (wt.% In)	Sd	Sp	Bn	Tenn	Mw	St	Gn	Others
Tada	+ (<0.02)	++	++	+	+	+		+	
Ohmidani	+ (<0.02)	+		++	+	+		+	Ag-minerals(1)
Omodani	++ (<0.05)	+	++	++	+	+			Rq, Lo(e), Ap(e), Ag(1)
Akenobe	+		++	+	++	+		+	Rq
Fukoku	++ (<0.04)	+	+		+	+			Rq, Md
Ashio	++ (<0.01)	+	+	++	+		+		Py, Cv(1), Dj(1)
Setoda	++ (<0.05)	+		++					Wt, Wf(e), Sc(e)
Ikuno	+	(<0.19)	+	+		+		+	Rq, Ap(e)
Konjo	++ (<0.34)	++			+		+	+	

Cp chalcopyrite, Sd stannoidite, Sp sphalerite, Bn bornite, Tenn tennantite-tetrahedrite-series mineral, Mw mawsonite, St stannite, Gn galena, Rq roquesite, Lo loellingite, Ap arsenopyrite, Ag native silver, Md matildite, Py pyrite, Cv covellite, Dj djurleite, Wt wittichenite, Wf wolframite, Sc scheelite. ++ common, + less common, (e) early stage, (1) late stage.

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF COEXISTING STANNOIDITE (sd) AND SPHALERITE (sp)

Ore Dep.		WEIGHT PERCENT								ATOMIC PROPORTIONS, TOTAL ATOMS = 25 (sd) or 2 (sp)								
		Cu	Ag	Fe	Zn	Cd	Mn	Sn	S	Total	Cu	Ag	Fe	Zn	Cd	Mn	Sn	S
Tada	sd	38.27	0.04	8.95	4.64	0.08	0.01	17.82	29.32	99.13	7.93	0.01	2.11	0.93	0.01	0.00	1.98	12.04
	sd <sup>1</sup>	39.7	0.8	11.5	4.5			15.5	28.8	100.8	7.83	0.08	2.58	0.86			1.63	11.26
	sp	0.24	0.01	0.17	65.32	0.62	0.16	0.00	33.43	99.95	0.00	0.00	0.00	0.97	0.00	0.01	0.00	1.01
Ohmidani	sd	38.87	0.03	9.03	4.51	0.03	0.03	19.23	28.67	100.40	8.05	0.00	2.13	0.91	0.00	0.01	2.13	11.77
	sd	38.95	0.03	9.54	4.10	0.03	0.00	19.24	29.17	101.06	7.99	0.00	2.23	0.82	0.00	0.00	2.11	11.85
Omodani	sp	0.63	0.00	0.42	65.90	0.47	0.02	0.00	32.37	99.81	0.01	0.00	0.01	0.99	0.00	0.00	0.00	0.99
	sd	38.0	9.8	3.5	0.1	0.0	19.3	29.1	99.8	7.89		2.31	0.70	0.01	0.01	2.14	11.94	
Akenobe	sd <sup>1</sup>	37.4	0.1	10.7	3.1			15.8	30.5	97.6	7.96	0.02	2.60	0.63			1.80	12.89
	sp <sup>2</sup>	0.2		0.3	66.0	0.6	0.1		33.0	100.2	0.00		0.01	0.98	0.01	0.00		1.00
Fukoku	sd	38.81	0.06	10.25	2.91	0.01	0.06	19.06	29.18	100.34	7.98	0.01	2.40	0.98	0.00	0.01	2.10	11.89
	sd <sup>1</sup>	41.5	0.2	9.7	3.5			18.3	28.6	101.8	8.19	0.02	2.18	0.68			1.93	11.20
	sp	1.28	0.03	0.87	64.78	0.25	0.07	0.00	32.37	99.65	0.92	0.00	0.02	0.97	0.00	0.00	0.00	0.99
Ashio	sd	38.59	0.03	10.99	2.91	0.10	0.03	18.63	28.17	99.45	8.05	0.00	2.60	0.98	0.01	0.01	2.08	11.65
	sp	2.33	0.00	1.93	63.44	0.71	0.05	0.00	32.57	101.03	0.04	0.00	0.03	0.94	0.01	0.00	0.00	0.99
Setoda	sd	38.88	0.01	11.02	2.24	0.31	0.03	19.03	29.03	100.55	7.96	0.00	2.57	0.45	0.04	0.01	2.09	11.90
Ikuno	sd	38.65	0.06	11.07	2.08	0.07	0.02	17.71	29.62	99.28	7.95	0.01	2.59	0.42	0.01	0.00	1.95	12.07
	sd <sup>1</sup>	38.2	0.1	9.4	4.2			15.5	31.7	99.1	8.11	0.02	2.26	0.86			1.76	13.34
	sd <sup>3</sup>	38.5		11.5	1.6			18.9	29.3	99.8	7.94		2.69	0.33			2.08	11.96
Konjo	sd	39.06	0.04	11.58	1.69	0.07	0.11	19.02	29.06	100.63	8.01	0.01	2.70	0.34	0.01	0.03	2.09	11.81
	sd <sup>4</sup>	37.2	0.1	12.5	1.2			16.5	31.2	98.7	7.54	0.01	2.88	0.24			1.79	12.54

<sup>1</sup> Kato & Fujiki (1969), <sup>2</sup> Shiozawa (1984), <sup>3</sup> Kissin & Owens (1979), <sup>4</sup> Kato (1969). Data obtained by electron microprobe.

The free energy  $\Delta G_r$  of reaction (1) as a function of temperature can be derived from the thermochemical data on chalcopyrite-bornite-pyrite-S<sub>2</sub> (gas) equilibrium (Schneeberg 1973) and FeS-pyrite-S<sub>2</sub> (gas) equilibrium (Barton & Skinner 1979). The activity coefficient of FeS in sphalerite is assumed to be 2.4, from the experimental data by Barton & Toulmin (1966). The relationship between temperature and FeS content of sphalerite in equilibrium with bornite and chalcopyrite was obtained on the basis of equation (4). Isotherms for FeS content of sphalerite in equilibrium with chalcopyrite and bornite were drawn on a log  $f(S_2)$  - temperature dia-

gram (Fig. 5). As summarized in Figure 5, sphalerite coexisting with stannoidite contains a mole fraction of FeS in a range from 0.002 to 0.011. The temperature of formation of a stannoidite-bearing assemblage cannot be estimated precisely. However, fluid-inclusion studies of the Japanese vein-type tin deposits considered here (e.g., Imai 1973) suggest that stannoidite-bearing assemblages formed in the temperature range 200 - 300°C. Accepting this temperature range, the probable  $f(S_2)$  region for stannoidite-bearing assemblages is estimated, as shown in Figure 5.

Lee *et al.* (1975) conducted an experimental study

TABLE 3. ATOMIC FFe/Zn RATIO OF STANNOIDITE

Location or Ore Dep.	Range (No. of analysis)	Reference(s)
eastern USSR	1.70 - 3.84 (5)	Botava et al. (1978) etc.
9 vein-type dep. in Japan*	2.03 - 14.4 (60)	
Mount Pleasant, Canada	2.03 - (?)	Petruk (1973)
Kidd Creek, Canada	2.21 (1)	Kissin & Owens (1979)
St. Michael's Mount	3.37 - 4.96 (8)	Moore & Howie (1984)
*) Tada		
	2.03 - 2.43 (9)	this study
	3.00 (1)	Kato & Fujiki (1969)
Ohmidani	2.27 - 2.37 (3)	this study
Omodani	2.33 - 2.97 (9)	this study
Akenobe	3.14 - 3.29 (2)	Shiozawa (1984)
	3.24 (1)	Yamanaka & Kato (1976)
	4.13 (1)	Kato & Fujiki (1969)
Fukoku	2.34 - 4.13 (5)	this study
	3.21 (1)	Kato & Fujiki (1969)
Ashio	3.76 - 5.58 (3)	this study
Setoda	5.17 - 6.28 (9)	this study
Ikuno	5.92 - 6.56 (7)	this study
	2.63 (1)	Kato & Fujiki (1969)
	8.41 (1)	Kissin & Owens (1979)
Konjo	8.04 - 14.4 (7)	this study
	12.2 (1)	Kato (1969)

TABLE 4. Fe/Zn RATIO OF SPHALERITE FROM TIN-BEARING VEIN-TYPE DEPOSITS IN JAPAN

Sphalerite + stannoidite	
Ore Dep.	Fe/Zn
Tada	0.002 - 0.007
Omodani	0.004 - 0.011
Akenobe	0.005 - 0.008
Fukoku	0.015
Sphalerite + stannoidite + stannite	
Ashio	0.036 - 0.041
Sphalerite + stannite (Shimizu & Shikazono 1985)	
Yatani	0.023 - 0.044
Ikuno	0.039 - 0.041
Akenobe	0.10 - 0.13
Takatori	0.17
Kaneuchi	0.20 - 0.23
Ohtani	0.22 - 0.24

on the equilibrium for the assemblage of stannoidite-chalcopryrite-bornite-mawsonite-S<sub>2</sub> (gas) in a temperature range from 430 to 300°C. Curves A and B in Figure 5 correspond to  $f(S_2)$  - temperature relationships for this equilibrium assemblage for  $a_{Fe} = 1$  and  $a_{Fe} = 0.1$ , in which  $a_{Fe}$  is the activity of the Cu<sub>3</sub>Fe<sub>2</sub>FeSn<sub>2</sub>S<sub>12</sub> component in stannoidite solid-solution. The uncertainty in  $f(S_2)$  for this assemblage at constant temperature, as deduced from the experimental study by Lee *et al.* (1975), increases with decreasing temperature. At 300°C, the uncertainty may be  $\pm 0.5 \log f(S_2)$ . Therefore, the  $f(S_2)$  estimated from this assemblage for a temperature below 300°C (in which range experimental

studies have not been carried out) might be large, probably more than  $\pm 0.5 \log f(S_2)$ . Unfortunately, we cannot estimate  $f(S_2)$  and temperature from the assemblage because a relevant experimental study has not been carried out at a temperature below 300°C, and no information is available on the thermochemical mixing-properties of the stannoidite solid-solution; however, note that theoretically it would be possible to estimate both  $f(S_2)$  and temperature based on the mawsonite-stannoidite-bornite-chalcopryrite-sphalerite assemblage if reliable experimental data on the assemblage and analytical data on sphalerite and stannoidite of the assemblage were available.

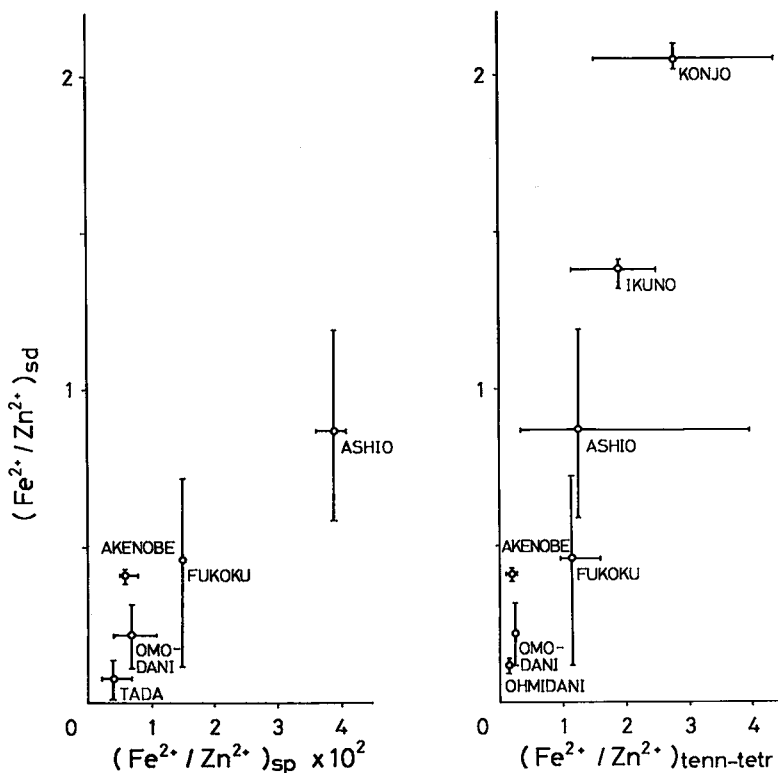
Shimizu & Shikazono (1985) have estimated the  $f(S_2)$  - temperature range for stannite-bearing assemblages from Japanese vein-type and skarn-type tin deposits. This estimated  $f(S_2)$  - temperature region is also shown in Figure 5. The  $f(S_2)$  - temperature range for the formation of these two types of tin sulfides is different. As discussed above, microscopic observations suggest that stannite formed earlier than stannoidite on the scale of one polished section, although in general coexistence of stannoidite and stannite cannot be observed in the same polished section. If stannite formed at an earlier stage than stannoidite, it could be inferred that  $f(S_2)$  increased or that temperature decreased (or both) with evolution of tin mineralization.

As shown in Table 4, the Fe<sup>2+</sup>/Zn<sup>2+</sup> ratio of coexisting stannoidite, sphalerite and tennantite-tetrahedrite-series minerals from the Tada, Omodani and Ohmidani deposits is low, compared with that from the other deposits such as the Ashio, Akenobe and Ikuno deposits. The Tada, Omodani and Ohmidani deposits are characterized by polymetallic (Zn-

TABLE 5. ATOMIC  $Fe^{2+}/Zn^{2+}$  RATIO OF COEXISTING STANNOIDITE (Sd), SPHALERITE (Sp) AND TENNANTITE-TETRAHEDRITE-SERIES MINERAL (Tenn)

Ore Dep.	Sd (avg; no. analysis)	Sp (avg; no. analysis)	Tenn (avg; no. analysis)
Tada	0.01 - 0.14 (0.08; 9)	0.002 - 0.007 (0.004; 8)	absent
Ohmidani	0.09 - 0.14 (0.12; 7)	absent	0.09 - 0.19 (0.14; 5)
Omodani	0.11 - 0.32 (0.22; 9)	0.004 - 0.011 (0.007; 8)	0.22 - 0.24 (0.23; 2)
Akenobe*	0.38 - 0.43 (0.41; 2)	0.005 - 0.008 (0.006; 3)	0.12 - 0.23 (0.18; 5)
Fukoku	0.11 - 0.72 (0.46; 9)	0.015 (0.015; 1)	0.94 - 1.61 (1.14; 4)
Ashio	0.58 - 1.19 (0.87; 3)	0.036 - 0.041 (0.039; 2)	0.34 - 3.97 (1.25; 4)
Setoda	1.06 - 1.43 (1.21; 9)	absent	absent
Ikuno	1.31 - 1.41 (1.38; 6)	absent	1.13 - 3.02 (1.90; 11)
Konjo	2.01 - 2.10 (2.05; 6)	absent	1.52 - 4.38 (2.77; 7)

\* Shiozawa (1984)

FIG. 4.  $Fe^{2+}/Zn^{2+}$  of sphalerite (left) and of tennantite-tetrahedrite-series mineral (right) as a function of  $Fe^{2+}/Zn^{2+}$  in stannoidite (atomic proportions).

Cu-Ag-Au; Zn-dominant) mineralization, and tungsten is not recovered from these deposits. On the other hand, the Akenobe, Ikuno and Ashio deposits are characterized by polymetallic (Cu-Zn-Pb-Sn-W-Ag-Au-Bi) mineralization, and tungsten is recovered from these deposits. The Fe/Zn ratio of coexisting stannoidite, sphalerite and tennantite from the tungsten-bearing polymetallic deposits is higher than in those from the tungsten-free polymetallic deposits.

High content of indium in chalcopyrite, shown in Table 1, probably indicates a high temperature of formation. Sphalerite rarely appears where the  $Fe^{2+}/Zn^{2+}$  ratio of the coexisting stannoidite exceeds approximately 1. These differences imply that the tungsten-bearing deposits formed under lower  $f(S_2)$  or higher temperature conditions (or both) than tungsten-free deposits.

More detailed investigations will be needed to clar-

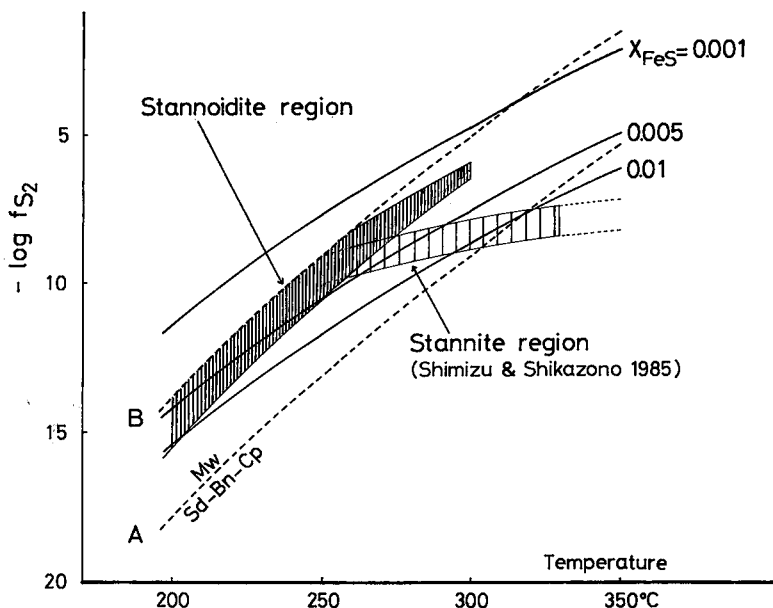


FIG. 5. Temperature -  $\log f(S_2)$  diagram for stannoidite-bearing ores from Japanese vein-type deposits.

ify the factors that lead to different  $f(S_2)$  and temperature conditions for different types of tin-bearing hydrothermal deposits.

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