Canadian Mineralogist
Vol. 29, pp. 207-215 (1991)

ROQUESITE-BEARING TIN ORES FROM THE OMODANI, AKENOBE, FUKOKU, AND IKUNO POLYMETALLIC VEIN-TYPE DEPOSITS IN THE INNER ZONE OF SOUTHWESTERN JAPAN

MASAAKI SHIMIZU
University Museum, University of Tokyo, Tokyo 113, Japan

AKIRA KATO
National Science Museum, Tokyo 169, Japan

ABSTRACT

Indium–tin mineralization is observed in the Omodani, Akenobe, Fukoku, and Ikuno deposits, which are Cu-dominant polymetallic veins of late Cretaceous to early Tertiary age in the Inner Zone of southwestern Japan. The indium–tin-bearing ores are commonly composed of roquesite ($CuInS_2$), stannoidite, sphalerite, tennantite-tetrahedrite, chalcopyrite and quartz, with local bornite, mawsonite, galena and arsenopyrite. The iron content of the sphalerite that coexists with roquesite, stannoidite and tennantite–tetrahedrite is very low. Temperatures of formation based on fluid-inclusion data on quartz from the Omodani and Akenobe deposits are in the range from 285° to 310°C. The $\delta^{34}S$ values of the roquesite-bearing tin ores are virtually constant (–0.8 to +0.3‰). Based on these descriptions, possible ranges in sulfur activity during formation of the roquesite-bearing tin ores are estimated to be approximately 10^{-8} to 10^{-6} atm., and the temperature was greater than 285°C.

Keywords: roquesite, polymetallic vein-type deposits, sulfur isotopes, activity of sulfur, temperature, Omodani, Akenobe, Fukoku, Ikuno, Japan.

SOMMAIRE

Une minéralisation à indium–étain a été documentée dans les gisements de Omodani, Akenobe, Fukoku et Ikuno, tous des systèmes de fissures polymétalliques à dominance de Cu, d'âge crétacé tardif à tertiaire précoce, situés dans la zone interne du Sud-Ouest du Japon. Le minerai à In–Sn contient couramment roquesite ($CuInS_2$), stannoïdite, sphalérite, tennantite–tétraédrite, chalcopyrite et quartz, ainsi que bornite, mawsonite, galène et arsénopyrite accessoires. La teneur en fer de la sphalérite en coexistence avec roquesite, stannoïdite et tennantite–tétraédrite est très faible. D'après les données sur les inclusions fluides du quartz des gisements d'Omodani et d'Akenobe, la température de formation du minerai aurait été entre 285 et 310°C. Les valeurs de $\delta^{34}S$ du minerai d'étain contenant de la roquesite sont à peu près constantes (–0.8 à +0.3‰). L'activité en soufre au cours de la formation du minerai aurait été d'environ 10^{-8} à 10^{-6} atm., et la température, supérieure à 285°C.

(Traduit par la Rédaction)

Mots-clés: roquesite, gisements polymétalliques en fissures, isotopes de soufre, activité du soufre, température, Omodani, Akenobe, Fukoku, Ikuno, Japon.

INTRODUCTION

Since the first report of the occurrence of roquesite in Japan, from the Eisei vein of the Akenobe deposit (Kato & Shinohara 1968), no additional roquesite has been described. This report documents new occurrences of roquesite in tin ores from the Omodani (Fukui Pref.), the Akenobe (Hyogo Pref.), the Fukoku (Kyoto Pref.), and the Ikuno deposits (Hyogo Pref.), in the Inner Zone of southwestern Japan. These deposits are subvolcanic-type (*e.g.*, Schneiderhöhn 1955) Cu-dominant polymetallic veins. The indium-bearing tin ores are characteristically composed of roquesite, stannoidite, sphalerite, members of the tennantite–tetrahedrite series, bornite and chalcopyrite. Stannite and kesterite have not been found. Information on possible activity of sulfur and temperature of formation of the roquesite-bearing ores can be estimated on the basis of electron-microprobe and thermochemical data, and fluid-inclusion data obtained on the coexisting quartz.

DESCRIPTION ON THE DEPOSITS AND ORE MINERALOGY

The Omodani, Akenobe, Fukoku, and Ikuno deposits are located in a former tectonically active zone called the Maizuru belt or the Hida marginal tectonic belt, between metamorphic and nonmetamorphic belts (Fig. 1). The Maizuru belt probably was a convergent plate margin during the late Paleozoic. Granitic batholiths, ultramafic rocks, and pelitic rocks with lignite exist in the vicinity of each deposit. The specimens are described below, and have been deposited at the University Museum of the University of Tokyo and National Science Museum. Some were collected by the present authors.

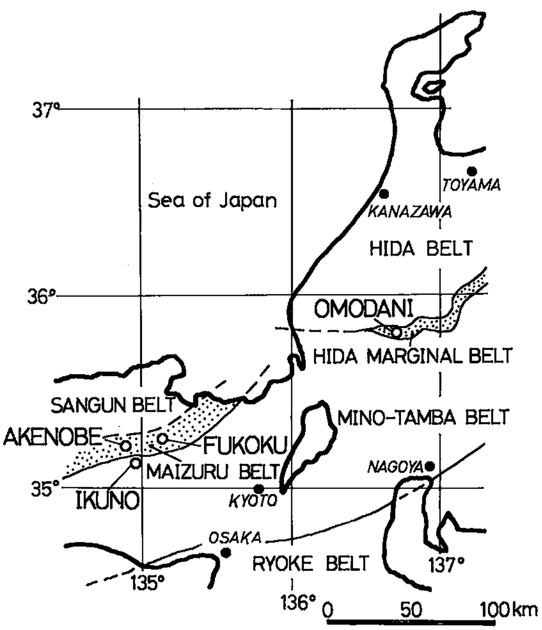

FIG. 1. Locations of the Omodani, Akenobe, Fukoku, and Ikuno deposits in the Inner Zone of southwest Japan.

Omodani Cu-Zn-Pb-Ag deposit

Omodani is located at Izumi-mura, Ono-gun, Fukui Prefecture, in the Hida marginal tectonic belt between the Hida metamorphic complex (Hida belt) and the nonmetamorphic rocks to the south (Mino–Tamba belt). The veins lie within the Omodani rhyolite (Kawai 1956), correlated with the Nohi rhyolite (Makiyama *et al.* 1975), which covers Mesozoic sedimentary rocks. The Omodani rhyolite is mainly composed of welded tuff (70–75 wt. % SiO_2), tuff breccia, tuff (71–75 wt.% SiO_2), and granite porphyry (*ca.* 77 wt.% of SiO_2). The K-feldspar from the welded tuff and granite porphyry gives K–Ar ages of 56.9 ± 2.8 Ma and 51.9 ± 2.6 Ma, respectively (Ministry of International Trade and Industry of Japan 1980).

Total production of the deposit from 1888 to 1966 was 4.4 × 10^5 tonnes of ore with average grades of 1-5 % Cu, 3-20 % Zn, 4-6 % Pb, and 85 grams per tonne of Ag. Ore specimens studied are largely composed of bornite, sphalerite, tennantite, stannoidite, chalcopyrite, and small amounts of löllingite, mawsonite, galena, and native silver (Table 1). Gangue minerals are quartz, chlorite, fluorite, K-feldspar of the adularia habit and calcite. Roquesite is associated with bornite, sphalerite, stannoidite, mawsonite, galena, and arsenopyrite (Fig. 2A).

Akenobe Cu-Zn-Sn-Ag deposit

The geology of the Akenobe mining district, Oya-cho, Yabu-gun, Hyogo Prefecture, has been studied by Kato (1920), Saigusa (1958), Muraoka & Ikeda (1968), Kojima & Asada (1973), Sato *et al.* (1977), and Shiozawa (1984). It is located in the Maizuru belt between the Sangun metamorphic belt to the north and the unmetamorphosed Mino–Tamba belt to the south. The products of mineralization are hosted in sedimentary and volcanic rocks of the Maizuru Group, of Permian age. K–Ar ages of dikes from the district indicate that the post-ore felsite (granophyre) is 57.8 ± 2.9 Ma and 52.6 ± 2.1 Ma, and the pre-ore rhyolite is 72.8 ± 2.9 Ma (Ishihara & Shibata 1972).

Total production from 1935 to 1986 is 1.7 × 10^7 tonnes of ore, and average grades are 1.1% Cu, 2.0% Zn, 0.4% Sn, and 20 g/t of Ag. Roquesite was discovered in the N 21 stope, -8th level of the Eisei vein of this deposit, where it occurs with chalcopyrite, quartz and siderite (Kato & Shinohara 1968). The roquesite-bearing ores used in this study were recently collected from the 14th level of the Chiemon No. 4 vein, and are principally composed of sphalerite, tetrahedrite, stannoidite, bornite, chalcopyrite, and lesser amounts of mawsonite, galena, ferberite, cas-

TABLE 1. MINERAL ASSEMBLAGE OBSERVED IN SPECIMENS STUDIED AND RANGE OF Fe^{2+}/Zn (ATOMIC)

Ore Deposit	Sp	Tn-Td	Bn	Rq	Sd	Cp	Others
Omodani	++	++	++	+	+	+	Lo,Ap,Mw,Gn,Ag
Fe^{2+}/Zn	0.005**	0.28-0.37			0.07-0.32		
max. wt.% In (*)	0.83 (16)	0.07 (19)	0.02 (62)	(8)	0.09 (10)	0.09 (13)	
Akenobe	++	++	+	+	++	+	Mw,Gn
Fe^{2+}/Zn	0.003-0.005	0.03-0.12			0.05-0.38		
max. wt.% In (*)	0.48 (9)	0.05 (19)	0.03 (9)	(10)	0.11 (11)	0.08 (8)	
Fukoku	++	+		+	++	+	Mw,Md
Fe^{2+}/Zn	0.004-0.015	0.88-1.25			0.45-0.72		
max. wt.% In (*)	0.08 (20)	0.98 (12)		(6)	0.30 (14)	0.21 (33)	
Ikuno	+	+		+	++	+	Ap,Gn
Fe^{2+}/Zn	0.016-0.036	1.65-2.00			0.97-1.49		
max. wt.% In (*)	1.61 (7)	0.09 (10)		(15)	0.13 (23)	0.31 (35)	

Abbreviations: Ag native silver, Ap arsenopyrite, Bn bornite, Cp chalcopyrite, Gn galena, Lo löllingite, Md matildite, Mw mawsonite, Rq roquesite, Sd stannoidite, Sp sphalerite, Tn-Td tennantite-tetrahedrite
++ common, + less common.
*) number of analysis
**) sphalerite poorest in Cu; there are many tiny chalcopyrite inclusions in sphalerite.

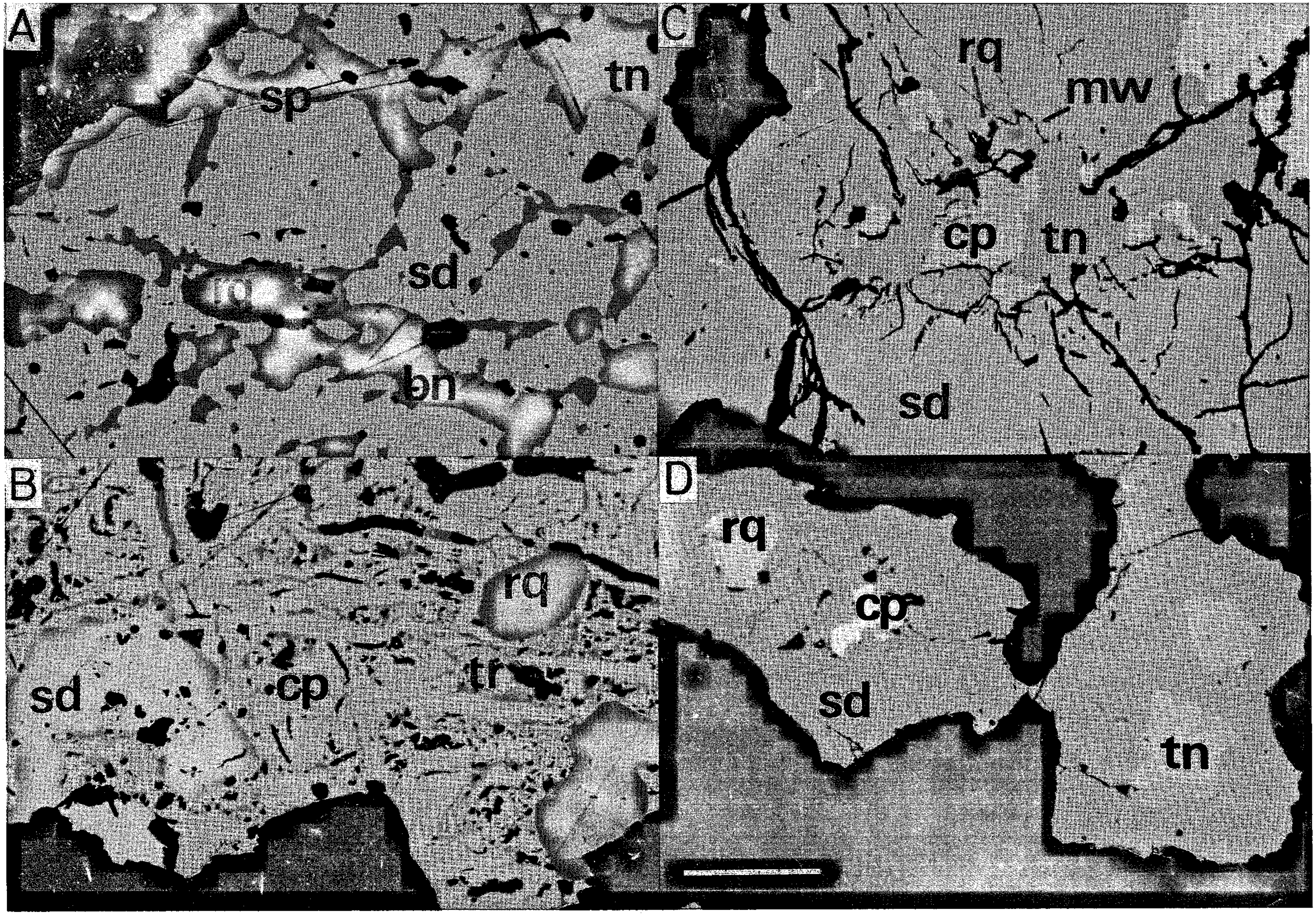

FIG. 2. Photomicrographs of roquesite-bearing ores from the Omodani (A), Akenobe (B), Fukoku (C), and Ikuno deposits (D). Abbreviations are the same as those in Table 1. The scale bar (in D) indicates 0.1 mm. Oil immersion.

siterite, scheelite, and an undetermined Ni-Co sulfide (Table 1, Fig. 2B). Gangue minerals are quartz, fluorite, and siderite.

Fukoku Cu-Zn-Ag deposit

Fukoku also is situated in the Maizuru belt, at Miyagai, Fukuchiyama City, Kyoto Prefecture. The mining district is geologically composed of sandstone with subordinate shales of the Triassic Yakuno Group. The Kumohara granite, of probable late Cretaceous age, and several masses of ultramafic rocks occur near the deposit.

The ore specimens studied consist of roquesite, sphalerite, stannoidite, tennantite, chalcopyrite, and small amounts of mawsonite, selenium-bearing matildite (up to 4.7 wt.% Se), and quartz (Table 1, Fig. 2C). Cosalite, boulangerite, and native bismuth have been reported in the deposit (Shimizu *et al.* 1966).

Ikuno Cu-Zn-Pb-Sn-Ag deposit

The Ikuno mining district, located at Ikuno-cho, Asako-gun, Hyogo Prefecture, 17 km southeast of the Akenobe deposit, occurs in Cretaceous rhyolitic and andesitic volcanic and pyroclastic rocks of the Ikuno Group. The geology and mineralization were described by Maruyama (1957). K–Ar ages from adularia from the deposit are 63.3 ± 1.9 Ma, 65.6 ± 2.0 Ma, and 70.5 ± 2.1 Ma (Ministry of International Trade and Industry of Japan, 1984).

Total production of the deposit during 1940–1973 was 6.9 × 10^6 tonnes of ore with average grades of 1.1 % Cu, 2.2 % Zn, 0.4 % Pb, 0.3 % Sn, 58.3 g/t Ag, and 0.3 g/t Au. The ore specimens used in this study are composed of roquesite, stannoidite, sphalerite, tennantite, chalcopyrite, and small amounts of arsenopyrite, galena and quartz (Table 1, Fig. 2D).

Chemical Composition of Coexisting Sulfide Minerals in In–Sn Ore

The chemical composition of coexisting minerals in the roquesite-bearing ore was determined using a JEOL 733II electron microprobe analyzer at the Geological Institute, Faculty of Science, University of Tokyo, using the methods of Shimizu *et al.* (1986).

Roquesite and chalcopyrite

Representative chemical compositions and atomic proportions of these minerals are given in Tables 2 and 3, respectively. All the grains examined are compositionally homogeneous. Slight substitution of Fe for In in roquesite is suggested, whereas that of In for Fe is very limited in the associated chalcopyrite.

Stannoidite

Stannoidite is essentially homogeneous in most cases, but the Fe^{2+}/Zn ratio varies significantly (Table 4), indicating the presence of material with the ideal formula $Cu_8(Zn,Fe)Fe_2^{3+}Sn_2S_{12}$, where Zn > Fe^{2+}, inferred following reference to the method of calculation of the Fe^{2+}/Zn ratio in this mineral by Shimizu & Shikazono (1987).

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITION OF ROQUESITE

Ore Dep.	WEIGHT PERCENT									ATOMIC PROPORTION (TOTAL ATOMS = 4)							
	Cu	Ag	Fe	Zn	Cd	Mn	In	S	Total	Cu	Ag	Fe	Zn	Cd	Mn	In	S
Omodani	26.44	0.03	0.34	0.30	0.03	0.01	46.21	26.00	99.36	1.014	0.001	0.015	0.011	0.001	0.000	0.981	1.976
	26.59	0.00	0.37	0.32	0.07	0.00	46.25	26.12	99.72	1.016	0.000	0.016	0.012	0.001	0.000	0.978	1.977
	26.54	0.00	0.48	0.25	0.04	0.02	45.82	26.03	99.18	1.018	0.000	0.021	0.009	0.001	0.001	0.972	1.978
Akenobe	26.28	0.11	0.30	0.34	0.06	0.01	46.19	26.49	99.78	1.000	0.002	0.013	0.013	0.001	0.000	0.973	1.997
	25.92	0.08	0.30	0.45	0.03	0.01	46.56	26.54	99.89	0.986	0.002	0.013	0.017	0.001	0.000	0.980	2.001
	26.17	0.01	0.41	0.40	0.06	0.01	45.74	26.25	99.05	1.003	0.000	0.018	0.015	0.001	0.000	0.970	1.993
*	24.9	-	1.8	0.1	-	0.2	46.3	25.7	99.0	0.96	-	0.08	0.00	-	0.00	0.99	1.96
Fukoku	26.21	0.13	0.46	0.10	0.04	0.02	46.83	26.67	100.46	0.992	0.003	0.020	0.004	0.001	0.001	0.981	2.000
	26.05	0.08	0.51	0.05	0.05	0.03	46.73	26.71	100.21	0.987	0.002	0.022	0.002	0.001	0.001	0.980	2.005
	26.57	0.15	0.86	0.06	0.06	0.03	46.23	26.09	100.05	1.012	0.003	0.037	0.002	0.001	0.001	0.974	1.969
Ikuno	26.30	0.09	0.46	0.31	0.05	0.04	45.86	26.17	99.28	1.007	0.002	0.020	0.011	0.001	0.002	0.972	1.985
	26.25	0.05	0.54	0.35	0.06	0.04	45.80	26.14	99.23	1.005	0.001	0.024	0.013	0.001	0.002	0.971	1.983
	26.35	0.33	0.90	0.19	0.05	0.02	45.96	26.39	100.19	0.999	0.007	0.039	0.007	0.001	0.001	0.964	1.982

*) Kato & Shinohara (1968)

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITION OF CHALCOPYRITE

Ore Dep.	WEIGHT PERCENT									ATOMIC PROPORTION (TOTAL ATOMS = 4)							
	Cu	Ag	Fe	Zn	Cd	MN	S	In	Total	Cu	Ag	Fe	Zn	Cd	Mn	S	In
Omodani	34.76	0.06	29.95	0.01	0.06	0.04	34.76	0.01	99.65	1.009	0.001	0.989	0.000	0.001	0.001	1.998	0.000
	34.79	0.03	29.82	0.03	0.03	0.03	34.96	0.06	99.75	1.007	0.001	0.982	0.001	0.001	0.001	2.005	0.001
	34.73	0.06	29.67	0.14	0.06	0.02	34.65	0.07	99.38	1.009	0.001	0.981	0.004	0.001	0.001	1.997	0.001
Akenobe	34.43	0.00	30.46	0.01	0.04	0.03	34.94	0.08	99.99	0.994	0.000	1.001	0.000	0.001	0.001	2.000	0.001
	34.69	0.07	30.49	0.04	0.05	0.03	34.93	0.01	100.31	1.000	0.001	1.000	0.001	0.001	0.001	1.995	0.000
	34.47	0.00	30.09	0.04	0.04	0.02	34.74	0.07	99.45	1.002	0.000	0.995	0.001	0.001	0.001	2.000	0.001
Fukoku	34.30	0.02	30.31	0.52	0.00	0.00	34.84	0.03	100.04	0.991	0.000	0.997	0.015	0.000	0.001	1.995	0.000
	34.38	0.00	30.24	0.08	0.03	0.03	34.89	0.04	99.69	0.996	0.000	0.996	0.002	0.000	0.001	2.002	0.000
	34.68	0.05	29.97	0.08	0.02	0.02	34.57	0.15	99.51	1.007	0.001	0.991	0.002	0.000	0.000	1.992	0.002
Ikuno	34.59	0.16	30.29	0.06	0.02	0.01	34.90	0.19	100.21	0.998	0.003	0.994	0.002	0.000	0.000	1.996	0.003
	34.50	0.02	30.06	0.03	0.06	0.02	34.68	0.19	99.57	1.002	0.000	0.993	0.001	0.001	0.001	1.997	0.003
	34.51	0.02	29.92	0.04	0.02	0.02	34.71	0.16	99.40	1.003	0.000	0.989	0.001	0.000	0.001	1.999	0.003

TABLE 4. REPRESENTATIVE CHEMICAL COMPOSITION OF STANNOIDITE

	WEIGHT PERCENT									
Ore Dep.	Cu	Ag	Fe	Zn	Cd	Mn	Sn	S	In	Total
Omodani	39.21	0.02	9.63	4.35	0.06	0.01	18.25	28.78	0.00	100.32
	39.16	0.01	9.50	4.23	0.09	0.02	18.51	28.79	0.09	100.40
	39.02	0.01	9.53	4.18	0.09	0.04	18.39	28.73	0.07	100.05
Akenobe	38.46	0.01	9.25	4.13	0.09	0.01	18.16	29.04	0.06	99.21
	38.84	0.06	9.27	4.43	0.06	0.01	18.13	29.41	0.00	100.20
	38.90	0.05	9.76	3.74	0.09	0.01	18.44	29.37	0.03	100.39
Fukoku	38.56	0.03	10.25	3.05	0.03	0.01	18.26	29.29	0.10	99.58
	38.81	0.06	10.25	2.91	0.01	0.06	18.56	29.58	0.17	100.41
	38.47	0.02	10.37	2.92	0.04	0.03	18.58	28.35	0.09	99.92
Ikuno	38.83	0.02	11.00	2.20	0.05	0.03	18.52	29.40	0.07	100.13
	38.77	0.00	11.13	2.10	0.03	0.02	18.44	29.46	0.00	99.95
	38.65	0.06	11.07	2.08	0.07	0.02	18.21	29.13	0.00	99.29

ATOMIC PROPORTIONS (TOTAL ATOMS = 25)									
Cu	Ag	Fe	Zn	Cd	Mn	Sn	S	In	Fe^{2+}/Zn
8.082	0.002	2.259	0.872	0.007	0.002	2.014	11.758	0.000	0.20
8.074	0.001	2.230	0.847	0.010	0.004	2.044	11.765	0.009	0.21
8.070	0.001	2.243	0.841	0.011	0.008	2.036	11.776	0.008	0.22
7.986	0.001	2.185	0.834	0.010	0.003	2.020	11.952	0.007	0.21
7.974	0.007	2.116	0.884	0.006	0.002	1.993	11.966	0.000	0.24
7.980	0.006	2.278	0.745	0.011	0.011	2.025	11.942	0.004	0.35
7.956	0.004	2.406	0.612	0.004	0.002	2.017	11.973	0.011	0.64
7.945	0.007	2.387	0.579	0.001	0.014	2.034	11.997	0.019	0.71
7.920	0.002	2.422	0.584	0.005	0.007	2.048	11.972	0.019	0.72
7.968	0.002	2.567	0.438	0.006	0.008	2.035	11.954	0.008	1.29
7.956	0.000	2.599	0.419	0.004	0.005	2.026	11.978	0.000	1.40
7.994	0.007	2.605	0.418	0.008	0.005	2.016	11.937	0.000	1.41

TABLE 5. REPRESENTATIVE CHEMICAL COMPOSITION OF TENNANTITE-TETRAHEDRITE-SERIES PHASE

	WEIGHT PERCENT												
Ore Dep.	Cu	Ag	Fe	Zn	Cd	Mn	Sn	As	Sb	Bi	S	Se	In	Total
Omodani	42.98	0.06	1.83	6.79	0.24	0.05	0.04	18.01	1.92	0.00	27.70	0.12	0.01	99.75
	43.47	0.06	1.90	6.74	0.25	0.03	0.00	18.46	1.36	0.00	28.03	0.02	0.04	100.35
	43.16	0.06	2.04	6.75	0.19	0.03	0.01	17.69	2.45	0.00	27.82	0.07	0.04	100.30
Akenobe	39.09	0.33	0.20	8.16	0.07	0.02	0.10	7.07	18.48	0.00	25.71	0.08	0.00	99.30
	39.65	0.25	0.42	7.97	0.09	0.01	0.03	8.11	17.06	0.00	25.78	0.07	0.00	99.44
	39.06	0.36	0.39	7.99	0.10	0.02	0.06	5.52	21.31	0.00	25.56	0.07	0.01	100.45
Fukoku	34.86	7.46	3.22	3.52	0.15	0.04	0.03	9.50	9.91	4.89	24.95	0.02	0.78	99.33
	35.43	6.66	3.25	3.41	0.12	0.06	0.04	10.01	9.00	5.58	25.18	0.04	0.72	99.50
	32.58	9.51	3.30	3.10	0.16	0.09	0.03	7.37	11.33	6.97	24.74	0.00	0.82	100.00
Ikuno	39.91	1.16	4.51	3.20	0.06	0.01	0.00	12.73	10.46	0.98	26.82	0.03	0.05	99.92
	41.23	0.82	4.66	3.12	0.05	0.01	0.03	13.70	8.80	0.00	26.78	0.06	0.07	99.31
	40.06	1.16	4.77	2.78	0.06	0.03	0.00	13.91	7.71	2.37	26.79	0.03	0.08	99.75

ATOMIC PROPORTIONS (TOTAL ATOMS = 29)												
Cu	Ag	Fe	Zn	Cd	Mn	Sn	As	Sb	Bi	S	Se	In	Fe/Zn
10.119	0.008	0.491	1.554	0.032	0.013	0.005	3.595	0.237	0.000	12.923	0.022	0.002	0.32
10.138	0.008	0.505	1.527	0.033	0.007	0.000	3.651	0.166	0.000	12.957	0.004	0.005	0.33
10.117	0.009	0.544	1.537	0.026	0.007	0.001	3.517	0.300	0.000	12.926	0.014	0.005	0.35
9.925	0.049	0.059	2.014	0.011	0.005	0.014	1.522	2.449	0.000	12.936	0.015	0.000	0.03
9.996	0.036	0.120	1.952	0.012	0.003	0.005	1.735	2.244	0.000	12.881	0.014	0.000	0.06
9.927	0.054	0.114	1.973	0.015	0.006	0.009	1.191	2.826	0.000	12.871	0.014	0.002	0.06
9.098	1.147	0.957	0.894	0.023	0.012	0.004	2.103	1.350	0.388	12.908	0.003	0.113	1.07
9.196	1.018	0.959	0.859	0.018	0.018	0.006	2.204	1.219	0.440	12.950	0.009	0.103	1.12
8.673	1.491	1.000	0.802	0.024	0.029	0.004	1.664	1.575	0.564	13.053	0.001	0.121	1.25
9.757	0.167	1.254	0.760	0.008	0.003	0.000	2.640	1.334	0.073	12.991	0.006	0.007	1.65
10.009	0.117	1.287	0.736	0.007	0.003	0.003	2.820	1.115	0.000	12.883	0.010	0.009	1.75
9.793	0.167	1.327	0.661	0.008	0.009	0.000	2.884	0.983	0.176	12.976	0.006	0.011	2.00

Tennantite–tetrahedrite

The grains examined are generally heterogeneous, although the general formula $(Cu,Ag)_{10}(Fe,Zn)_2(As,Sb,Bi,In)_4S_{13}$ is applicable to all of them (Table 5). Tennantite from the Fukoku deposit shows the highest silver, bismuth and indium contents of the materials studied. The total of As + Sb + Bi + In is very close to 4, which suggests that the In^{3+}, though low in content, can lodge in a trigonal prism.

Sphalerite

Compositional homogeneity is confirmed in the

TABLE 6. REPRESENTATIVE CHEMICAL COMPOSITION OF SPHALERITE

	WEIGHT PERCENT								ATOMIC PROPORTIONS (TOTAL ATOMS = 2)							
Ore Dep.	Cu	Fe	Zn	Cd	Mn	S	In	Total	Cu	Fe	Zn	Cd	Mn	S	In	Fe/Zn
Omodani	0.82	0.39	64.45	0.66	0.02	32.14	0.72	99.21	0.013	0.007	0.975	0.006	0.000	0.991	0.006	0.007
	0.84	0.44	65.22	0.66	0.01	32.36	0.78	100.31	0.013	0.008	0.977	0.005	0.000	0.989	0.007	0.008
	0.69	0.65	65.41	0.67	0.03	32.45	0.21	100.11	0.011	0.011	0.979	0.006	0.001	0.991	0.002	0.011
Akenobe	0.30	0.19	65.23	0.58	0.03	33.08	0.30	99.74	0.005	0.003	0.975	0.005	0.001	1.008	0.003	0.004
	0.38	0.29	65.63	0.67	0.03	33.04	0.36	100.41	0.006	0.005	0.977	0.006	0.001	1.002	0.003	0.005
	0.39	0.30	64.74	0.59	0.03	32.71	0.48	99.24	0.006	0.005	0.974	0.005	0.001	1.004	0.004	0.005
Fukoku	0.47	0.44	66.40	0.20	0.14	32.62	0.08	100.35	0.007	0.007	0.989	0.001	0.002	0.991	0.001	0.007
	0.46	0.44	65.93	0.25	0.09	33.01	0.02	100.20	0.007	0.008	0.979	0.002	0.002	1.000	0.000	0.008
	1.28	0.87	64.78	0.25	0.07	32.37	0.05	99.68	0.020	0.015	0.971	0.002	0.001	0.990	0.000	0.015
Ikuno	0.48	0.91	65.58	0.41	0.05	32.49	0.04	99.96	0.007	0.016	0.981	0.004	0.001	0.991	0.000	0.016
	0.57	0.97	65.01	0.49	0.04	32.62	0.05	99.75	0.009	0.017	0.973	0.004	0.001	0.996	0.000	0.017
	0.49	1.05	65.17	0.51	0.05	32.70	0.04	100.01	0.008	0.018	0.973	0.004	0.001	0.996	0.000	0.018

TABLE 7. REPRESENTATIVE CHEMICAL COMPOSITIONS OF BORNITE

	WEIGHT PERCENT						ATOMIC PROPORTIONS (TOTAL ATOMS = 10)				
Ore Dep.	Cu	Ag	Fe	S	Se	Total	Cu	Ag	Fe	S	Se
Omodani	45.86	20.19	10.18	23.41	0.06	99.70	3.961	1.027	1.000	4.007	0.004
	47.42	18.46	10.25	23.57	0.01	99.71	4.064	0.932	0.999	4.004	0.001
	49.38	16.04	10.30	23.69	0.06	99.47	4.201	0.804	0.997	3.993	0.004
Akenobe	62.01	0.27	11.24	25.47	0.03	99.01	4.936	0.013	1.018	4.018	0.002
	62.54	0.27	11.62	25.59	0.12	100.15	4.931	0.013	1.042	3.998	0.008
	62.23	0.27	11.39	25.45	0.13	99.48	4.939	0.013	1.028	4.002	0.008

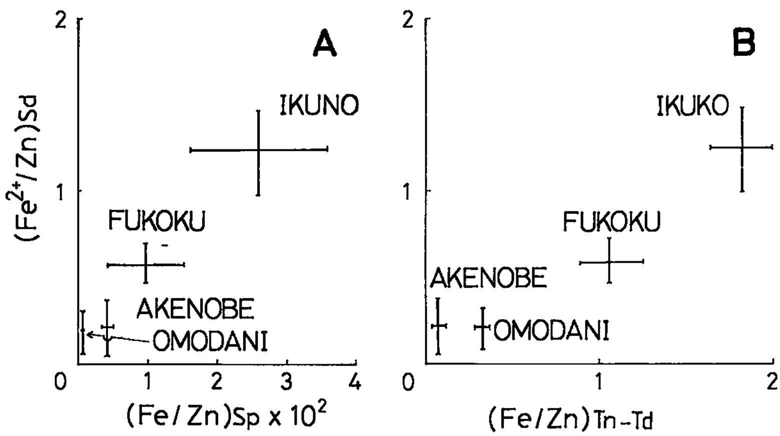

FIG. 3. Atomic Fe^{2+}/Zn ratio of sphalerite (A) and of tennantite–tetrahedrite (B) as a function of Fe^{2+}/Zn in stannoidite. Symbols: Sp sphalerite, Sd stannoidite, Tn–Td tennantite–tetrahedrite.

grains examined. As shown in Table 6, the iron contents are very low in all of them. Note that the iron content of sphalerite associated with stannite is quite high (Shimizu & Shikazono 1985, 1987).

Bornite

Bornite is common in the roquesite-bearing ores from the Omodani and Akenobe deposits (Table 1), although it is not found in the ores studied by Kato & Shinohara (1968). The material from the latter deposit fits the ideal formula, but that from the former has an unusually high Ag content, giving an ideal formula $AgCu_4FeS_4$ (Table 7). It is accompanied by native silver. It is tentatively handled as bornite here in favor of its optical similarity to ordinary bornite, but it may be a discrete species from bornite, if it is found to be compositionally discontinuous with bornite, or structurally different from it.

DISCUSSION

Mineral assemblages of the specimens studied and ranges of atomic Fe^{2+}/Zn ratios are summarized in Table 1. There is a wide range of Fe^{2+}-for-Zn substitution in coexisting stannoidite, sphalerite, and tennantite–tetrahedrite (Figs. 3A, B). The Fe^{2+}/Zn ratio of stannoidite is positively correlated with that of sphalerite and tennantite–tetrahedrite. No experimental data bearing on the influence of temperature on iron and zinc partitioning among these minerals have been obtained yet, but could be of use

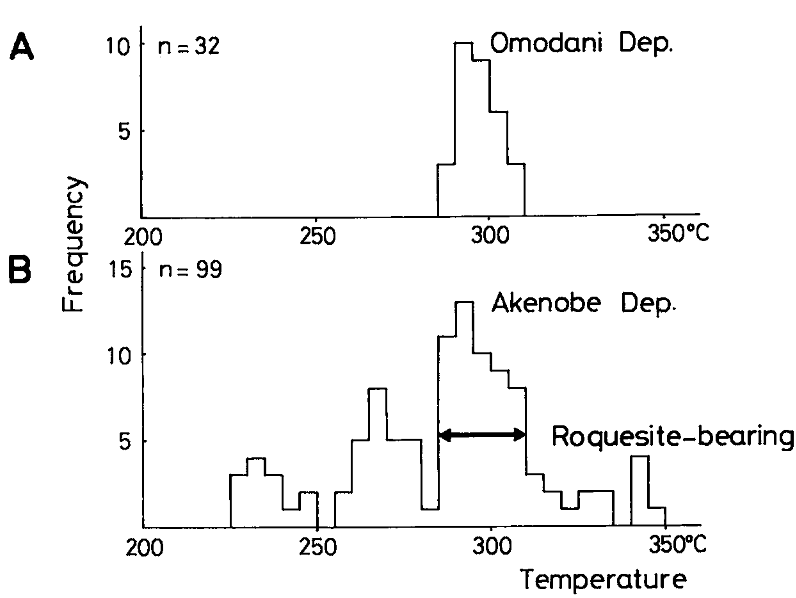

FIG. 4. Histograms of filling temperatures of fluid inclusions in quartz associated with roquesite from the Omodani (A) and Chiemon No. 4 vein, Akenobe deposits (B).

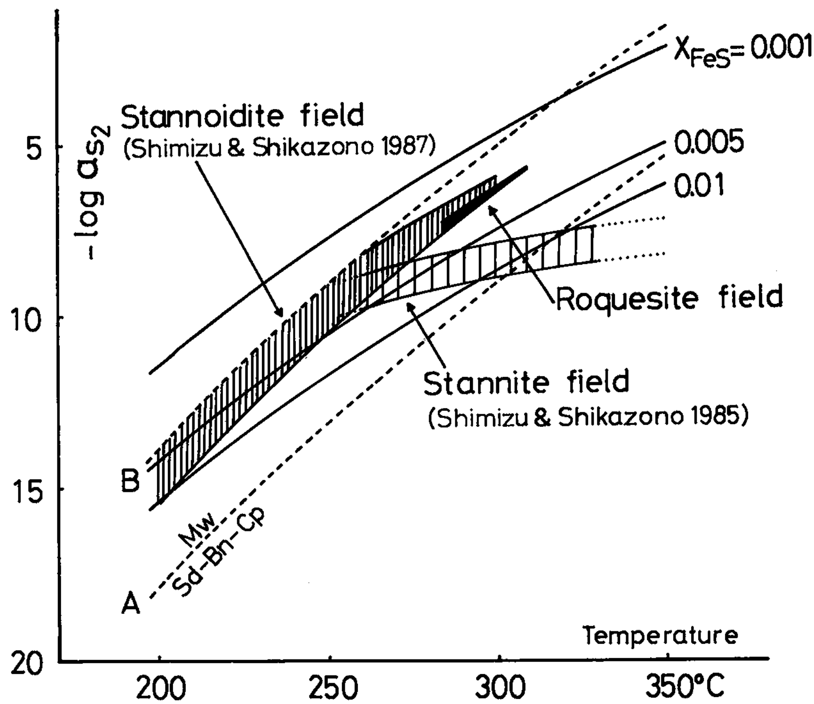

FIG. 5. Temperature – log $a(S_2)$ diagram for roquesite-bearing ores. Curves A and B correspond to $a(S_2)$ – temperature relationships for the assemblage of stannoidite – chalcopyrite – bornite – mawsonite – S_2(gas) for a(Fe) = 1 and a(Fe) = 0.1 a(Fe) is defined as the activity of the $Cu_8Fe_2^{3+}Fe^{2+}Sn_2S_{12}$ component in the stannoidite solid solution. Symbols: Mw mawsonite, Sd stannoidite, Bn bornite, Cp chalcopyrite.

TABLE 8. SULFUR ISOTOPIC COMPOSITIONS OF ROQUESITE-BEARING BULK ORES

Ore Deposit	$\delta^{34}S$ (per mil)
Omodani	-0.8
Akenobe	-0.9 (average, n=32)*
Fukoku	-0.5
Ikuno	+0.3

*) Shiozawa's unpublished data

as a geothermometer. The comparison of estimated temperatures of formation of roquesite-bearing ores from the geological standpoint enables the grouping of four deposits into two pairs, Ikuno–Fukoku and Akenobe–Omodani; the estimated temperature of formation of the former is higher than the latter.

The indium contents of sphalerite, tennantite–tetrahedrite, stannoidite, and chalcopyrite from the Ikuno and Fukoku deposits generally tend to be higher than those from the Omodani and Akenobe deposits (Table 1). The high indium contents of these minerals are probably favored by higher temperatures of formation, provided that the degree of concentration of indium in all the deposits was approximately equal. Filling temperatures of fluid inclusions in the coexisting quartz from the Omodani and Akenobe deposits give a temperature ranging from 285 to 310°C (Fig. 4).

Shimizu & Shikazono (1985, 1987) estimated the probable physicochemical environment of formation of stannoidite- and stannite-bearing tin ores in Japan (Fig. 5). In this figure, the log $a(S_2)$ - temperature field of the roquesite-bearing tin ores from the Omodani and Akenobe deposits can be estimated to be approximately 10^{-8} atm. at 285°C to 10^{-6} atm. at 310°C, based on the thermochemical data on the mineral assemblage, FeS contents of sphalerite, and fluid-inclusion data. The approach referred to here is the same as that used by Shimizu & Shikazono (1987). The field of the roquesite-bearing ores falls within that of the stannoidite-bearing ores.

The isotopic compositions of sulfur in the Akenobe and Ikuno deposits have been reported by Yamamoto (1974), Sasaki & Ishihara (1980), and Ishihara *et al.* (1981), but those of the roquesite-bearing ores are reported here for the first time. It is worthy of note that preliminary sulfur isotope study on the roquesite-bearing ores indicates a very narrow range of $\delta^{34}S$ values, from -0.9 to +0.3‰ (Table 8). This could indicate a magmatic origin, and suggests either that the physicochemical environment of the deposits did not change during the indium mineralization, or that the metal/sulfur ratios in the ore fluids responsible for the indium mineralization were too small to change the isotopic compositions in the fluids significantly.

Roquesite also occurs in the Ulsan Fe–W–As skarn-type deposit in the Republic of Korea (Imai & Choi 1984). The deposit is located about 80 km NNE of Busan, and is related to the emplacement of the Bulgugsa granite. We believe that the indium mineralization there is of the same age as that in Japan, on the other side of the Sea of Japan.

ACKNOWLEDGEMENTS

We are grateful to Professor Akio Tsusue of Kumamoto University for the organization of this project, Mr. Takuya Shiozawa, whose previous work stimulated this study, and Professor R.F. Martin, Drs. Chris Stanley, M. Gunnesch and anonymous referees for their comments, which served to improve the manuscript. This work was partly supported by Grant-in-Aid for Scientific Research (Nos. 623030 and 01740471) from the Ministry of Education, Science, and Culture of Japan, and by the Fujiwara Foundation of Natural History.

REFERENCES

IMAI, N. & CHOI, S. (1984): The first Korean occurrence of roquesite. *Mineral. J.* **12**, 162-172.

ISHIHARA, S., SATO, K. & TSUKIMURA, K. (1981): Some aspects on the tin–polymetallic veins in the Akenobe mine area, southwest Japan. *Mining Geol.* **31**, 147-156 (in Japanese with English abstr.).

______ & SHIBATA, K. (1972): Re-examination of the metallogenic epoch of the Ikuno–Akenobe province in Japan. *Mining Geol.* **22**, 67-73.

KATO, A. & SHINOHARA, K. (1968): The occurrence of roquesite from the Akenobe mine, Hyogo Prefecture, Japan. *Mineral. J.* **5**, 276-284.

KATO, T. (1920): A contribution to the knowledge of the cassiterite veins of pneumato–hydatogenetic or hydrothermal origin. A study of the copper–tin veins of the Akenobe district in the province of Tajima, Japan. *J. Coll. Sci., Tokyo Imperial Univ.* **43**, Art. 5, 1-60.

KAWAI, M. (1956): On the late Mesozoic movement in the western part of the Hida plateau. I. Geological study in the southern mountainland of Arashimadake, Fukui Prefecture. *J. Geol. Soc. Japan* **62**, 559-573 (in Japanese).

KOJIMA, Y. & ASADA, I. (1973): The Akenobe ore deposits: their geologic structure and fracture patterns. *Mining Geol.* **23**, 137-151 (in Japanese with English abstr.).

MAKIYAMA, J., MORISHITA, A. & ITOIGAWA, J. (1975): *Regional Geology of Japan, Chubu-chihou* (revised edition). Asakura Shoten, Tokyo (in Japanese).

MARURUMA, S. (1957): The relations between ore veins and igneous intrusives. *Mining Geol.* **7**, 281-284 (in Japanese with English abstr.).

MINISTRY OF INTERNATIONAL TRADE AND INDUSTRY OF JAPAN (1980): *Report on Regional Geological Survey in the Hida District. Part I* (in Japanese).

MINISTRY OF INTERNATIONAL TRADE AND INDUSTRY OF JAPAN (1984): *Report on Regional Geological Survey in the Bantan District* (in Japanese).

MURAOKA, N. & IKEDA, S. (1968): Recent geologic exploration and development of the Akenobe mine. *Mining Geol.* **18**, 79-91 (in Japanese with English abstr.).

SAIGUSA, M. (1958): Geology and mineralization of the Akenobe mine, Hyogo Prefecture, Japan. *Mining Geol.* **8**, 218-238 (in Japanese with English abstr.).

SASAKI, A. & ISHIHARA, S. (1980): Sulphur isotope characteristics of granitoids and related mineral deposits in Japan. *Proc. 5th Quart. IAGOD Symp.* **1**, 325-335.

SATO, N., ASADA, I. & KASAMATSU, S. (1977): Geological structure and ore deposits of the Akenobe mine, Hyogo Prefecture, Japan. *Mining Geol.* **27**, 245-262 (in Japanese with English abstr.).

SCHNEIDERHÖHN, H. (1955): *Erzlagerstätten, Kurzvorlesung zur Einfuhrung und zur Wiederholung.* Gustav Fischer Verlag, Stuttgart, Germany.

SHIMIZU, M., KATO, A. & SHIOZAWA, T. (1986): Sakuraiite: chemical composition and extent of (Zn,Fe)In-for-CuSn substitution. *Can. Mineral.* **24**, 405-409.

______ & SHIKAZONO, N. (1985): Iron and zinc partitioning between coexisting stannite and sphalerite: a possible indicator of temperature and sulfur fugacity. *Miner. Deposita* **20**, 314-320.

______ & ______ (1987): Stannoidite-bearing tin ore: mineralogy, texture and physicochemical environment of formation. *Can. Mineral.* **25**, 229-236.

SHIMIZU, T., KATO, A. & MATSUO, G. (1966): Minerals from the Fukoku mine, Kyoto Prefecture, with special reference to cosalite, boulangerite, hexastannite and some secondary arsenic minerals. *Chigaku Kenkyu* **17**, 201-209 (in Japanese with English abstr.).

SHIOZAWA, T. (1984): *Mineralization of the Akenobe Tin - Polymetallic Deposits, Hyogo Prefecture, Central Japan.* M.S. thesis, Univ. Tokyo, Tokyo, Japan.

YAMAMOTO, M. (1974): Distribution of sulfur isotopes in the Ryusei vein of the Akenobe mine, Hyogo Prefecture, Japan. *Geochem. J.* **8**, 75-76.

Received April 4, 1990, revised manuscript accepted October 12, 1990.