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Indium and other trace elements in volcanogenic massive sulfide ores from the Kuroko, Besshi and other types in Japan

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Abstract: By analyzing trace elements of massive sulfide ores from rhyodacite-related Kuroko deposits (35 samples) and Yanahara pyrite deposits (10 samples), andesite-related Taro deposits (4 samples), and basalt-related non-metamorphosed Shimokawa, Tsuchikura and Makimine deposits (6 samples) and metamorphosed Besshi-type deposits (25 samples), potentiality of indium resource was evaluated. In the major Hokuroku Basin for Kuroko deposits, those of the eastern side, such as the Kosaka-Uchinotai (avg. 26 ppm In), the Hanawa and Furutobe are relatively rich in indium, and the indium contents are correlated with not zinc but copper content. This indium may be contained in tetrahedrite-group minerals of the Kuroko horizon in a narrow sense. Based upon an average content of indium in the Kosaka-Uchinotai deposits and In-production in the 1970's, a recoverable amount in the Kosaka deposits is estimated to be 50 tons In, which are smaller two orders of magnitude than the world-class In-bearing massive sulfides deposits. On the contrary, In-anomalies are observed in the zinc concentrates of the Sazare and Shirataki mines, implying that indium in the Besshi-type deposits are mainly contained in sphalerites. Zinc grades of the crude ores of the Besshi-type deposits are low as 0.n% level. A large potentiality cannot be expected on the Besshi-type ore deposits. The high In-values up to 207 ppm were obtained on the Cu-pyrrhotite-rich ores at Yanahara hosted in the Permian rhyolites. Sporadic In-anomalies, up to 167 ppm, have also been observed in ores from the thermally metamorphosed lower levels of the Besshi deposits. These are considered due to later hydrothermal In-enrichment along fractures by Miocene intrusion of the ilmenite series-granitoids of the Outer Zone of SW Japan.

Keywords: Kuroko, Besshi type, massive sulfides, indium, resource evaluation

1. Introduction

Significance of indium in the modern high-technology industry has been increased drastically in the past years, because of strong demand of liquid crystals for electronic and communication apparatus. Major primary source for indium of the world is by-products of (1) massive sulfide deposits (Ishihara, 2005) and (2) granite-related vein, skarn and dissemination, where trace amounts of indium are extracted from zinc concentrates of In-Sn-bearing basemetal ores (Ishihara *et al.*, 2006a). The major massive sulfide examples include Archean Kid Creek deposit (<50 ppm, 3,400 tons In) in Canada, Proterozoic Sallivan deposit (50 ppm, 8,000 tons In) in Canada, Ordovician Brunswick deposit (50 ppm, 8,000 tons In) in Canada, Devonian Gaiskoye deposit (24 ppm In, 7,200 tons) in the Ural, Russia, and Neves Corvo deposit (>18 ppm, 7,000 tons In) in Portugal (Schwarz-S and Herzig, 2002). About the granite-related deposits, 6,000 tons In are estimated in the Northeast Japan Arc including the Toyoha vein-type deposits, while 3,000 tons In may be possible in veins of the Southwest Japan Arc (Ishihara *et al.*, 2006a). Larger tonnage of indium may be concentrated in the Southern China including Dachang (6,000 tons In), Dulong (4,000 tons In) and other some hundreds tons-class deposits, and middle size deposits are also known in the Inner Mongolia, China (Zhang *et al.*, 2006; Ishihara *et al.*, 2006b).

Trace amounts of indium and other rare metal contents were first examined in Japan by Takahashi (1963) at Ashio copper deposits using spectrographic method with the sensitivity of 10 ppm In. Systematic analyses were made later by the MMAJ (Metal Mining Agency of Japan) projects in the early 1990s. Kuroko (black ore) deposits were studied mostly in the 1990 - 91 fiscal year and partly in the 1992 fiscal year. The analytical methods applied to the In-analyses were AAS (atomic absorption spectrometry) for the 1990 project, but ICP (inductively coupled plasma mass-spectrometry) for the 1991 and later years. The results indicated almost no anomalies discovered in the Japanese mas

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sive sulfide ores, except for few Kuroko-type ores from Fukazawa mine (zinc concentrates, 38 ppm In), Takara mine (10 ppm In), Kunitomi and Minami-Shiraoi mines (6 and 4 ppm In) (MITI, 1992, 1993).

Analytical methods for indium and other trace elements have been improved since that period. Here we re-examined the trace elements using ICP/MS analytical instrument with "a total digestion" employing HF, $HClO_4$, HNO_3 and HCl at the Actlabs, Ltd. The samples used were from our own collection and ores stored in the Geological Museum of the Geological Survey of Japan, AIST, and powdered at the crushing laboratory by conventional agate mortar powdering.

From Miocene Kuroko deposits of the Northeast Japan, 35 ore samples were selected from 11 mines. From the pre-Cretaceous massive sulfide deposits, 4 samples from Cretaceous Taro deposits and 10 samples from the Permian Yanahara deposits, which are associated with andesitic and felsic volcanic rocks, respectively, whereas the rest of 31 samples are from non-metamorphosed (Shimokawa and Tsuchikura, 5 samples) and metamorphosed Besshi-type massive sulfides (26 samples from 11 mines), all of which are associated with basaltic rocks. The sample localities are given in Fig. 1 and also listed in Table 1. The analytical results are given in Table 2.

2. Indium of Miocene Kuroko deposits

The Japanese Kuroko deposits occur mostly in the back-arc basins of the Northeast Japan arc, and hosted in submarine pyroclastic rocks called "Green Tuff". The major ore deposits, such as Kosaka and Shakanai-Matsumine, all occur in the "Hokuroku Basin" of the northern Akita (Fig. 1). These ore deposits can be grouped into the eastern group including Kosaka-Motoyama, -Uchinotai, -Uwamuki; Ainai, Furutobe and Hanawa, and the western group of Shakanai, Matsumine and Hanaoka, and the central group of Fukazawa and Ezuri.

Indium was first studied for the dressing budgetary at the Kosaka-Uchinotai dressing plant (Maeshiro, 1978 in Tatsumi, 1987). From the 2.5 ppm In-bearing Kuroko of the Uchinotai ore deposits, Maeshiro (1978) obtained 14.4 ppm In in both the copper and zinc concentrates, 2.5 ppm in the lead concentrates, 0.6 ppm in the pyrite concentrates, and 0.3 ppm in the tailing. Indium is recovered generally from zinc concentrates (George, 2005), because of scavenging ability of sphalerite. A main reason for the high content of indium in the copper concentrates at the Uchinotai deposits may be due to rather dominant tetrahedrite-group minerals (Matsukuma and Horikoshi, 1970), which tend to occur in Kuroko (black ore) horizon of a narrow sense above Oko (yellow ore) horizon (Watanabe, 1973).

Mill-concentrates could tell us average values of given deposits. In our study, copper concentrates of the Kosaka mine are as high as 20 ppm In. In contents of the zinc concentrates are lower than those of the copper concentrates as 11 ppm. Lead (3 ppm In) and pyrite concentrates (1 ppm In) are much lower than the zinc concentrates. Individual ores of the Kosaka-Uchinotai deposits are also high in copper-rich ores, 37 ppm In (22.4 % Cu) to 15 ppm In (11.2 % Cu). An average of the Uchinotai deposits is 26 ppm In (n=2).

Among the neighboring mines, indium is high as 20 - 12 ppm in the Furutobe deposits, but is low (8 - 4 ppm In) in the Ainai deposits. Indium contents of the Hanawa deposits, occurring in the easternmost small basin, are higher than those of the Kosaka deposits, because the copper concentrates contain 26 ppm In (Table 2). Tetrahedrite-group minerals, which typically occur in the kuroko horizon (in narrow sense), are rather rich in many orebodies here, such as Motoyama-Ajiro, Motoyama-Shin-Higashi No.1 and Tsutsumi, Akedoushi-NE, SW and Toumei orebodies (Nippon Mining Group, 1981). Tetrahedrite-group minerals are heterogeneous in composition (Yui, 1971) and can contain many metal elements. Thus, predominance of indium in copper concentrates rather than zinc concentrates are considered due to these sulfosalts.

On the contrary, ore deposits of the western group are lower in the indium contents, although they have a whole sequence of vertical zoning downwards. At the Shakanai mine, copper and zinc concentrates contain 9 and 7 ppm In, respectively. At the Matsumine mine, copper and zinc concentrates revealed 6 and 9 ppm In, respectively. Individual ores vary from 1 to 17 ppm In. Tetrahedrite contents may be lower in the Kuroko horizons of the Shakanai-Matsumine ore deposits, relative to the mineral contained in those of the Kosaka mine.

Among the central group of Kuroko deposits, indium is low at Fukazawa (4 - 7 ppm In). One sample of copper-zinc-rich ore (9.9 % Cu, 8.1 % Zn) from the Ezuri mine is as high as 22 ppm In. The analytical results of individual ores in the Hokuroku basin gives the following average: 11.3 ppm In at 15.0 % Zn, 1.6 % Pb, and 8.9 % Cu.

From the Okuaizu region of Fukushima Prefecture (Fig. 1), two deposits were selected. At the Tashiro mine, yellow ore (6.3 % Cu) of 17 ppm In is higher than 1 ppm In of Kuroko (20.5 % Zn +3.7 % Pb). At the Yokota mine, the high-grade yellow ore (18 % Cu) revealed the highest value as 52 ppm In, a middle-grade ore (6 % Cu) gives 16 ppm In, and Kuroko (18.3 % Zn + 3.8 % Pb, 0.6 % Cu) is determined as 5 ppm In. The high-grade yellow ores are extremely high in Mo (3,010 - 3,140 ppm).

Because an indium anomaly was reported previously (MITI, 1992) in the Takara deposits of the southern

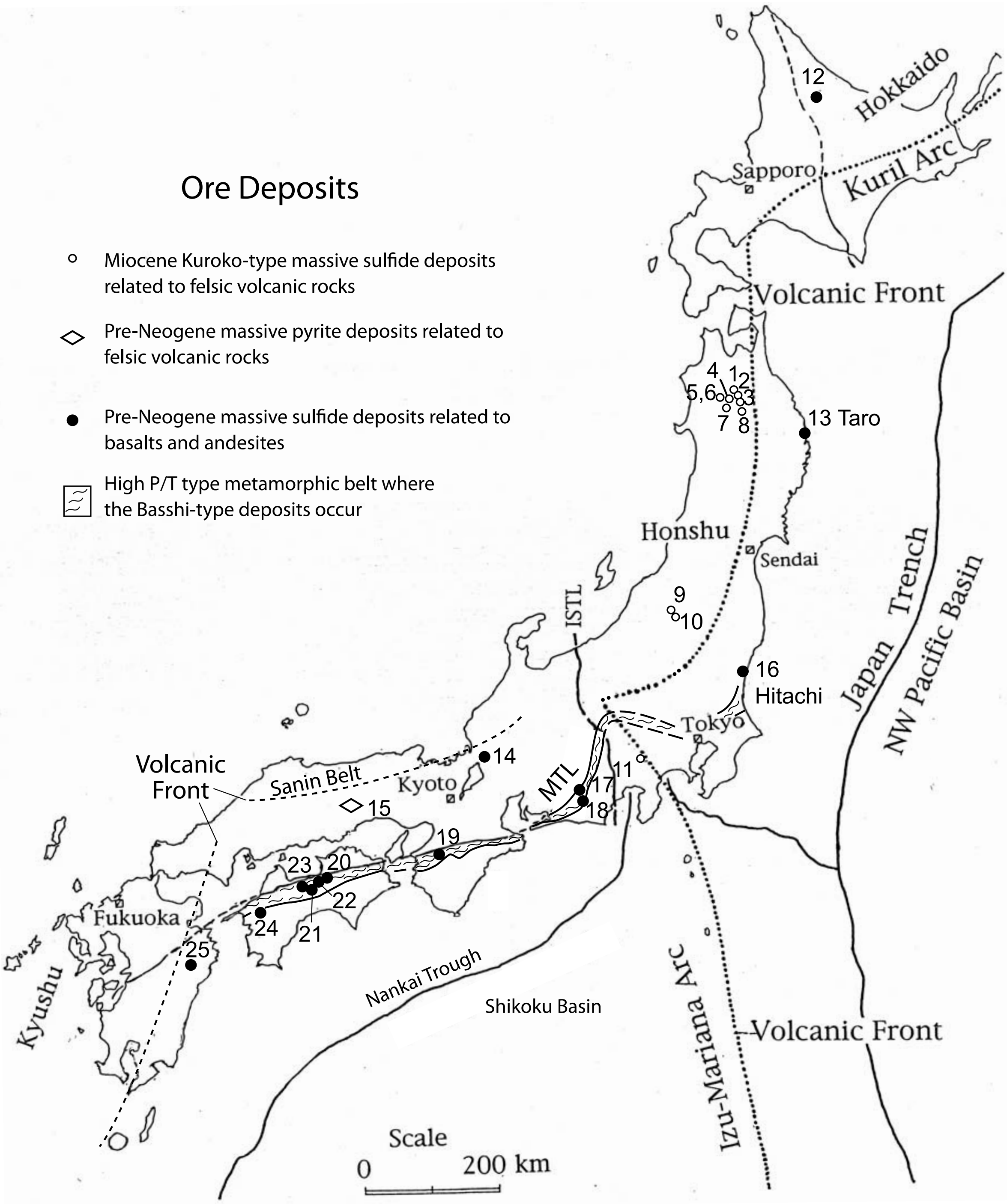

Fig. 1 Locality map of the studied sulfide ores. Numbers correspond to those in Tables 1 and 2. MTL, Median Tectonic Line; ISTL, Itoigawa-Shizuoka Tectonic Line.

Fossa magna region (Fig. 1), the representative samples of the three ore types of Yakushi and Enjoji (2004) were analyzed from this small deposit. The chalcopyrite-type ore gives 3 ppm In, and chalcopyrite-sphalerite type and galena-sphalerite-type ores are lower than 2 ppm (Table 2), indicating no anomalous values.

Correlation coefficient of indium with other metal elements in the whole Kuroko ores on 35 samples from 11 ore deposits, are the highest in In-Cu (0.64)(Fig. 3), then In-Se (0.59), In-Bi (0.57) and In-Mo (0.55). Indium is highly correlated with the chalcophile elements, implying that indium could be concentrated in copper sulfosalts, such as tetrahedrite instead of sphalerite, in many of the Japanese Kuroko deposits. Correlation coefficient of In-Zn is negative as -0.43,

Table 1 Locality and type of the massive sulfide ores analyzed.

Sample nos. Locality: Ore types
Miocene Kuroko-type deposits
1. AIN1 Akita, Ainai: Fine, massive cp-py ore with some sp-gn
AIN2 ditto: Fine, massive Kuroko with some py mingled
2. FUR2 Akita, Furutobe: 2L W10; Fine, massive sp-bearing yellow ore
FUR3 ditto: Daikokuzawa East orebody: Fine, Kuroko-bearing yellow ore
3. KOSCu Akita, Kosaka: Copper concentrates (May, 1983)
KOSZn ditto: Zinc concentrates (ditto)
KOSPy ditto: Pyrite concentrates (ditto)
UCH1 Akita, Kosaka-Uchionotai: Fine and massive yellow ore
UCH2 ditto: Medium, drusy yellow ore
UWA ditto, Uwamuki No.4 orebody: Fine massive cp-py-rich Kuroko
4. EZR Akita, Ezuri, No. 1323: Fine, cp-rich massive Kuroko,
5. SHACu Akita, Shakanai: Copper concentrates (May, 1983)
SHAZn ditto: Zinc concentrates (ditto)
SHA1 ditto: Fine and massive cp-py yellow ore
SHA2 ditto: Very fine massive Kuroko with coarse sp and barite layering
6. MATCu Akita, Matsumine: Copper concentrates (May, 1983)
MATZn ditto: Zinc concentrates (ditto)
MAT1 ditto: Fine, py-rich Kuroko0
MAT2 ditto: Fine and massive cp-rich yellow ore
7. FUK1 Akita, Fukazawa: Barite and quartz-rich Kuroko, middle grade
FUK2 ditto, No. 4 orebody,80091217: Py-rich Kuroko, low grade
FUK3 ditto, No. 4 orebody, 80081207: Fine high-grade Kuroko
8. HNACu Akita, Hanawa: Copper concentrates (May, 1983)
HNAZn ditto: Zinc concentrates (ditto)
HAN1 ditto, Akedoushi orebody: Very fine massive yellow ore
HAN2 ditto, Akedoushi orebody: Medium, massive Kuroko
9. TAS1 Fukushima, Tashiro-Oshio orebody: Fine massive cp-py ore
TAS2 ditto, Tashiro: Fine, Kuroko with pyrite crystals
TAS3 ditto, YA7111: Medium, low grade Kuroko
10. YOK1 Fukushima, Yokota, 720228: Medium cp-py ore, brecciated
YOK2 ditto: Very fine massive Kuroko
YOK3 ditto: Brecciated Kuroko with pyrite
11. T8 Yamanashi, Takara: Cp-type ore (Yakushi and Enjoji, 2004)
T2 ditto: Cp-sp type ore (ditto)
T1 ditto: Gn-sp type ore (ditto)
Pre-Miocene massive sulfide deposits
12. SIMCu Hokkaido, Shimokawa: Copper concentrates
SIM Zn ditto: Zinc concentrates
SIM1 ditto: Upper 1st adit, S32: Fine, cp-rich po massive ore
SIM2 ditto: Lower 2nd adit (1967.9.14): Very fine, cp-py-po massive ore
13. TROCu Iwate, Taro: Copper cponcentrates
TROZn ditto: Zinc concentrates
TRO1 ditto: Taro-Honko –11 L: Banded sp>py ore
TRO2 ditto, Taro-Sinkabu-ko –14 L: Coarse py ore, cracked
14. TUK Shiga, Tsuchikura: Very fine, cp-bearing py ore
15. YAN1 Okayama, Yanahara, Upper Orebody: Very fine, massive py ore
YAN2 ditto, Lower Orebody: Cp-rich po massive ore
YAN3 ditto, Lower Orebody, L27: Fine massive py ore

Table 1 Continued.

Sample nos. Locality: Ore types
YAL4 ditto: Laminated ore, with black matter (cf., Fig. 2)
YAL5 ditto: Laminated ore, pure massive py ore (cf., Fig. 2)
YAN6 ditto, Lower Orebody: Cp-po-bearing py ore
YAN7 ditto, margin, 27 L,24 section, 4-go: Po-rich py ore
YAN8 ditto, Shimo-Yanahara orebody, SL 8: Cp-bearing massive py ore
YAN9 ditto: Lower Orebody(?): Cp-rich po ore
YAN10 ditto: Pure cp aggregate
16. HTCCu Ibaraki, Hitachi: Copper concentrates
HTCZn ditto: Zinc concentrates
HTCPy ditto: Pyrite concentrates
HTC1 ditto, Takasuzu orebody: Coarse, cp<< py massive ore
17. KNE Shizuoka, Kune: Cp<<py banded ore
18. MIN ditto, Minenosawa: Very fine, cp-py massive ore
19. IMR Wakayama, Iimori: Very fine, cp-rich py massive ore
20. SIG Ehime, Shingu: Very fine, cp<<py banded ore
21. SIRCu Kochi, Shirataki: Copper concentrates
SIRZn ditto: Zinc concentrates
SIR1 ditto, Sam. no. 20702: Cp<<py-po massive ore
22. SZACu Ehime, Sazare: Copper concentrates
SZAZn ditto: Zinc concentrates
SZA ditto: Very fine, cp-bearing py ore
23. SMM1 Ehime, Besshi, Honzan: Typical cp-py ore donated by Sumitomo Mining Co.
SMM2 ditto, Ikadatsu: ditto
SMM3 ditto, Sekizen: ditto
BSS1 ditto, Besshi, Upper orebody: Very fine, cp-py massive ore
BSS3 ditto, Ikadatsu –21L: Very fine, (cp-)py massive ore
BSS7 ditto, Honzan 26L: Cp-py-po ore, donated by Prof. K. Kase
BSS2 ditto, Honzan 28L, E8: Fine sp-po ore
BSS4 ditto, Honzan 29 L: Cp-py-po ore
BSS5 ditto, Honzan 29 L: Cp-po ore
BSS6 ditto, Honzan 33L, E3: Cp-po ore
24. OKK Ehime, Okuki: Very fine, cp-py ore
25. MKIPy Makimine, Miyazaki: Pyrite concentrates. Taken at the broken mill site.

Abbreviations: cp-chalcopyrite, gn-galena, po-pyrrhotite, py-pyrite, sp-sphalerite.

3. Indium of the pre-Neogene massive sulfide deposits

Pre-Neogene massive sulfide deposits can be divided into non-metamorphosed massive sulfide deposits occurring everywhere in the accretionary complexes and metamorphosed Besshi-type occurring exclusively in the Sanbagawa metamorphic belt. The former group is further subdivided into those associated with mafic, andesitic and felsic volcanic rocks.

3.1 Massive sulfides associated with diabase and andesite

The Shimokawa deposits in Hokkaido are stratabound copper deposits associated with diabase in sediments of the Cretaceous-Paleogene Hidaka Group. The copper ores (average of 2.5 % Cu) contain always 0.2 - 0.3 % Co, which is exsolved in pyrite and pyrrhotite, and also contained as Co-bearing pentlandite (Japan Mining Association, 1965).The analyzed high-grade copper ores (13.0 - 16.7 % Cu) are also high in Co (3,260 - 5,600 ppm). The ores are high in trace amounts of indium (4 - 21 ppm) and tin (55 - 68 ppm). Bamba and Motoyoshi (1985) reported hexagonal pyrrhotite in the lower level and monoclinic pyrrhotite in the upper level, which may indicate later thermal effect by hidden granitic intrusion of Miocene age of the Hidaka belt (Ishihara *et al.*, 1998). The trace amounts of cobalt were possibly derived from the host diabase, but the indium and tin may have been added possibly during hydrothermal effect of the Miocene ilmenite-series granitic activities.

Table 2 Analytical results of the ore components of the volcanogenic massive sulfide deposit in Japan.

Element:	In	Sn	Cd	Zn	Pb	Cu	Fe	Mn	Cr	V	Ni	Co	Ga	W	Mo	Se	As	Bi	Ag	Sb	Tl
Detect. Lmt.	0.1	1	0.1	0.2	1	0.2	100	1	0.5	1	0.5	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
Miocene Kuroko-type deposits																					
1. AIN1	8.4	3	1.2	111	90	71400	194000	8	2.0	2	0.8	6.3	3.1	0.7	16.0	17.7	38.4	16.0	11.6	2.9	1.3
AIN2	4.3	< 1	1360.0	303000	34500	25900	35700	25	4.4	4	3.9	0.6	30.3	0.7	12.5	15.9	97.6	12.8	266.0	216.0	1.8
2. FUR2	19.7	3	16.8	2860	152	98200	195000	16	3.4	3	6.5	0.3	5.7	1.6	170.0	3.9	605.0	254.0	36.6	96.3	29.5
FUR3	12.4	5	95.0	51100	1500	165000	224000	24	1.4	3	2.6	1.0	7.1	0.7	37.5	18.5	525.0	76.7	87.3	35.8	34.2
3. KOSCu	20.4	5	144.0	22000	23200	167000	198000	26	29.1	5	14.2	5.5	11.1	1.6	358.0	16.4	399.0	85.0	447.0	123.0	19.1
KOSZn	10.5	3	2110.0	421000	13000	8700	36200	228	30.4	10	10.4	4.9	56.7	1.8	180.0	21.9	676.0	59.0	198.0	767.0	7.5
KOSPy	1.0	2	13.0	2580	884	2410	382000	55	39.6	3	22.8	27.5	1.2	1.4	118.0	6.1	608.0	72.1	40.9	122.0	35.0
UCH1	14.7	1	6.3	720	692	112000	270000	29	12.6	98	30.3	20.2	11.0	2.7	432.0	18.5	48.7	410.0	276.0	32.8	6.4
UCH2	37.2	2	7.4	571	259	224000	245000	3	2.6	< 1	7.6	3.9	3.7	1.3	119.0	5.6	49.5	162.0	71.6	24.8	2.0
UWA	0.3	1	1460.0	296000	37200	10700	8500	13	2.5	2	5.1	< 0.1	20.9	0.5	22.6	16.2	574.0	1.5	344.0	5550.0	1.3
4. EZR	22.1	1	409.0	81000	2510	98700	124000	47	1.6	1	23.8	0.5	7.9	3.1	370.0	5.1	714.0	63.2	124.0	337.0	111.0
5. SHACu	8.7	3	164.0	32700	30800	154000	205000	39	8.7	4	10.5	22.6	11.1	1.2	272.0	24.4	1060.0	129.0	417.0	238.0	23.1
SHAZn	7.4	3	1930.0	411000	17000	10900	32600	429	14.6	5	6.0	8.2	74.0	6.0	158.0	24.0	464.0	38.6	202.0	512.0	9.7
SHA1	17.2	3	161.0	28600	1520	112000	265000	22	3.1	4	20.6	0.4	9.6	1.3	200.0	4.8	2260.0	3.4	319.0	2330.0	3.9
SHA2	0.9	< 1	1940.0	391000	33400	22500	25300	338	2.0	4	2.3	0.2	36.5	67.2	34.8	16.1	2650.0	1.7	228.0	1200.0	2.2
6. MATCu	6.1	3	56.4	9900	22200	162000	209000	33	10.5	5	9.8	27.7	13.9	3.1	407.0	25.3	470.0	119.0	177.0	63.1	32.4
MATZn	9.3	13	2070.0	436000	3250	9840	40900	750	14.0	7	7.0	9.4	90.8	4.0	230.0	24.0	155.0	64.8	85.6	251.0	11.2
MAT1	8.7	< 1	20.1	5710	2370	41200	234000	39	3.4	< 1	12.2	0.9	1.5	1.8	90.2	4.8	90.4	310.0	31.0	28.4	10.4
MAT2	6.6	3	97.0	9800	9490	239000	221000	63	2.7	1	6.7	1.2	6.9	1.2	17.9	21.8	15.9	194.0	86.4	21.5	1.5
7. FUK1	3.5	< 1	1060.0	270000	12200	7560	19500	1490	1.7	15	11.3	0.7	17.0	4.5	99.6	13.9	37.6	3.1	44.8	59.4	0.4
FUK2	5.4	< 1	1540.0	312000	37700	11100	24900	459	3.4	24	6.3	0.1	35.2	28.0	60.7	17.6	2940.0	0.5	90.1	615.0	42.5
FUK3	7.3	< 1	932.0	173000	24000	107000	201000	74	4.4	9	25.6	58.9	47.1	1.1	599.0	15.3	3150.0	471.0	254.0	890.0	22.0
8. HNACu	25.7	3	245.0	53700	35800	170000	231000	48	15.8	2	11.0	2.1	14.8	1.7	129.0	18.2	4270.0	156.0	270.0	4020.0	11.5
HNAZn	13.5	2	1580.0	421000	26500	13000	50300	216	12.2	4	9.4	1.5	108.0	3.2	168.0	25.7	1700.0	44.6	164.0	774.0	13.6
HAN1	19.8	5	901.0	169000	31100	130000	191000	111	1.2	< 1	0.7	0.4	50.5	0.7	59.7	22.5	309.0	7.2	267.0	273.0	2.9
HAN2	2.7	< 1	2380.0	453000	37400	28600	34900	336	0.9	< 1	< 0.5	< 0.1	110.0	0.4	15.0	30.8	14.2	0.5	98.3	39.4	0.8
9. TAS1	16.7	1	3.7	383	15	62600	260000	2	2.1	< 1	0.9	18.8	3.6	2.1	285.0	3.2	540.0	516.0	5.7	21.1	0.5
TAS2	0.6	< 1	1630.0	205000	36500	3360	6700	13	1.4	< 1	0.9	4.2	0.9	0.8	6.7	9.3	619.0	7.3	323.0	627.0	1.7
TAS3	7.9	< 1	856.0	146000	35800	1260	67400	21	1.1	12	3.4	0.5	14.1	5.8	38.0	7.1	292.0	11.2	117.0	67.4	1.4
10. YOK1	52.2	3	16.0	11100	629	177000	199000	29	2.4	< 1	1.5	49.3	1.6	0.8	3010.0	330.0	95.7	4744.0	21.6	13.7	7.5
YOK2	16.0	2	2.2	1620	96	60300	238000	123	3.1	< 1	2.2	98.4	2.2	3.2	3140.0	139.0	243.0	3135.0	8.1	7.0	18.4
YOK3	4.5	< 1	736.0	183000	38300	5780	140000	9	0.7	< 1	1.8	12.7	2.2	0.7	77.6	9.0	135.0	14.0	227.0	312.0	1.7
11. T8	2.9	8	14.6	3230	202	28300	396000	111	5.4	19	7.4	1.0	8.0	1.3	67.1	4.6	812.0	23.9	58.8	19.8	n.d.
T2	1.8	7	2510.0	443000	74	3370	40000	44	5.4	6	2.8	1.2	62.6	15.4	4.8	51.8	691.0	0.9	188.0	25.4	n.d.
T1	< 0.1	11	400.0	230000	10300	800	6600	22	3.7	6	3.6	0.5	3.4	1.2	3.6	26.3	170.0	0.5	203.0	328.0	n.d.
Pre-Miocene massive sulfide deposits																					
12. SIMCu	10.4	41	44.5	28600	108	149000	256000	146	8.8	7	19.0	1630.0	5.4	< 0.1	9.6	76.5	92.3	4.6	25.7	9.3	0.9
SIMZn	23.1	17	448.0	340000	41.7	17800	76400	1050	1.8	3	5.6	1280.0	13.9	< 0.1	6.8	63.2	< 0.1	0.8	17.5	3.0	0.3
SIM1	4.2	55	32.9	14300	303	130000	347000	164	5.6	49	18.6	3260.0	7.0	0.5	23.8	37.1	643.0	7.1	68.3	22.0	2.0
SIM2	21.1	58	9.2	6960	55	167000	323000	18	4.3	< 1	27.0	5600.0	4.9	0.4	5.1	154.0	298.0	7.0	22.7	4.3	0.4
13. TROCu	0.4	235	101.0	31000	37000	230000	203000	458	6.9	< 1	4.0	0.7	30.9	< 0.1	14.7	15.0	791.0	5.0	215.0	65.4	0.8
TROZn	0.9	11	1430.0	482000	31200	5200	17500	5350	38.7	1	26.7	1.3	39.4	0.2	17.3	35.0	18.6	3.5	25.0	8.1	0.4
TRO1	0.7	18	492.0	179000	38400	192	197000	4740	8.3	21	19.0	5.8	7.4	2.4	29.2	182.0	77.0	29.0	53.9	40.6	2.7
TRO2	0.4	2	21.9	7480	103	324	401000	43	5.2	2	2.6	37.6	0.9	0.3	2.6	20.7	216.0	39.3	1.8	1.3	0.2
14. TUK	1.1	1	0.7	305	133	24700	362000	186	17.2	24	16.6	505.0	2.9	0.4	125.0	8.6	144.0	1.9	26.7	1.4	19.8

Table 2 Continued.

Element:	In	Sn	Cd	Zn	Pb	Cu	Fe	Mn	Cr	V	Ni	Co	Ga	W	Mo	Se	As	Bi	Ag	Sb	Tl
Detect. Lmt.	0.1	1	0.1	0.2	1	0.2	100	1	0.5	1	0.5	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
15. YAN1	0.6	1	2.2	531	104	1920	457000	36	4.3	7	6.0	209.0	1.5	0.9	53.0	26.1	513.0	5.1	2.2	8.9	4.7
YAN2	207.0	55	169.0	11000	16	152000	394000	202	4.3	12	11.8	89.2	3.1	0.5	72.7	309.0	33.5	41.8	231.0	4.9	1.1
YAN3	0.1	2	4.0	1520	35	1040	517000	64	3.5	6	4.9	626.0	1.2	0.5	51.0	96.9	335.0	18.5	1.7	19.2	2.7
YAL4	0.2	4	3.3	1890	70	14300	493000	115	5.1	93	6.7	528.0	5.8	1.0	58.5	42.4	21.5	25.7	9.2	8.0	0.9
YAL5	0.6	2	7.5	4390	59	4700	435000	79	4.9	48	10.1	577.0	1.2	0.4	82.2	24.2	2.6	9.1	6.5	2.6	0.9
YAN6	13.1	45	122.0	10500	9	132000	375000	185	1.7	10	11.7	78.3	2.4	0.4	103.0	193.0	17.1	23.2	240.0	3.4	0.9
YAN7	< 0.1	1	1.1	78.4	7	4260	546000	58	2.5	< 1	26.2	50.2	0.3	0.3	18.5	43.8	8.0	15.8	7.4	2.8	0.1
YAN8	0.8	11	31.8	4840	80	7120	463000	146	4.4	8	7.5	73.6	1.6	0.5	34.0	24.4	239.0	13.5	9.2	15.4	7.4
YAN9	28.4	65	160.0	11200	24	185000	409000	64	1.4	2	11.4	197.0	1.5	0.2	61.6	236.0	16.3	26.8	242.0	2.8	1.5
YAN10	2.8	13	22.3	2720	32	217000	347000	178	4.7	8	12.1	3.7	5.2	0.4	21.7	37.2	1440.0	12.6	212.0	4.7	2.9
16. HTCCu	5.3	4	70.4	25700	1160	168000	185000	262	26.9	15	17.4	9.0	5.3	9.0	61.2	52.7	21.9	29.0	36.6	5.6	1.1
HTCZn	14.7	2	929.0	385000	1330	15200	91200	1410	12.8	2	9.7	5.6	27.3	1.1	19.4	48.2	19.7	22.5	15.6	4.0	0.9
HTCPy	< 0.1	1	1.6	821	173	687	295000	95	40.3	10	28.7	116.0	1.0	1.9	34.4	16.1	67.4	8.8	2.8	2.9	0.7
HTC1	0.4	1	1.1	259	15	20100	415000	75	6.0	14	30.7	431.0	1.6	0.5	119.0	47.6	39.4	14.3	3.5	0.7	1.0
17. KNE	0.8	2	7.7	804	49	83300	259000	46	25.8	124	21.5	269.0	3.7	0.6	169.0	149.0	25.7	3.2	8.3	18.4	1.2
18. MIN	3.9	2	7.5	1230	72	74800	337000	118	10.5	38	19.3	805.0	2.3	0.4	38.9	34.3	26.0	2.2	18.0	19.9	4.9
19. IMR	1.5	1	15.2	2170	371	35700	343000	633	18.1	105	59.4	184.0	10.8	0.5	55.5	15.6	16.5	2.1	5.3	1.5	1.7
20. SIG	0.5	2	2.0	813	77	33200	421000	144	5.6	83	17.0	488.0	10.8	1.3	138.0	118.0	13.6	2.4	8.6	0.6	0.5
21. SIRCu	6.5	3	33.3	5860	92.7	174000	235000	149	20.1	16	46.5	225.0	1.4	0.2	37.7	147.0	29.0	7.9	36.8	1.8	1.0
SIRZn	48.1	3	1840.0	440000	81.8	5390	47200	136	13.1	5	8.6	123.0	10.4	< 0.1	27.8	206.0	50.6	2.6	24.7	1.8	0.5
21. SIR	1.5	1	13.7	1540	39	39500	389000	63	11.8	158	43.4	484.0	3.4	0.5	61.9	46.9	10.3	1.8	8.0	0.4	0.4
22. SZACu	15.7	3	220.0	48300	542	202000	29000	42	7.4	5	9.2	214.0	2.4	< 0.1	44.0	163.0	135.0	26.9	68.7	11.6	0.2
SZAZn	79.5	2	2040.0	501000	261	17400	45400	88	1.3	3	7.9	63.3	11.1	< 0.1	33.9	120.0	29.9	3.4	12.7	1.1	0.2
SZA	3.5	2	13.1	3060	52	33000	400000	92	15.5	80	31.5	757.0	3.6	0.5	58.7	33.5	7.3	0.8	4.1	0.4	0.6
23. SMM1	1.5	7	23.9	3790	416	19400	451000	203	14.2	96	16.1	590.0	7.4	0.5	14.1	93.2	64.6	6.4	32.8	8.6	0.4
SMM2	3.0	9	20.8	3720	190	44300	443000	115	12.0	55	22.8	359.0	4.6	0.3	55.7	58.2	129.0	3.3	42.9	13.5	0.4
SMM3	2.6	4	9.9	1520	74.3	15200	438000	112	22.6	75	55.2	563.0	0.9	0.2	22.1	72.9	28.8	3.1	6.9	2.3	0.2
BSS1	2.5	2	54.9	14700	177	201000	317000	280	3.0	21	32.6	864.0	3.3	0.7	19.8	201.0	34.6	2.5	84.3	14.8	0.3
BSS3	3.9	17	75.6	20400	31	42300	336000	136	10.4	58	16.5	203.0	12.9	0.5	30.2	12.0	14.6	1.9	6.6	1.5	0.8
BSS7	167.0	3570	903.0	100000	4040	10100	300000	22000	3.2	10	6.5	27.8	3.7	1.6	0.5	43.5	34400.0	225.0	280.0	1290.0	0.4
BSS2	45.1	447	35.6	2940	14	64400	276000	534	53.7	156	112.0	782.0	14.4	2.8	26.8	138.0	400.0	36.1	127.0	8.6	1.7
BSS4	5.6	6	101.0	29200	261	33300	401000	530	20.7	64	35.3	1190.0	6.9	0.7	44.1	79.1	29.9	3.7	21.3	12.8	0.9
BSS5	4.7	16	72.7	17900	216	104000	486000	586	10.2	81	57.3	1740.0	12.6	0.5	43.0	242.0	< 0.1	9.7	72.8	8.8	0.9
BSS6	1.2	58	11.5	1290	89	1360	581000	108	2.4	< 1	116.0	101.0	< 0.1	0.2	1.1	31.9	5.1	1.1	6.9	1.1	< 0.05
24. OKK	2.9	2	72.2	20300	521	218000	241000	65	7.0	27	5.8	1470.0	5.9	0.2	27.1	319.0	376.0	2.1	47.6	5.0	2.8
25.MKIPy	1.3	5	1.9	591	151	64000	341000	61	7.0	12	18.1	1580.0	2.7	0.3	76.2	27.6	76.0	2.7	47.4	14.5	0.8

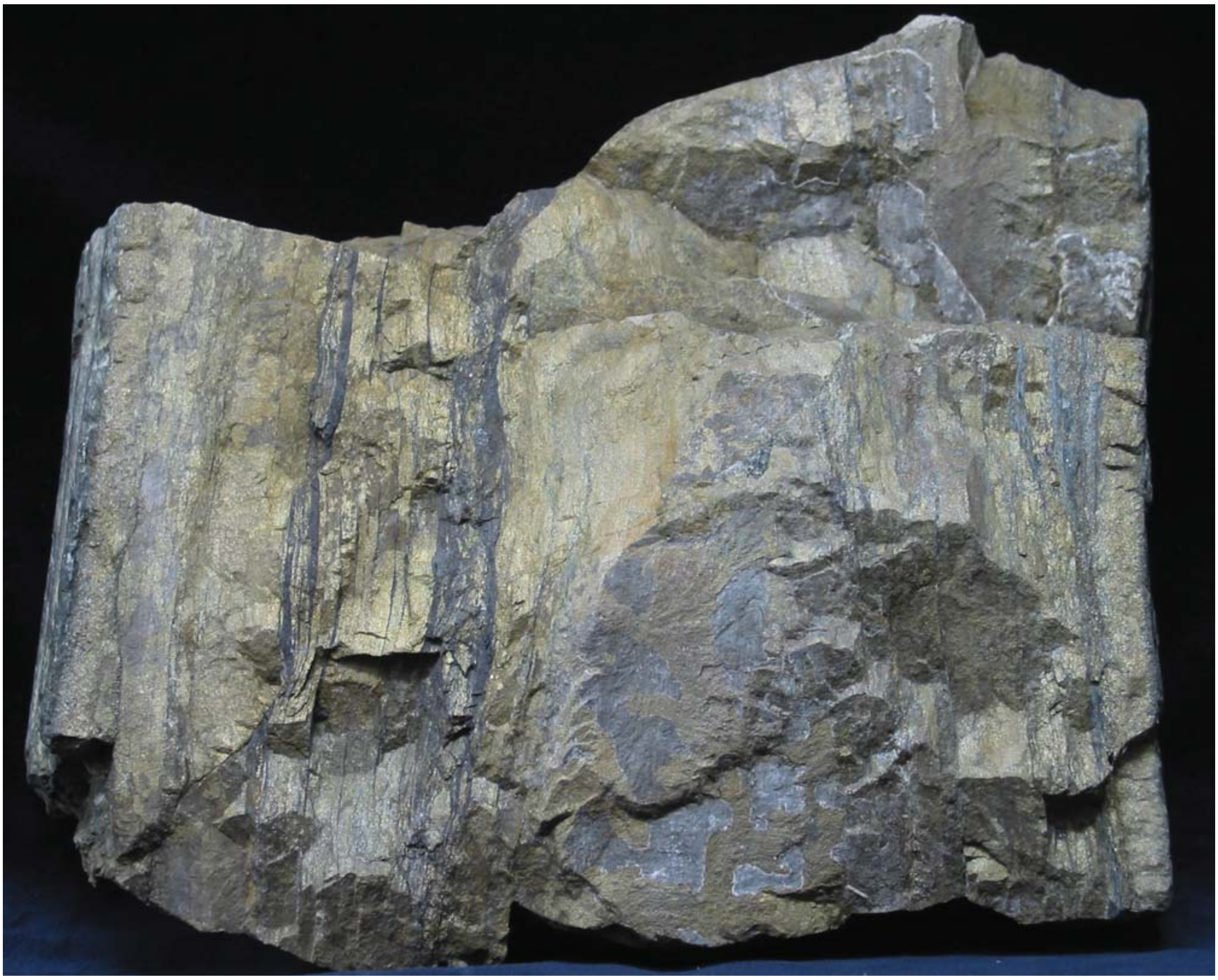

Fig. 2 Laminated pyrite-pyrrhotite-magnetite ore from the Yanahara mine. The magnetic susceptibility vary from 20 x 10^{-3} (yellow pyrite dominant part) to 268 x 10^{-3} SI (black magnetite banded part). The samples YAL 4 and 5 (Table 1) are taken from this specimen. Width of the sample is 22 cm. Collection of the Geological Museum of AIST (D33-301).

The Taro deposits in the Kitakami Mountains are rich in lead and zinc, and are considered as a Cretaceous Kuroko type. The mineralization, however, is associated with not dacitic like in the Hokuroku Basin, but mainly andesitic activities of the Taro belt. The indium contents are very low as below 1 ppm.

Unmetamorphosed massive sulfide deposits also occur in the Inner Zone of Southwest Japan. Tsuchikura deposits of Shiga Prefecture are located in brecciated basalts and melange of the Jurassic Tanba Group. The largest, Eastern orebody, which is intercalated between bedded chert and massive chert, occurs as lenses in the olistostrome, The ores are copper-rich pyrite, and these sulfides are rich in cobalt having two concentration peaks at 1,000 - 2,000 ppm and around 300 ppm (Itoh and Kanehira, 1967). Nickel is also dominant as 15 - 250 ppm. One analysis of our study showed only 1 ppm In.

3.2 Massive sulfides associated with rhyolite

Yanahara deposits of Okayama Prefecture are huge one rich in pyrite, and are often compared with ores of the Rio Tinto mine in Spain (e.g., Mitsuno, 1986). Representative ore contains 45 % Fe, 47 % S, 0.2 % Cu and 0.3 % Zn (Dowa Mining Co., 1981). The Yanahara deposits occur with sediments of the upper Paleozoic Maizuru Group and diabase intrusion. The direct host rocks, which are related genetically to the mineralization, however, are altered rhyolitic complexes occurring between the two units, and major No. 1, No. 2, No. 3 and Lower Orebodies, and several small orebodies were known in the N-S alignment to the west. The ores are generally massive but may be laminated locally (Fig. 2).

No pyrite ores but copper-pyrrhotite-rich ore (15.2 % Cu) gives the highest value of 207 ppm In; the other weak anomalies (13 and 28 ppm In) are also found in copper-pyrrhotite-rich ores (13.2 and 18.5 % Cu). These anomalous ores are high in trace amounts of tin (45 - 65 ppm Sn). These rocks are taken the Lower orebody of the main ore deposits.

Calculation of correlation coefficients of the analyzed components of the Yanahara ores (n=10) indicates that high values are obtained on In-Bi (0.80), In-Se (0.78), In-Cd (0.69), In-Sn (0.61) and In-Zn (0.59), In-Mn (0.52), and In-Ag (0.50) . The indium is correlated with zinc more than copper in the ore deposits and the high correlation coefficient between In and Cd, imply that the indium is contained in sphalerite in the ore deposits.

3.3 Besshi-type deposits

The Besshi-type metamorphosed massive sulfide deposits, associated with Jurassic submarine basaltic volcanism, occur along the Sanbagawa metamorphic belt from Shizuoka Prefecture (Kune, Minenosawa etc), through Wakayama (Iimori) to Ehime Prefecture (Shingu, Besshi). Makimine deposit is similar type occurring with the upper Cretaceous basaltic activity of the Shimanto Supergroup. The Hitachi massive sulfides are usually grouped into the Besshi type. But the ore deposits contain variety of gangue and ore minerals, because of contact metamorphism with Cretaceous granitoids belonging to the Abukuma Belt (Tagiri, 1973), which are generally tin-free (Ishihara and Terashima, 1977). Here, zinc concentrates are high in indium as 15 ppm, but copper concentrates are lower as 5 ppm In, which are different from abundance in the concentrates from the Kuroko deposits at the Kosaka-Uchinotai mine.

The same tendency with even higher values have been found in Shirataki and Sazare mines. Zinc vs. copper concentrates are 48 ppm vs. 7 ppm In at the Shirataki mine, and 80 ppm vs. 16 ppm In at the Sazare mine. The Besshi deposits are the largest of this type, composed of the Honzan implying the main part (29,940 Kt, 2.36 % Cu), Ikadatsu (3,149 Kt, 1.49 % Cu) and small other deposits (Sumitomo Metal Mining, Co. Ltd., 1981). Representative ores from these deposits contain only 1.2 - 5.6 ppm In, but one zinc- and arsenic-rich ore (10.0 % Zn, 3.4 % As, BSS7, Table 2) from 26 L contains 167 ppm In and one copper-rich ore (6.4 % Cu) from the lower level (28 L) of the Honzan deposit, shows 45 ppm In (BSS2, Table 2). These samples are rich in pyrrhotite and gives high tin values as 3,570 and 447 ppm, respectively.

According to Sumitomo Metal Mining Co. (1981), the Besshi Honzan deposit was mined down to 2,100 meters (1 - 32 L) from the surface. The host rocks have been thermally metamorphosed below 22 L, which became stronger below 26 L. Quartz micro-veining and silicification with tin and arsenic minerals became obvious below 26 L. Pyrrhotite occurs abundantly, which is dominantly monoclinic in the 24 - 26 L and hexagonal in the 26 - 28 L, and all hexagonal between 28 and 32 L. It is obvious that the lower part of the Besshi deposits has been thermally metamorphosed by hidden later granitic intrusion. Tin, arsenic and antimony are typical ore elements related to the Miocene ilmenite-series granitic activities of the Outer Zone of SW Japan (Fig. 1). It is therefore possible to think that the high indium-bearing ores (e.g., BSS7 and 2) were formed by the original pyrite ores metasomatized and hydrothermally altered to the Cu-Zn pyrrhotite ores by high-temperature fluids released through cracks from the hidden Miocene granitic body (Kase, 1988).

Indium is very low at gabbroid-related the Okuki massive sulfide deposits of the Mikabu Belt, which is located at south of the Sanbagawa Belt. Copper-pyrite mill head of basalt-related massive sulfide deposits at Makimine of the Cretaceous Shimanto terrain is also low in indium (1.3 ppm).

Correlation coefficient of ore components on the pre-Neogene deposits, which are associated with basaltic volcanic rocks, are as follows: In-Sn (0.86), In-As (0.85), In-Sb (0.84), In-Bi (0.84), In-Mn (0.79), In-Ag (0.62), and In-Cd (0.55)(see also Fig. 3). These high values indicate that most of these ore-elements were derived from Miocene ilmenite-series granitic activities of the Outer Zone of the SW Japan.

4. Other ore components

Other ore components analyzed here (Table 2) have shown regional characteristics on their correlation coefficients of all the analyses and also absolute amounts of individual ores even ignoring the amounts of major components such as copper, zinc, lead and iron sulfides. Among common sulfide minerals, sphalerite has the largest capacity to contain other elements for its crystal structure. Iron can be contained up to 26 %, and Cd, In, Ge and Ga occur in large amounts, which could be extracted from sphalerite concentrates for industrial purposes.

The highest correlation coefficient, 0.90 - 0.93, was obtained on Cd-Zn throughout all the types of ores (Fig. 4A), reflecting a complete solid solution between ZnS and CdS (Deer *et al.*, 1992). The other solid solutions on ZnS-HgS and ZnS-ZnSe are not observed in the bulk chemistry, because of much less contents of mercury and selenium. The correlation coefficient of Zn-Ga (0.82) is also high on the Kuroko ores (Fig. 4B); accordingly, Ga-Cd is again highly correlated (0.79). However, these correlations are poor in the pre-Neogene ore deposits. Absolute amounts of Cd are generally lower in the pre-Neogene ores than in the Miocene ores.

Arsenic is high in the Miocene Kuroko deposits (Fig. 4C), ranging up to 3,150 ppm, but the contents of the Yanahara and other pre-Neogene massive sulfide ores are generally below 400 ppm, except for the BSS7

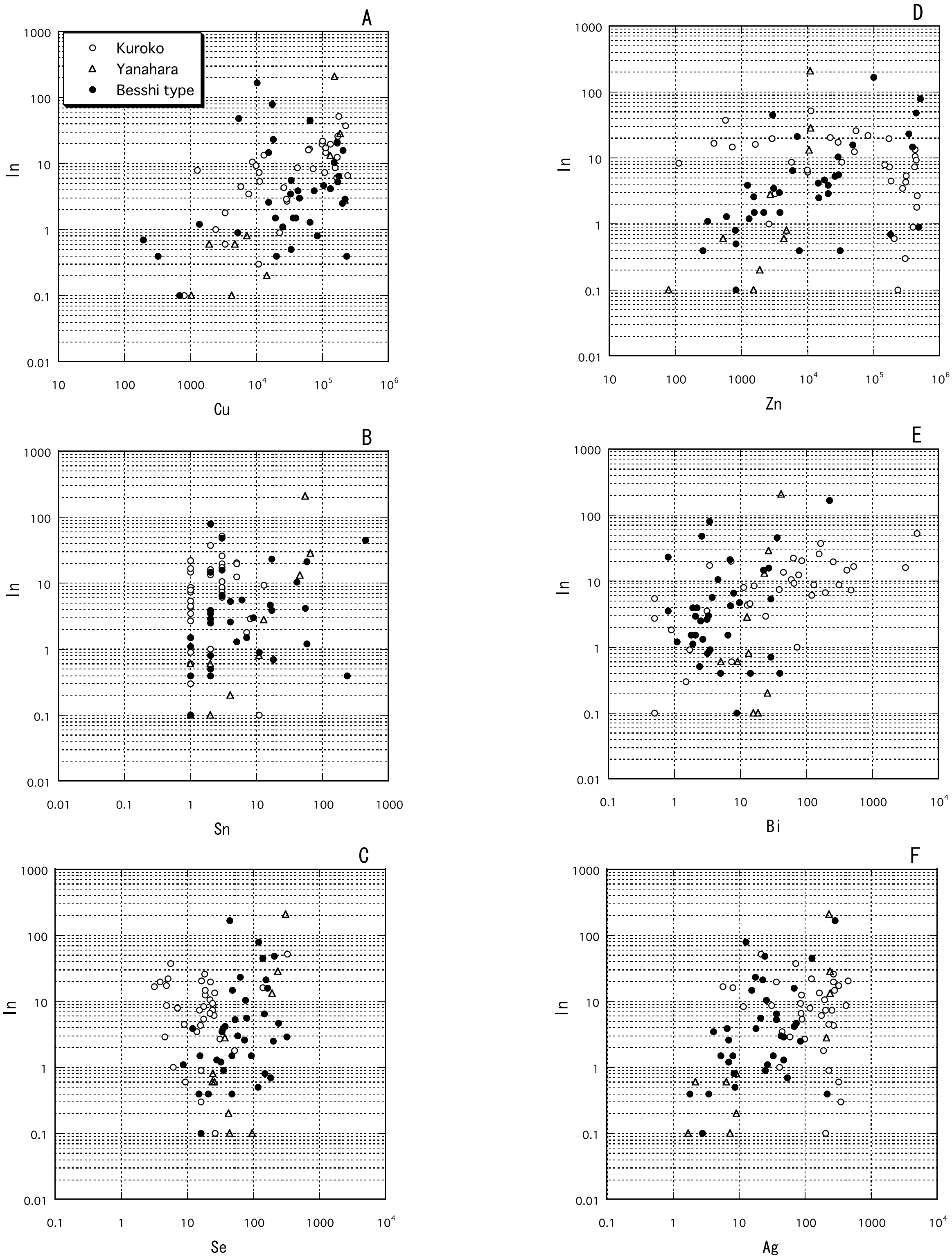

Fig. 3 Indium vs. copper, tin, selenium, zinc, bismuth and silver (in ppm) of the Miocene Kuroko, Yanahara and Besshi-type ores. The Besshi type includes the ores from the Taro, Shimokawa and Tsuchikura mines.

(3.44% As). Cobalt is very high in amount and positively correlated with copper in the Besshi-type ores, implying the basalt-related genesis, but very low on the Kuroko ores (Fig. 4D).

Mo is highly correlated with Bi (0.96) and Se (0.95) in the Miocene Kuroko deposits (Fig. 4E). These elements are especially abundant in copper ores from the Yokota deposits (3,010 - 3140 ppm Mo, 3,135 - 4,744 ppm Bi and 139 - 330 ppm Se), whose basement is supposed to be late Cretaceous granitoids. These com-

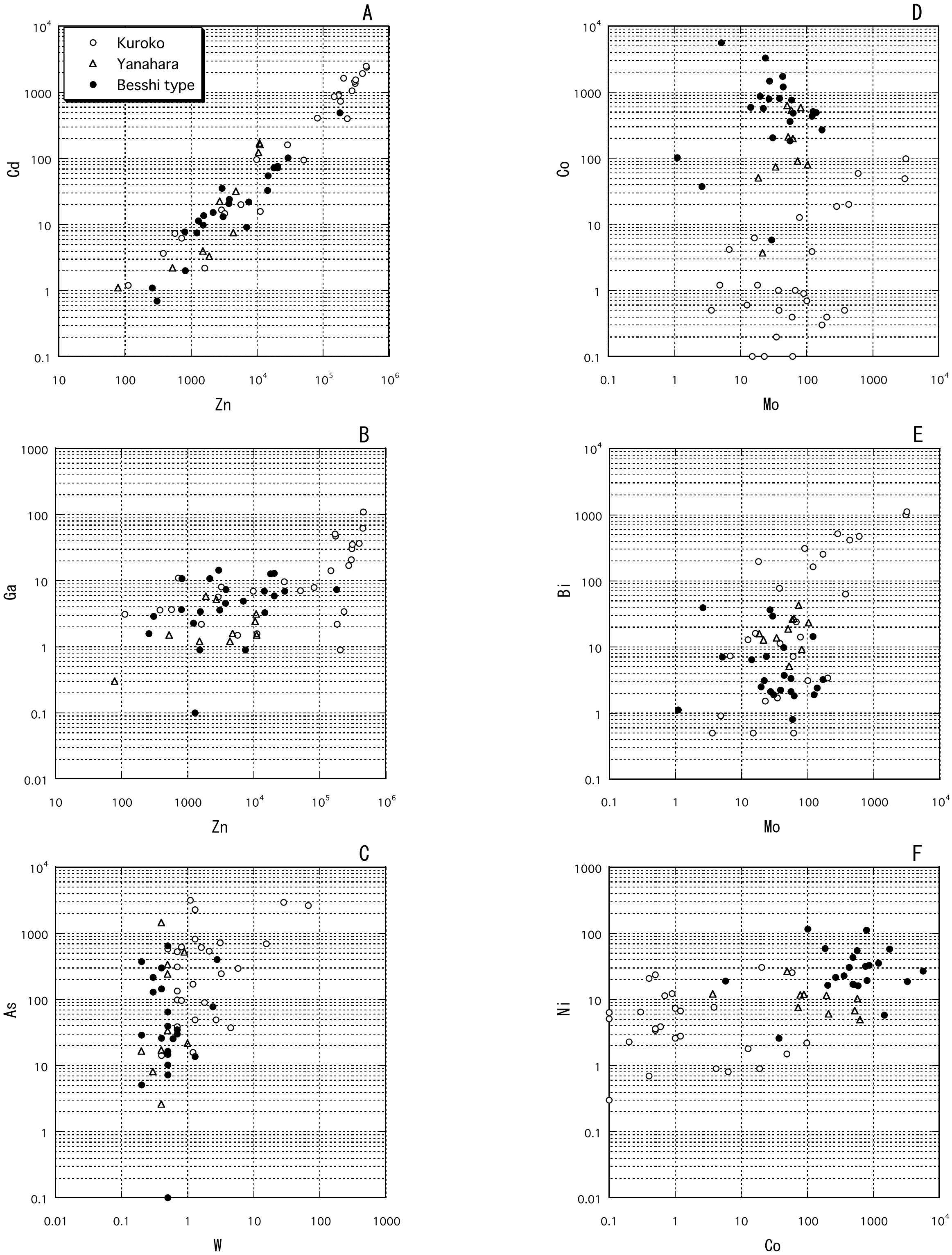

Fig. 4 Relationship among Cd-Zn, Ga-Zn, As-W, Co-Mo, Bi-Mo and Ni-Co (in ppm) of the Miocene Kuroko, Yanahara and the Besshi-type ores. The Besshi type includes the ores from the Taro, Shimokawa and Tsuchikura mines.

ponents are much less in the Yanahara pyrite ores and the other pre-Neogene massive sulfide ores. Antimony is also high in the Miocene Kuroko ores of the Hokuroku basin, up to 2,330 ppm, but is lower in those of the Okuaizu District (<627 ppm). The content is even lower in the Yanahara ores (<19 ppm) and the other pre-Neogene massive sulfide ores (<41 ppm).

Among mafic components associated with massive sulfides of basaltic affinity, Co and Ni, are contained widely in the Tsuchikura ore deposits (Ito and Kanehira,

Table 3 Production tonnage and In-contents of copper and zinc concentrates of the major Kuroko and other volcanogenic massive sulfide deposits in Japan.

Mine (age)	Production	Ore grade		In in concentrates	
		Cu	Zn	Copper	Zinc
Kuroko type in Japan					
1) Akita, Kosaka (mio)	12,186 Kt	2.5%	4.1%	20 ppm	11 ppm
2) ditto, Shakanai (mio)	9,390 Kt	1.4	2.1	9	7
3) ditto, Matsumine (mio)	30,000 Kt	2.4	3.6	6	9
4) ditto, Hanawa (mio)	3,787 Kt	1.1	3.2	26	14
Besshi and other types					
5) Hokkaido, Shimokawa (K)	6,850 Kt	2.0	0.4	10	23
6) Okayama, Yanahara (P)	35,240 Kt	0.4	tr	No ore dressing	
7) Ibaraki, Hitachi (J)	29,482 Kt	1.4	0.6	5	15
8) Ehime, Besshi (J)	29,190 Kt	1.2	0.3	Not available	
9) ditto, Sazare (J)	5,598 Kt	1.7	0.4	16	80
10) Kochi, Shirataki (J)	3,104 Kt	1.1	0.3	7	48

Abbreviations for the age: mio, Miocene; K, Cretaceous; J, Jurassic; P, Permian. Data source: Watanabe (1973), Geological Survey of Japan (1980), Aoki (2000).

1967). Cobalt is the highest in amount on the Shimokawa deposits (3,260 - 5,600 ppm), which has been known during the operation stage, then Makimine (1,580 ppm), Okuki (1,470 ppm), and all the Besshi-type ores (101 - 1740 ppm), and is very low (<20 ppm) on the Miocene Kuroko deposits (Fig. 4D) except for the Yokota ores which contains 13 - 98 ppm. Nickel, on the other hand, has the same tendency but smaller variations depending upon the geological background. The contents of the Besshi type ores vary from 6 to 116 ppm, while those of the Yanahara ores range 5 - 26 ppm. Miocene Kuroko ores of the Hokuroku basin contain 1 - 30 ppm Ni, and those of the Okuaizu are very low as 1 - 4 ppm Ni (Fig. 4F). On the contrary to Ni and Co, both Sb and As are rich in Kuroko ores but poor in the Besshi-type and other pre-Neogene ore deposits.

5. Potentiality of Indium Resources

Industrial indium has been extracted mostly from zinc concentrates of various In-contents, depending upon each mining and smelting situations. The mill concentrates also give an average In-contents of that ore deposit. Zinc concentrates of the Toyoha vein-type deposits, where many In-Cu and In-Zn ore minerals and In-bearing sphalerite have been discovered (Ohta, 1989) contain more than 1,000 ppm In (Ishihara *et al.*, 2006a). In-contents of mill concentrates from major Japanese massive sulfide deposits are given in Table 3.

Kuroko deposits of the Hokuroku basin are concentrated in the eastern margin of the Kosaka mine area and western margin of the Shakanai-Matsumine mines area. Indium contents of the main Kosaka deposits of the Uchinotai orebodies are as high as 37 ppm, and the copper concentrates contain 20 ppm In. The indium was recovered at the Kosaka smelter since 1976 fiscal year, and by 1983, the recovered indium metal is reported as 18.5 tons (Dowa Mining Co. Ltd., 1985). Total ores produced at the Kosaka mine between 1884 and 1983 are 7,488 Kt (1.92 % Cu) at Motoyama, and 8,064 Kt (2.25 % Cu) at the Uchinotai and 2,283 Kt (0.83 % Cu) at Uwamuki orebodies (Dowa Mining Co. Ltd., 1985). The total crude ores produced were 17,835 Kt.

An averaged contents of the main Uchinotai orebodies studied is calculated to be 26 ppm In and 16.8 % Cu. If this In/Cu ratio is applied to the whole ores, the indium contents become 4 ppm; then the total content of the Uchinotai orebodies is calculated to be 32 tons In, which seems a reasonable estimate, compared with the indium production recorded as 18.5 tons in the short period between 1976 and 1983, and low recovery rate of indium during the processing. The early-developed (1884 - 1946) Motoyama orebody is similar in size to the Uchinotai orebodies and rich in copper but the Uwamuki deposits are rich in lead and zinc and poor in indium. If the average feed ore grade of 2.5 ppm of Maeshiro (1978) were applied to the total crude ores produced of 17,835 Kt, the In-content would be 44.5 tons. Therefore, the total content for the Kosaka mine may be around 50 tons In, which may be the largest among massive sulfide deposits in Japan (Table 4).

Copper and zinc concentrates of the Hanawa mine in the eastern Hokuroku basin are also high in indium, 25.7 ppm and 13.5 ppm, respectively (Table 2), which are higher than those of the Kosaka mine. Other high values discovered in individual ore samples are those of the Furutobe mine, eastern Hokuroku basin, and Yokota mine of the Aizu District (Table 2). These ore

Table 4 In-grade and base metal tonnage of representative volcanogenic massive sulfide deposits of the world.

Locality	Age	Tonnage	In content
Lau Basin, SW-Pacific	Recent	2.5 MT	40 ppm
TAG, Mid-Atlantic Ridge	Recent	3.8	1.3
Kosaka, Japan	Miocene	17.8	2.5
(Uchinotai, Japan	Miocene	8.1	4)
Neves-Corvo, Portugal	Late Devonian	262	18
Gaiskoye, Russia	Devonian	300	24
Sibaiskoye, Russia	Devonian	100	10
Brunswick #12, Canada	Ordovician	161	50
Heath Steele, Canada	Ordovician	34	50
Kidd Creek, Canada	Archean 2.71 Ga	135	50
Maranda J, South Africa	Archean, 3.02 Ga	2.7	50

Data source: Schwarz-S. and Herzig (2002) and this study.

deposits are much smaller in size than the Kosaka deposits. Therefore, Miocene Kuroko deposits of the Miocene Green Tuff Belt seem to have low potentiality of indium.

The highest indium content, 207 ppm, was obtained in the Yanahara pyrite deposits in this study. This ore sample is also high in copper (15.2 % Cu) and zinc (1.1 % Zn). An average of the analyzed 10 samples from this deposit is 25 ppm In, 7.2 % Cu and 4,867 ppm Zn. Such copper and zinc concentration, however, is only seen locally in and around the major ore deposits of No. 1 (5,433 Kt), No. 2 (3,084 Kt), No.3 (7,818 Kt) and Lower (18,905 Kt) orebodies, and small orebody group; the total copper-iron sulfide ore is reported to be only 300,000 tons (Dowa Mining Co., Ltd., 1981, 1985). Although high In-values were obtained erratically, indium potentiality may be small in the Yanahara deposits.

Among massive sulfides associated with basaltic rocks, the largest Besshi deposits may have the highest estimated indium content for the largest tonnage produced, although the distribution of indium is sporadic in the deposits. Copper and zinc concentrates of the neighboring Sazare deposits, however, revealed 15.7 ppm and 79.5 ppm In, respectively; those of Shirataki deposit 6.5 ppm and 48.1 ppm In, respectively. Indium is highly concentrated in sphalerite in this metamorphosed massive sulfide ores, rather than copper sulfides in the Kosaka deposits.

Sphalerite was also recovered at the Besshi mine, although we were not able to obtain the concentrates. It is said that the sphalerites occurred mostly 0.n% Zn, locally n% Zn level in the ore deposits of lower stratigraphic horizon of the host Minawa Group (K. Uchida, personal communication, 2006). From the Sazare and Shirataki mines, we learnt that zinc contents are one order of magnitude lower than copper content, but indium contents of the zinc concentrates are one-order of magnitude higher than those of the copper concentrates. Some amounts of indium may be therefore expected in the Besshi-Sazare-Shirataki deposits.

6. Genetic aspects of the Indium anomalies in Southwest Japan

Week indium anomalies have been detected in the Yanahara and Besshi deposits of Southwest Japan. In the Yanahara deposits, two sources can be considered: one is ore fluids released from the host rhyolitic rocks, while the other is much later addition by hidden granitic intrusion. The immediate host rocks for the Yanahara deposits are altered rhyolites of possibly Permian in age. Since indium occurs with felsic volcanic rocks (e.g., Neves Corvo deposit, Ishihara, 2005; Brunswick No. 12 deposit, Ishihara and Murakami, 2007), it is possible to assume that indium was derived from the In- and Sn-rich rhyolitic activities.

The Yanahara ore bodies are located in the Sanyo Sn-rich ilmenite-series granitic province of late Cretaceous age where Sn-W ore deposits also occur (Ishihara and Terashima, 1977). The ore bodies have been cut by quartz porphyry dikes, which may be apophysis of hidden granites, and the ore pyrites are converted to magnetite and pyrrhotite by this intrusion (Higashimoto, 1958). The anomalous In-values were found in pyrrhotite-rich ores from the Lower Orebody. It is possible therefore to speculate that the orebody is closest to the hidden intrusion and trace amounts of indium and tin may have been added from the hidden ilmenite-series granitic bodies during the late Cretaceous time. We need further detailed study here to identify these two possibilities.

Sporadic In-anomalies were found in the thermally metamorphosed lower part in the Besshi deposits. The BSS7 anomaly from the 26^{th} level reveals 167 ppm In,

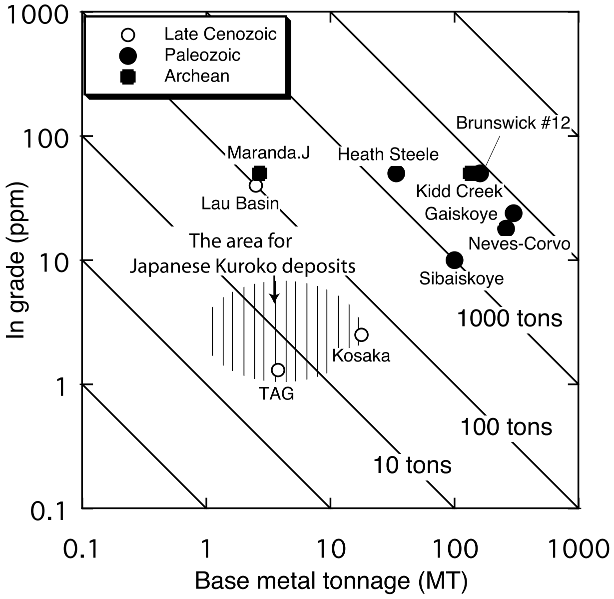

Fig. 5 Grade-tonnage model selected volcanogenic massive sulfide deposits of the world. The dara from Schwarz-S. and Herzig (2002) and this study.

3,570 ppm Sn and 34,400 ppm As (Table 2), and the BSS2 sample with 45.1 ppm In, 127 ppm Ag, 138 ppm Se, 447 ppm Sn and 400 ppm As, but the other three samples from the deep levels revealed no such anomalies. Kase (1988) reported Sn-As-Zn-Ag vein mineralization at the 26th Level of the Besshi mine, and considered that the metals were brought by hidden intrusion of the Miocene granitic activities belonging to the Outer Zone of Southwest Japan. Indium is dominant in the base-metal-rich deposits of the Hoei (Pb-Zn) and Kishu (Cu) deposits in the Outer Zone (Ishihara *et al.*, 2006a). Arsenic, antimony, indium and tin are common mineralized components related to the Outer Zone granitoids. Therefore, these ore components were supplied from the depth through fractures into the lower part of the Besshi deposits whose primary pyrites have been converted to pyrrhotite by thermal metamorphism.

7. Concluding Remarks

Indium contents of individual massive sulfide deposits were estimated based upon new analytical data, and general low values were reconfirmed in the Japanese massive sulfide deposits, including the Kuroko, Yanahara and Besshi types. Even the Miocene Kuroko deposits related to felsic volcanic rocks (cf., Table 3) are low in indium, on the contrary to similar Kuroko types in Paleozoic and Archean terrains in North America and Europe (Fig. 5). Compared with the ores from the Brunswick No. 12 deposits, whose general environment is much dominant in C-bearing reducing agent, the Japanese Kurokos are low in the trace amounts of indium and tin (Ishihara and Murakami, 2007). This fact is impressive considering many high values on base metal deposits of vein and skarn type deposits of granitic affinities in Japan (Ishihara *et al.*, 2006a) and East Asia (Ishihara *et al.*, 2007).

Felsic volcanism related to the Kuroko mineralizations is a part of the Miocene bimodal volcanism erupted through the Kuroko Rift (Yamada and Yoshida, 2005). The basalts are originated in undepleted upper mantle (Nakajima *et al.*, 1995). Andesitic and felsic volcanic rocks and some granitoids with low Sr_0 of 0.704 to 0.706 may have been derived from the mafic lower crust. Rhyodacitic rocks related to the Kuroko mineralization contain only 0.9 to 2.6 ppm Sn (Ishihara and Terashima, 1983). This juvenile nature of the related igneous activities to the Japanese Kuroko deposits may be one of the reasons for the low concentration of indium. Strangely enough, a high value of 40 ppm (Schwarz-S. and Herzig, 2002) was reported from the sea-floor mineralization under similar tectonic setting of the Lau Basin (Hawkins, 1995).

Within the low level of concentration, indium has been concentrated in ores containing tetrahedrite-group minerals in the Miocene Kuroko deposits (e.g., Hanawa, Kosaka-Uchinotai and Furutobe). On the other hand, indium appears to be concentrated in sphalerite in the pre-Neogene massive sulfide deposits. Weak and sporadic anomalies were found in the massive sulfides of the Yanahara deposits, whose source may be either the host rhyolite or later granitic intrusion. The In-anomalies in the deeper level of the Besshi deposits is considered due to overlapping vein-type mineralization related to the Miocene ilmenite-series granitic activities of the Outer Zone of Southwest Japan.

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黒鉱型・別子型などの火山性塊状硫化物鉱床のインジウム含有量

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要　旨

黒鉱鉱床（35試料），柵原鉱床（10試料），田老鉱床（4試料），下川，土倉と槇峰鉱床（6試料），別子型鉱床からの25試料について硫化物鉱石成分を誘導結合プラズマ質量分析法で測定し，インジウムの資源的評価を実施した．北鹿盆地の黒鉱鉱床群では東部の小坂内の岱，花輪，古遠部などがインジウムを多く含み，かつ亜鉛よりも銅との相関性が良い特徴を示し，インジウムが四面銅鉱系サルフォソールトに含まれている可能性を暗示する．小坂鉱山では，内の岱鉱石の含有量，選鉱産物の含有量に基づき約50トンのインジウムが鉱床の含有量として推定されるが，これは世界的にインジウムを生産している大鉱床より2桁低く，我が国にはインジウムに富む塊状硫化物鉱床はないと言える．別子型鉱床の個々の分析値やインジウムに富む亜鉛精鉱で明らかなように，このタイプの鉱床ではインジウムは閃亜鉛鉱に含まれている．佐々連・白滝鉱床の亜鉛精鉱はインジウムに富むが，原鉱のZn品位は0.n%であるから，資源的には期待できない．二畳紀流紋岩中に胚胎する柵原鉱床からは最高値207 ppm Inが得られた．当鉱床に見られるインジウム異常は母岩の流紋岩類か後期白亜紀の貫入岩起源と推察される．別子鉱床下部には散点的な異常（167 ppm以下）が認められるが，これらは中新世の西南日本外帯のチタン鉄鉱系花崗岩の貫入に伴って割れ目規制を受けた熱水鉱化作用が生じ，インジウムが付加されたものと考えられる．