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MERCURIAN GOLD FROM THE TSUGU GOLD–ANTIMONY VEIN DEPOSIT IN JAPAN

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Abstract

Electron-microprobe analyses of ores from the Tsugu gold–antimony vein deposit, Japan, revealed the first find of mercurian gold in Japan; the gold contains up to 7.7 atomic % Hg. The high mercury content and the opaque minerals coexisting with the mercurian gold indicate that aS_2 during formation of the Tsugu deposit was lower than that of epithermal gold–silver vein-type deposits. Opaque minerals from other similar deposits also indicate low aS_2 as a condition for the precipitation of such gold.

Keywords: mercurian gold, microprobe analyses, epithermal vein deposits, depositional conditions, Tsugu deposit, Japan.

Sommaire

Des analyses à la microsonde électronique du minerai d'or et d'antimoine du gisement en fissures de Tsugu (Japon) mettent en évidence pour la première fois la présence de l'or mercurifère au Japon; l'or peut contenir jusqu'à 7.7% Hg (base atomique). La teneur élevée en mercure et les minéraux opaques qui coexistent avec l'or indiquent une valeur de l'activité du soufre aS_2 inférieure à ce qu'elle serait dans les gisements Au–Ag épithermaux en fissures. L'assemblage des minéraux opaques dans des gisements semblables concorde avec l'hypothèse d'une faible activité de soufre requise pour la précipitation d'un or enrichi en mercure.

(Traduit par la Rédaction)

Mots-clés: or mercurifère, analyses à la microsonde électronique, gisement épithermal en fissures, conditions de formation, gisement Tsugu, Japon.

Introduction

Electron-microprobe analyses of gold from several ore deposits have revealed that some gold contains more than 30 atomic % mercury (Naz'mova & Spiridonov 1979, Ozerova *et al.* 1980, Basu *et al.* 1981, Nysten 1986, Oberther & Saager 1986). However, the presence of mercury in gold from gold vein deposits in Japan had not been reported despite extensive electron-microprobe analyses (Shikazono 1981, 1985b, 1986).

In this paper, the first occurrence of mercurian gold from the Tsugu gold–antimony vein deposit in central Japan is reported. Mineralogical characteristics of gold deposits in which mercurian gold occurs are summarized, and depositional conditions in terms of aS_2 and temperature are estimated. We suggest that the mercury content of gold is a useful indicator of aS_2 and temperature.

General Features of the Tsugu Deposit

The Tsugu gold–antimony deposit is located in the central part of Honshu Island, Japan (Fig. 1). Geologically, the Tsugu deposit occurs in the Ryoke metamorphic terrane, adjacent to the outer zone of southwestern Japan. In this zone and in the Ryoke metamorphic terrane, gold deposits are rare, whereas there are many mercury–antimony deposits. On the other hand, in the Tertiary submarine volcanic region (Green tuff region) and Quaternary volcanic region, many epithermal vein-type deposits occur. Epithermal vein-type deposits are the main gold producers of Japan. Mines which have produced both antimony and gold are very rare. Therefore, the Tsugu deposit is an unusual type of gold deposit for Japan. Igneous activity related to the mineralization indicates that the age of mineralization was middle Miocene. This age is different from that of epithermal-type gold–silver mineralization (mostly late Miocene to Pleistocene; Shikazono & Tsunakawa 1982, Shikazono 1985a).

The previous studies on the Tsugu deposit by Tsuboya (1936), Tatsumi (1948) and our own work have demonstrated that: (1) opaque minerals include stibnite, jamesonite, cinnabar, gold, pyrite, pyrrhotite, arsenopyrite, marcasite, sphalerite, galena and chalcopyrite. (2) The ore minerals display a zonal distribution: gold and cinnabar are enriched in the upper parts of the veins, and sphalerite, galena and chalcopyrite are more abundant in the deeper parts. Pyrrhotite and arsenopyrite are distributed throughout. (3) From the mode of occurrences of opaque

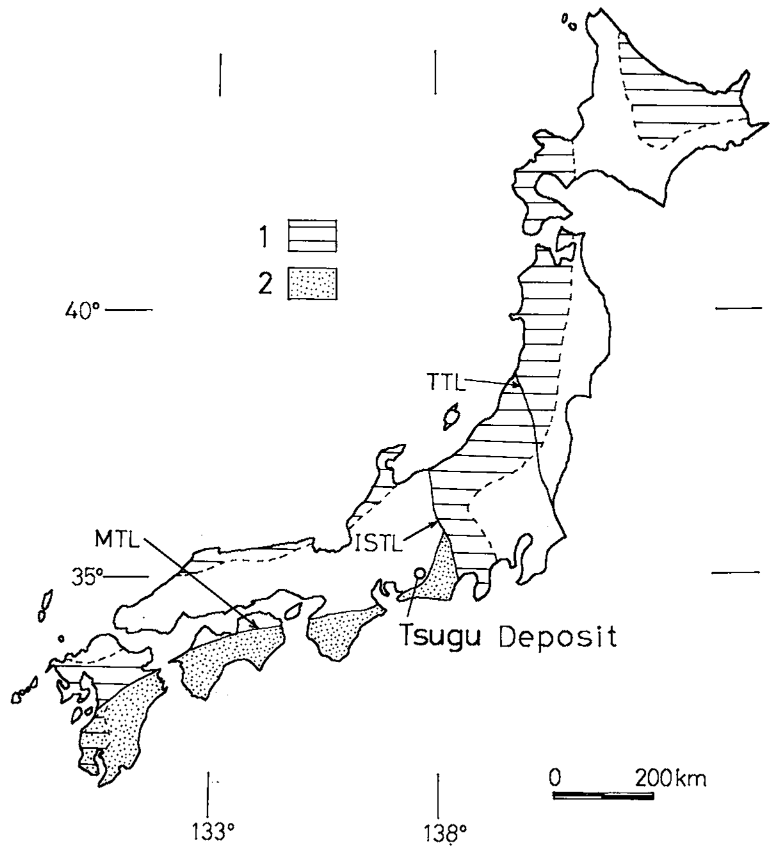

FIG. 1. Map showing location of the Tsugu gold-antimony deposit. 1: Green tuff region, 2: outer zone of southwestern Japan, TTL: Tanakura tectonic line, ISTL: Itoigawa-Shizuoka tectonic line, MTL: Median tectonic line.

TABLE 1. REPRESENTATIVE COMPOSITIONS (EPMA DATA) OF MERCURIAN GOLD FROM THE TSUGU GOLD-ANTIMONY DEPOSIT, CENTRAL JAPAN

	weight percent					atomic percent			
	Au	Ag	Cu	Hg	Total	Au	Ag	Cu	Hg
Sample I	79.95	10.91	0.04	8.53	99.43	73.78	18.38	0.11	7.72
	79.37	11.47	0.09	8.20	99.13	73.06	19.27	0.25	7.42
	81.62	10.31	0.06	7.77	99.76	75.40	17.40	0.16	7.04
	81.10	11.11	0.08	7.66	99.95	74.29	18.59	0.23	6.89
	81.52	10.73	0.05	7.16	99.46	75.28	18.08	0.15	6.49
	82.03	10.79	0.07	6.78	99.67	75.53	18.14	0.20	6.13
	82.63	10.22	0.05	6.35	99.25	76.73	17.33	0.15	5.80
	82.55	10.96	0.07	6.05	99.63	75.92	18.41	0.20	5.47
	83.70	10.47	0.06	5.27	99.50	77.38	17.67	0.16	4.79
	83.17	10.92	0.05	5.03	99.17	76.86	18.42	0.15	4.57
	84.42	10.84	0.05	4.69	100.00	77.46	18.17	0.14	4.23
	84.97	10.33	0.05	4.23	99.58	78.58	17.43	0.15	3.84
	84.97	10.65	0.08	3.90	99.60	78.32	17.92	0.24	3.52
	85.66	10.78	0.08	3.42	99.94	78.63	18.07	0.24	3.07
	86.29	10.34	0.05	3.18	99.86	79.56	17.40	0.15	2.89
	85.81	10.97	0.09	2.90	99.77	78.74	18.38	0.25	2.62
	86.36	10.65	0.07	2.22	99.30	79.81	17.97	0.20	2.02
	87.58	10.25	0.07	1.87	99.77	80.84	17.27	0.20	1.69
	88.19	10.62	0.08	0.32	99.21	81.55	17.92	0.24	0.29
av.	83.78	10.70	0.06	5.03	99.58	77.25	18.01	0.19	4.55
Sample II	86.61	5.98	0.01	7.39	99.99	82.63	10.41	0.04	6.92
	89.19	6.14	0.00	4.66	99.99	84.97	10.68	0.00	4.35
	90.14	6.24	0.00	3.43	99.81	85.93	10.85	0.00	3.21
	89.76	6.23	0.02	3.29	99.30	85.96	10.89	0.06	3.09
	90.21	6.37	0.03	2.85	99.46	86.14	11.10	0.09	2.67
	91.15	6.34	0.01	2.30	99.80	86.78	11.03	0.04	2.16
	91.34	6.20	0.01	1.84	99.39	87.39	10.84	0.04	2.02
	92.05	6.72	0.00	0.93	99.70	87.48	11.66	0.00	0.86
	92.02	6.71	0.01	0.55	99.29	87.78	11.67	0.00	0.51
	93.09	6.52	0.03	0.07	99.71	88.53	11.32	0.09	0.06
av.	90.56	6.35	0.01	2.73	99.64	86.36	11.05	0.04	2.59

Instrumentation: JEOL electron microprobe at the Ocean Research Institute, University of Tokyo, run at 25 kV. Standards: pure elements (for Au and Ag), natural chalcopyrite (Cu), and cinnabar (Hg). Lines: Au*Lα*, Ag*Lα*, Cu*Kα* and Hg*Lα*.

minerals it is considered that pyrrhotite and sphalerite were precipitated at an early stage; gold, pyrite, marcasite, stibnite and cinnabar were precipitated at a late stage, and arsenopyrite was precipitated throughout the mineralization period. (4) The main gangue minerals are sericite and quartz. Accessory minerals are tourmaline and apatite.

ANALYTICAL RESULTS

Samples from the University Museum, University of Tokyo, used in this study demonstrate that gold is associated with quartz, sericite, pyrite and arsenopyrite. The gold grains are irregular in form and range from 5 to 130 μm in size. Such fine-grained gold is scattered in quartz and is not in direct contact with pyrite and arsenopyrite.

Analyses of many gold grains were obtained with a JEOL electron microprobe at the Ocean Research Institute, University of Tokyo. Representative analytical results of mercurian gold from the Tsugu deposit are presented in Table 1. Mercury content of gold ranges from nil to 8.5 wt.%, and silver con-

TABLE 2. REPRESENTATIVE COMPOSITIONS (EPMA DATA) OF SPHALERITE FROM THE TSUGU GOLD-ANTIMONY DEPOSIT, CENTRAL JAPAN

weight percent							atomic ratio based on total atoms = 2					
Zn	Fe	Mn	Cd	Cu	S	Total	Zn	Fe	Mn	Cd	Cu	S
51.52	13.25	1.77	0.12	0.02	33.25	99.93	0.752	0.226	0.031	0.001	0.000	0.990
48.84	15.03	2.43	0.12	0.02	33.47	99.91	0.710	0.256	0.042	0.001	0.000	0.991
51.25	13.73	1.55	0.15	0.02	33.56	100.26	0.744	0.233	0.027	0.001	0.000	0.994
50.59	14.34	1.55	0.16	0.02	33.32	99.98	0.737	0.245	0.027	0.001	0.000	0.990
49.16	14.88	2.04	0.14	0.03	33.47	99.72	0.716	0.254	0.035	0.001	0.001	0.994
47.54	15.73	2.50	0.09	0.02	33.34	99.22	0.694	0.269	0.043	0.001	0.000	0.993
46.70	15.95	2.73	0.11	0.06	33.60	99.15	0.681	0.272	0.047	0.001	0.001	0.998
45.12	16.79	3.65	0.11	0.05	33.72	99.44	0.654	0.285	0.063	0.001	0.001	0.997
46.40	15.72	3.58	0.10	0.02	33.30	99.12	0.677	0.269	0.062	0.001	0.000	0.991
46.65	15.45	4.04	0.07	0.04	33.48	99.73	0.677	0.262	0.070	0.001	0.001	0.990

Instrumentation: JEOL electron microprobe at the Ocean Research Institute, University of Tokyo, run at 25 kV. Standards: synthetic $Zn_{0.6}Fe_{0.4}S$, MnS, CdS and natural chalcopyrite. Lines: $ZnK\alpha$, $FeK\alpha$, $MnK\alpha$, $CdL\alpha$, $SK\alpha$.

tent ranges from 6.0 to 11.5 wt.%. The chemical compositions of gold of the Tsugu deposit can be expressed as $Au_{73.1-89.6}Ag_{10.4-19.1}Hg_{0-7.7}$. Averaged chemical compositions of gold from the Tsugu deposit are plotted in terms of Au, Ag and Hg, together with data from the literature (Fig. 2). The Au/Ag ratios of gold from the Tsugu deposit are high compared with those from the other mercurian gold occurrences. Note that mercury content varies inversely with gold content (Fig. 3), implying that Hg substitutes for Au. This type of substitution has not been reported previously, although the substitution of Hg for Ag has been reported (Nysten 1986).

During the last decade numerous analyses for gold from gold deposits in Japan have been reported (*e.g.*, Shikazono 1981, 1985b, 1986). A frequency histogram of the silver content of gold from epithermal gold–silver vein-type deposits and the Tsugu deposit (Fig. 4) clearly indicates that the Au/Ag of gold from the Tsugu deposit is higher than that from epithermal vein-type deposits.

Factors Controlling Mercury Content of Gold

Gold and cinnabar occur in the same part of the vein, although coexistence of these minerals on a hand-specimen scale is not observed. It is thus assumed here that these minerals were in equilibrium. The following reaction can be used to determine which factors are important for controlling mercury content of gold in equilibrium with cinnabar:

$$(Hg) + \tfrac{1}{2}S_2 = HgS \qquad (1)$$

in which (Hg) denotes the Hg component in the gold.

From the equilibrium relation for reaction (1), we obtain:

$$N_{Hg} = 1/(K_1 a(S_2)^{1/2}\, \gamma_{Hg}) \qquad (2)$$

in which N_{Hg} is the atomic fraction of the Hg component, K_1 is the equilibrium constant of reaction (1), aS_2 is the activity of sulfur, and γ_{Hg} is the activity coefficient of the Hg component.

From (2) it is clear that the mercury content of

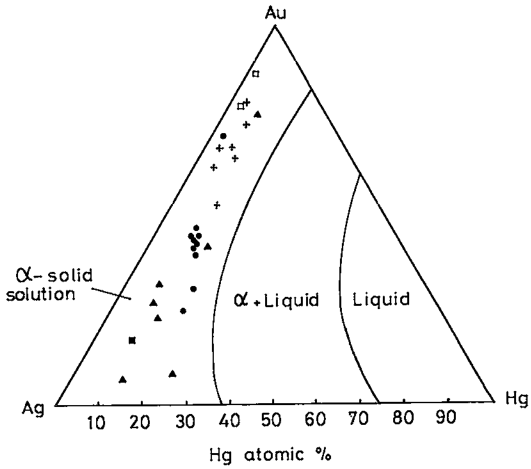

FIG. 2. Chemical composition of mercurian gold plotted on a Au–Ag–Hg triangular diagram. Data sources: Tsugu (open square), this study; Långsele (solid circle), Nysten (1986); Aitik (solid triangle), northern Sweden, Nysten (1986); Kazakhstan (cross), Naz'mova & Spiridonov (1979); Bajupura–Dariba (solid square), Basu *et al.* (1981). Phase boundaries (solid lines) at 450°C were drawn from Basu *et al.* (1981).

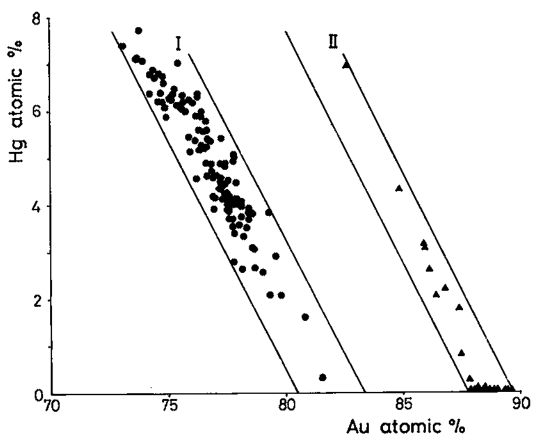

FIG. 3. Relationship between mercury and gold contents of mercurian gold from the Tsugu gold–antimony deposit. Solid triangles: sample II collected by the late Prof. T. Watanabe, 1950; dots: sample I collected by Mr. T. Nakano, 1941.

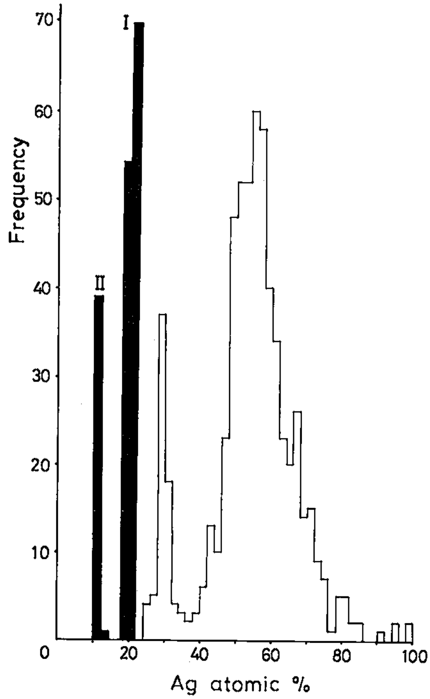

FIG. 4. Frequency (number of analyses) histogram for Ag (atomic %) of gold from the Tsugu deposit (solid) and epithermal gold–silver vein-type deposits in Japan (open). I: sample I; II: sample II. Data sources: Tsugu deposit, this study; epithermal gold–silver vein-type deposits in Japan (Shikazono 1981, 1986).

gold is related to aS_2 and K_1. Using the thermochemical data for reaction (1) by Barton & Skinner (1979), isoactivity lines for Hg in gold may be drawn on a log aS_2– temperature diagram (Fig. 5). At a given temperature, the activity of Hg in gold increases with a decrease in aS_2. Therefore, the aS_2 for the mercurian gold of the Tsugu deposit is inferred to be relatively low.

Ranges in Sulfur Activity and Temperature

The iron content of sphalerite is a useful indicator of aS_2 and temperature (Barton & Toulmin 1966). Microprobe analyses of sphalerite (Table 2; Fig. 6) indicate that sphalerite from the Tsugu deposit is markedly higher in iron than that from the epithermal gold–silver vein-type deposits in Japan.

Measurements of homogenization temperatures of fluid inclusions were obtained from quartz coexisting with sphalerite, pyrrhotite and chalcopyrite of the early stage of sulfide mineralization, and from quartz coexisting with gold, arsenopyrite, pyrite and sericite of the late stage of mineralization. Homogenization temperatures of fluid inclusions are 281–345°C for the early sulfide stage, and 275–295°C for the late stage of gold mineralization. These fluid inclusion data, stability fields of arsenopyrite, pyrite and pyrrhotite, and the iron content of sphalerite can define the possible ranges of aS_2 and temperature for the Tsugu mineralization (Fig. 7).

The ranges of aS_2 and temperature for epithermal gold–silver vein-type deposits in Japan have been clearly defined on the basis of the chemical compo-

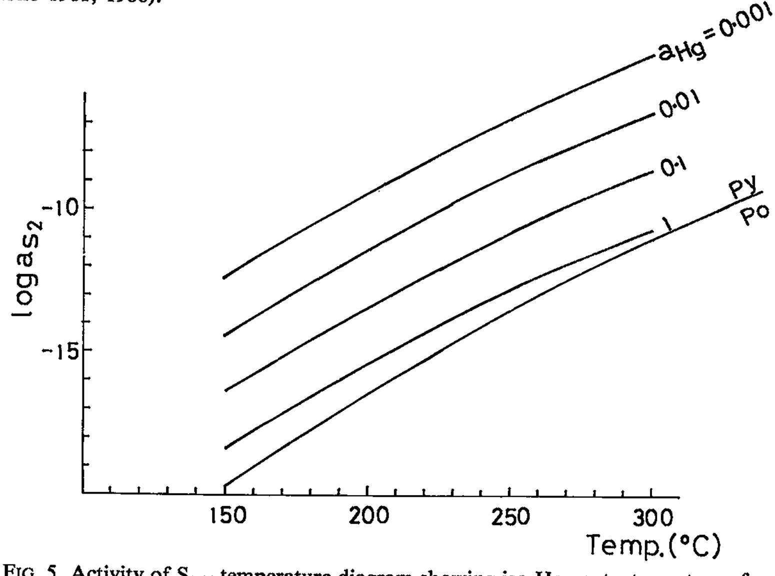

FIG. 5. Activity of S_2 – temperature diagram showing iso-Hg contents contours for gold. The calculations were carried out using thermochemical data of Craig & Barton (1973).

TABLE 3. OPAQUE MINERALS THAT COEXIST WITH MERCURIAN GOLD IN GOLD DEPOSITS

Name of deposit	Opaque minerals	References
Rajpura-Dariba, India	gl,cp,sulfosalts,cb,po, ow,py	Basu et al. (1981)
Langsele, Sweden	po,py,gl,cp,au,bo,ap,he	Nysten (1986)
Kazakhsten, USSR	st,py,sp,ja,ch,fr	Naz'mova & Spiridonov (1979)
Tsugu, Japan	po,py,ap,st,ja,cn,cp,gl, sp	this study

Mineral abbreviations: ap arsenopyrite, au aurostibite, bo bournonite, cb cubanite, ch chalcostibite, cn cinnabar, cp chalcopyrite, fr freibergite, gl galena, he hessite, ja jamesonite, ow owyheeite, po pyrrhotite, py pyrite, sp sphalerite.

sition of sphalerite and electrum, and homogenization temperatures of fluid inclusions (Shikazono 1985b). Values of aS_2 for the Tsugu deposit are lower than the typical ranges of values for the epithermal gold–silver vein-type deposits in Japan (Fig. 7). We conclude that such a low aS_2 is in accord with the high mercury content of the gold in the Tsugu deposit.

Mercurian gold has been reported from several gold deposits: Långsele, Aitik, Kazakhstan, and Bajpura-Dariba (Naz'mova & Spiridonov 1979, Basu *et al.* 1981, Nysten 1986). The nature of the opaque minerals coexisting with mercurian gold in these deposits is summarized in Table 3. The common opaque minerals are pyrrhotite, galena, sphalerite, stibnite, and jamesonite, and less common are cubanite, arsenopyrite, pyrite, and owyheeite. Pyrrhotite, cubanite, and arsenopyrite suggest relatively low aS_2 conditions, but the temperatures of formation of these deposits have not been estimated.

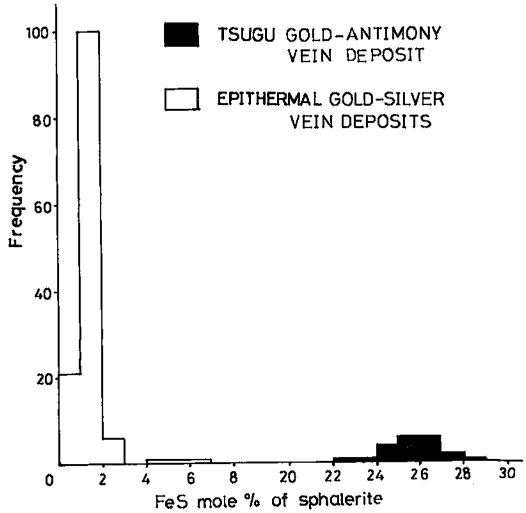

FIG. 6. Frequency (number of analyses) histogram for FeS mole % of sphalerite from the Tsugu deposit and epithermal gold–silver vein-type deposits in Japan. Data sources: Tsugu deposit, this study; epithermal gold–silver vein-type deposits in Japan, Shikazono (1977).

SUMMARY

Gold from the Tsugu gold–antimony vein deposit

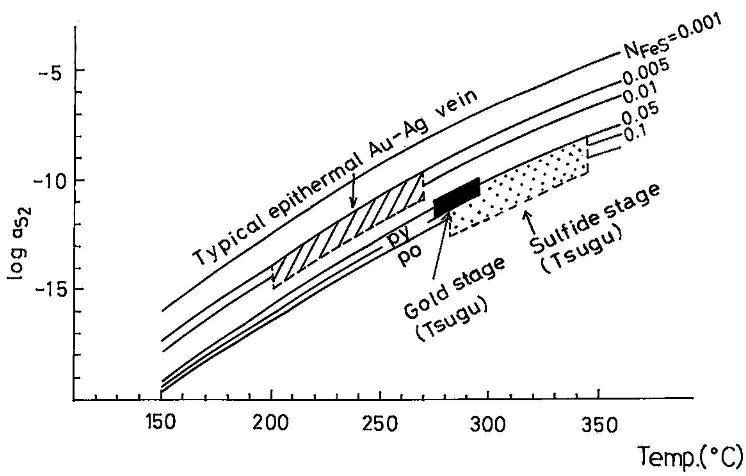

FIG. 7. Possible ranges of activity of S_2 and temperature for the Tsugu deposit (solid and dotted areas) and epithermal gold–silver vein-type deposits in Japan (shaded area). Iso-FeS lines for sphalerite and iso-Hg activity lines for gold were drawn based on Barton & Skinner (1979) and Craig & Barton (1973). Hatched area: typical epithermal gold–silver vein-type deposits in Japan. Dotted area: early stage of the Tsugu deposit. Solid area: gold stage of the Tsugu deposit. The upper and lower limits of aS_2 for the gold stage were determined by univariant sulfidation reactions 2 pyrite + arsenic = 2 arsenopyrite + S_2, and pyrite = pyrrhotite + $\frac{1}{2}S_2$, respectively. Mineral abbreviations: py pyrite, po pyrrhotite.

has the composition, $Au_{73.1-89.6}Ag_{10.4-19.1}Hg_{0-7.7}$. This is the first occurrence of mercurian gold in Japan. The iron content of sphalerite is high (22.6–28.5 mole % FeS). The occurrence of pyrrhotite and arsenopyrite, iron content of sphalerite, mercury content of gold, and homogenization temperatures of fluid inclusions indicate that the gold mineralization of the Tsugu deposit occurred under lower aS_2 and higher temperature than in the more common epithermal gold–silver vein-type deposits in Japan. Other gold deposits from which mercurian gold has been reported are also characterized by low aS_2.

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