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Article

Chemical characteristics of the indium-polymetallic ores from the Toyoha mine, Hokkaido, Japan

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Abstract: High-grade indium-polymetallic ores of the Toyoha deposits, Hokkaido, which mainly belong to the stage IV mineralization, were studied chemically at E-W trending Shinano-Izumo-Iwami Veins, WNW-ESE trending Soya Vein , and N-S-trending Sorachi-Nemuro Veins. The indium contents go up to 1.0 wt % in the ores (Sorachi, -430 mL). Averaged indium contents and 1000 In/Zn ratio are obtained as follows: Shinano Vein(n=29): 568 ppm and 9.0; Izumo Vein (n=7): 582 ppm and 1.9; Iwami Vein (n=17): 371 ppm and 6.4 (n=16, excluding the highest value of 444.6); Soya Vein (n=4) 1,467 ppm and 3.1; and Nemuro-Sorachi Vein (n=5): 4,050 ppm and 9.1. The whole average is 854 ppm (n=62) and 7.1 (n=61). These indium-rich ores occur in the southeastern part of the Toyoha deposit, where the hydrothermal ore solutions were considered flown out from the depth.

Indium contents of the ores are positively correlated with zinc contents on the Shinano Vein (correlation coefficient of 0.65), but unclear on the whole veins (correlation coefficient of 0.51). Positive correlation between indium and tin is only seen locally (e.g., Iwami Vein). Within available level of 500 meters, zinc content decreases but tin and arsenic contents increase with the depth. Distribution of indium has some similarity with that of tin and arsenic vertically. These chemical characteristics suggest that indium was closely associated with tin and arsenic, besides zinc and cadmium in the hydrothermal fluids. Compared with similar indium-rich ore deposits in sedimentary terrains in Bolivia, indium-contents are similar in the two regions. Mafic components such as iron, copper, nickel, cobalt, arsenic, and silver are, however, richer in the Toyoha deposits than in the Bolivian deposits. Manganese, antimony, bismuth and tin are predominant in the Bolivian ore deposits. These chemical characteristics reflect general difference of the host rocks, juvenile mafic volcanics vs. sedimentary and felsic volcanics, of the two regions.

Keywords: Toyoha deposit, Miocene, mafic host rocks, vein type, lead-zinc, indium, tin

1. Introduction

There are two sources for industrial use of indium: one is submarine volcanogenic massive base-metal sulfides, while the other is vein-type base-metal sulfides. The massive sulfides such as Kidd Creek and Brunswick deposits, Canada, are large in the tonnage of base-metal but low in indium grade. The tin-polymetallic vein-type deposits such as Toyoha and Ikuno-Akenobe deposits in Japan, and many in Bolivian tin-polymetallic belt, are moderate to small in the base-metal size, but the indium grades are high in general. These ore deposits are also volcanogenic occurring mostly in terrestrial volcanic environment. The Toyoha deposit is the largest in Japan, containing ca. 5,000 tons of indium (Ishihara *et al*., 2006).

Toyoha lead-zinc pyrite ores were cropped out along the upper stream (Shirai river) of the Toyohira river, southwest of Sapporo (Fig. 1), which were discovered by geological survey of either by Ikutaro Asai or Kotora Jinbo during 1890-1891s. The property was acquired and developed by the Kuhara Mining Co. in 1914-1921. The Nippon Mining Co. was the successor and re-opened the mine in 1934, and continued the silver-lead-zinc mining up to 1950s. In 1950s, the mining license was shifted to the present owner of the Toyoha Mining Co. Ltd. (Toyoha Mining Co. Ltd., 1981), who developed most of polymetallic ores and ceased the mining on the 31st March, 2006.

Mineralogical studies were most advanced in indium-

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bearing ore deposits of the early days in Japan, including Toyoha deposits (e.g., Kato and Shinohara, 1968; Shimizu *et al*., 1986; Shimizu and Kato, 1991; Ohta, 1989). Yoshie *et al*. (1986), however, tried to evaluate valuable trace components including Au, Cu, Zn, W, In and Co for the mining purpose of the Toyoha mine. Genetic model for the polymetallic deposits was proposed by Yajima *et al*. (1993). Extraction of these useful components during the dressing and smelting processes made the Toyoha ores the most valuable than any other lead-zinc ore deposit in the Japanese Islands and of the world (Ishihara, 2005).

We collected various ores from drilling cores for exploration of major veins of the southeastern part of the Toyoha mine, and analyzed major and trace elements by ICP/MS methods paying special attention to the indium contents. This mine has had largest indium production in the past, over 5,000 tons metal, among major indium-bearing tin-polymetallic ore deposits of Ikuno, Akenobe and Ashio mines in the Japanese Islands (Ishihara *et al*., 2006). This paper reveals chemical characteristics of trace and some major elements of this largest indium-bearing ore deposit in Japan and compare them to similar Miocene tin-polymetallic ores in Bolivia.

2. Geology and mineralization stages

Toyoha mine is situated in Miocene volcano-sedimentary area in the southwestern part of Hokkaido (Fig. 1), and is located very close to Quaternary volcanic front. The famed Jozankei hot spring occurs about 10 km east of this mine and dormant volcano of Muine-yama (1,461m) and Nagao-yama (1,211m) are seen 5 km to the south. Because of the young and active volcanic circumstance, the mining tunnels of the southeastern corner of the Toyoha mine was very hot to the limit of dynamite blasting (170°C) on the wall rocks, and over 40°C in the air temperature.

According to Yoshie *et al*. (1986), the mine area is underlain by Miocene volcanic and sedimentary rocks of three units. The lowest Koyanagizawa Formation is composed of the lowest andesite lava, middle basaltic lava and upper dacite lava and its pyroclastics with very local intercalation of conglomerate and mudstone. Motoyama Formation overlies unconformably the Koyanagizawa Formation and consists of alternative conglomerate, sandstone and mudstone. The uppermost

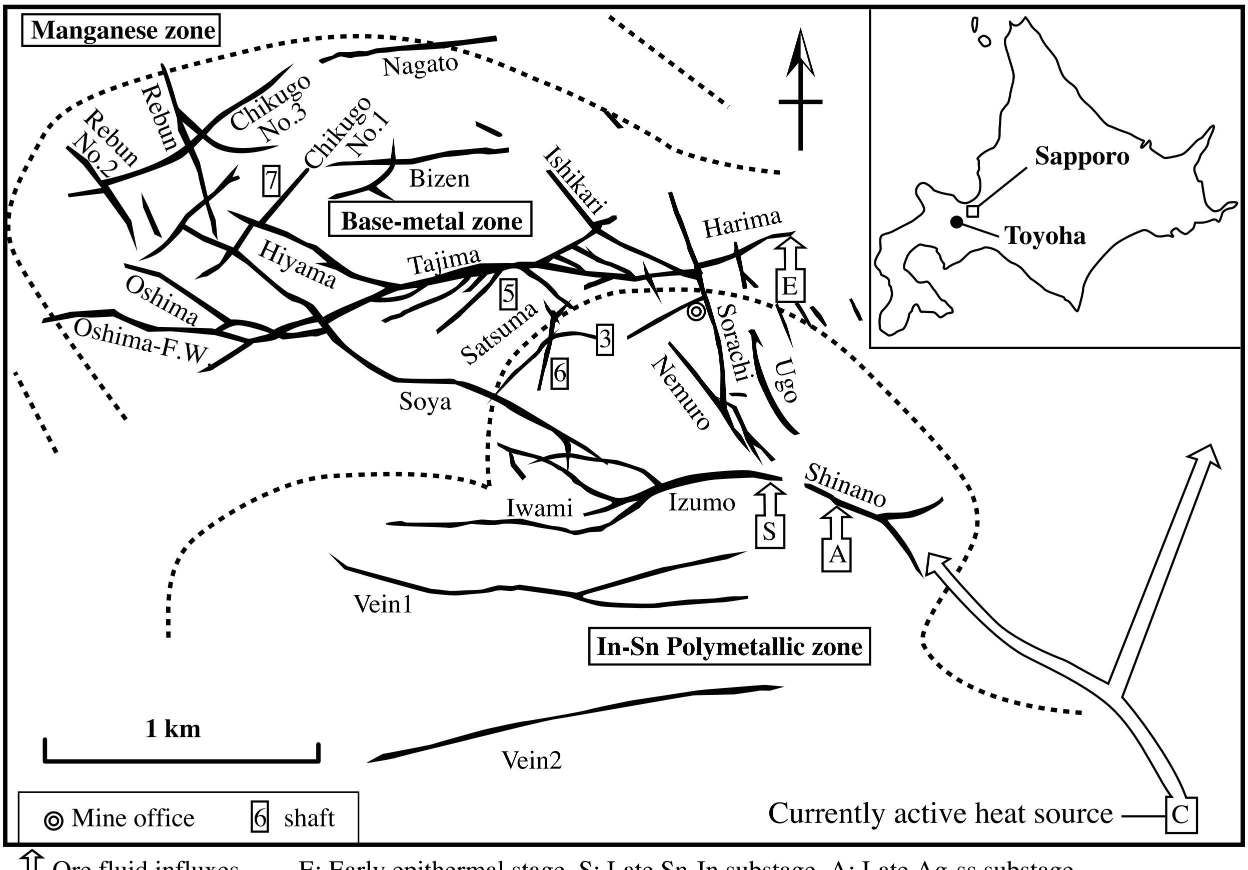

Fig. 1 Location and vein system of the Toyoha mine showing the indium polymetallic zone, base metal zone and manganese zone from the southeast to northwest (originally from Yajima *et al*., 1993).

Nagato Formation, composed of lower fine tuffs and upper andesite lava and its tuff breccia, overlies conformably on the Motoyama Formation. All of these rocks host the ore veins. No large Miocene intrusions have been observed, but small Miocene felsic dikes ("quartz porphyry", 12.8 Ma U-Pb age on zircon, Ishihara *et al*., 2010a) intrude into these host rocks, which is considered branched dikes of the main quartz porphyry (E-W 4 km and N-S 4 km) located in the Jozankei township with the satellitic bodies southward.

The ore deposits are vein type with more than 50 named and un-named veins. Major veins are E-W trending Oshima footwall-Tajima-Harima Vein and Iwami-Izumo-Shinano Veins, WNW-ESE trending Soya Vein, and N-S trending Sorachi Vein (Fig. 1). The mineralizations occurred more than 700 m vertically in blind condition (Fig. 2), which made the Toyoha mine large in production. Vein-type deposits of the Toyoha mine are composed of silver-lead-sphalerite-rhodochrosite ores in the northwestern area, where a part of the ores was cropped out. Moving toward southeastern corner, these ores became polymetallic containing tin, tungsten and indium in the base metal ores. For example, cassiterite and stannite and a new mineral of sakuraiite $(Cu,Zn,Fe)_3(In,Sn)S_4$ were discovered in the Giant Shinano Vein (Yajima, 1977). Zinc-indium mineral of $Cu(Zn, Fe)_2InS_4$ and silver-indium mineral of $AgInS_2$ were reported from Izumo and Sorachi Veins (Ohta, 1980).

These veins were originally classified into the first stage of silver-bearing galena-sphalerite assemblage and the second stage of chalcopyrite-pyrite assemblage, both intruded by the latest rhodochrosite-calcite-silver-quartz veins (Akome and Haraguchi, 1963). The two-stage classification was modified by Yajima and Ohta (1979) who pointed out the characteristic minerals of the first stage as sphalerite, galena, pyrite, arsenopyrite and hematite, and those of the second stage as pyrrhotite, graphite, tin and tungsten minerals, besides sphalerite, galena and pyrite. Thus, both the oxygen fugacity and temperature during the formation are quite different between two stages.

Yoshie *et al*. (1986) and Narui *et al*. (1988) classified crystallization history of the ore minerals into seven stages, which are slightly modified by Sanga *et al*. (1992). They showed the geographic distribution of the stage I and II mineralizations in the E-W veins of the northwestern part, and the main polymetallic veins of the stage III to V in all the NW-SE and N-S veins of the southeastern part. The stage VI and VII veins are seen along NW-SE striking veins as the whole but mainly in the northern area.

Main vein-forming minerals of each stage are seen as follows (Yoshie *et al*., 1986). They also showed average and range of indium contents of the vein width of each stage as follows:

Stage I: Large amounts of quartz containing galena, sphalerite, pyrite, rhodochrosite, hematite, magnetite replacing hematite and argentite. Average indium-contents vary from 10 to 60 ppm In in this stage, but the indium-bearing minerals have not been identified yet.

Stage II: Mainly rhodochrosite and Mn-calcite, together with small amounts of quartz, Mn-silicates, and pyrrhotite-containing pyrite. Indium content of this stage is as low as below 10 ppm.

Stage III: Mainly quartz and pyrite, with small amount of hematite. Indium contents are also as low as

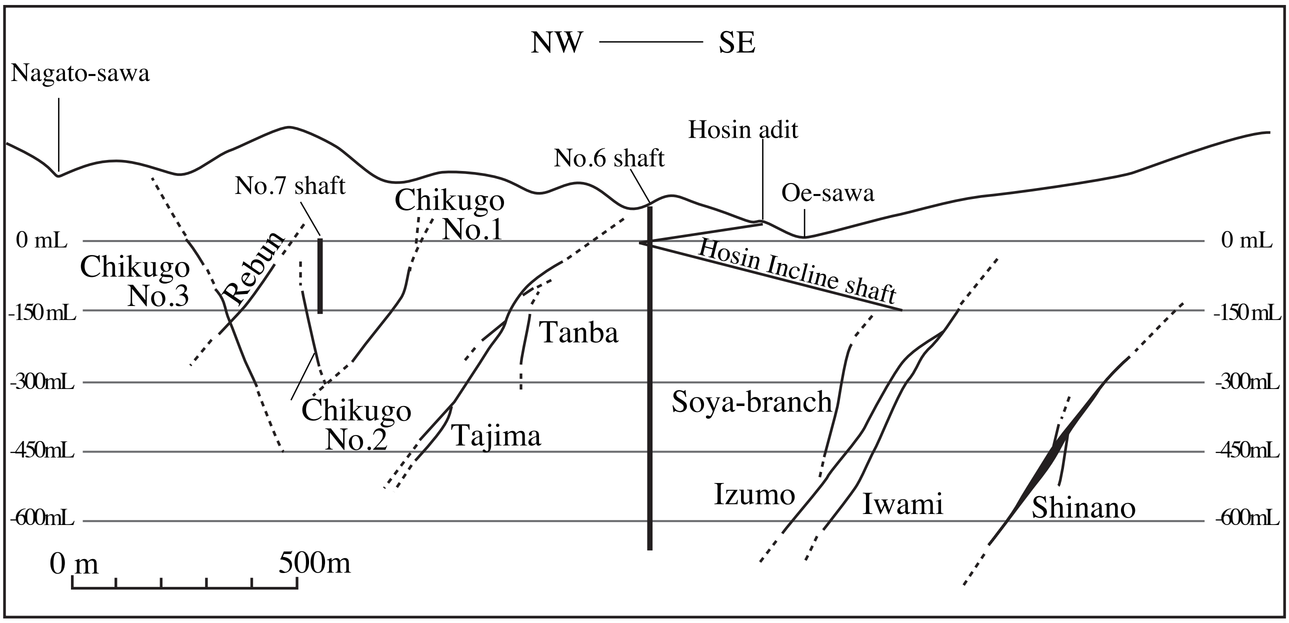

Fig. 2 Idealized E-W section of the Toyoha vein system (from guidebook of Toyoha mine, 1994 edition).

Table. 1 Analytical results of indium-polymetallic ores from the Toyoha mine. Detection limit in ppm.

Elements and ratio	In	1000	Sn	Cd	1000	Zn	Pb	Cu	Fe	Mn	V	Cr	Ni	Co	Ga	W	Mo	As	Bi	Ag	Se	Sb	Ge	Tl
Detection Limit (ppm)	0.1	In/Zn	1	0	Cd/Zn	0.2	0.5	0.2	10.0	1	1.0	0.5	0.5	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1
Shinano Vein (n=29)																								
KO 220-1 -300mL	263	1.4	398	867	4.6	190000	1330	781	181000	95	2	4	1.7	10	15.7	6.9	2.9	2160	1.8	115.0	13.9	56.8	0.1	0.4
KO 220-1 do.	817	2.0	1090	1850	4.5	414000	363	2410	102000	312	1	6	0.9	65	12.4	95.8	2.2	998	1.2	84.5	8.9	27.6	0.2	0.1
KO 221-1 do.	44	0.7	127	281	4.3	65300	48700	433	141000	679	21	12	13.4	14	2.9	14.3	2.3	610	1.5	146.0	22	23.8	0.1	0.5
KO 221-2 do.	453	1.6	395	1590	5.6	282000	3660	1120	169000	163	< 1	3	0.9	21	7.4	5.5	1.7	695	9.0	24.4	7.1	15.1	0.1	< 0.05
KO 217-1 350mL Shita III	892	3.2	737	1310	4.7	279000	24000	1870	200000	499	1	14	1	55	7.5	10.3	14.3	1720	5.0	73.0	3.2	82.8	0.2	5.6
KO 217-7 do.Shita-IV	258	3.7	299	398	5.7	69900	632	59200	186000	65	2	8	5.6	38	25.2	8.8	3.4	2970	2.7	302.0	43.1	46.1	0.1	0.6
KO 212-1 do., 450 mL	563	12.7	5370	179	4.0	44200	2350	91900	198000	80	7	18	224	3150	19.1	122	4	68900	557.0	>100	21.6	841	3.2	0.5
KO 213-2 do., do.	2550	29.2	5900	1020	11.7	87200	749	112000	236000	56	4	12	127	1300	136	118	2.4	21300	54.0	756.0	43.5	258	1.1	0.4
KO 215-1 do., do.	824	18.4	6040	304	6.8	44700	2650	37900	217000	165	10	24	127	1700	43.7	906	45.9	25800	62.3	281.0	84	348	0.7	0.7
KO 218-1 do., 550 mL	220	33.1	11500	103	15.5	6640	10800	46300	215000	61	22	42	62.6	672	29.7	427	2.4	12400	873.0	953.0	16.1	213	0.4	1.0
KO 218-3 do., do.	154	0.7	257	715	3.1	233000	84800	308	47900	153	11	11	2.7	8	53.2	4.5	1.9	3280	10.3	486.0	4	467	1	1.3
KO 218-5 do., do.	94	10.8	1070	56	6.4	8740	6400	25000	262000	41	22	36	198	2500	31.9	275	3	72300	526.0	724.0	8.9	1060	0.7	0.7
KO 218-6 do, do..	222	1.4	236	777	4.8	163000	880	743	252000	76	1	3	0.8	55	33.5	93.6	1.8	1740	7.4	109.0	3.6	84	0.5	0.9
KO 218-6 do., do.	516	1.8	298	2020	7.2	282000	64200	1080	131000	82	< 1	6	0.5	196	109	173	11.8	663	45.3	434.0	23	161	1.7	0.2
KO 219-1 do., -590 mL	2800	6.1	508	2940	6.4	461000	36500	2650	31400	169	< 1	4	1.4	191	168	14.8	11.1	2160	9.2	1190.0	193	540	3.5	0.2
KO 219-2 do., do.	177	1.1	550	1330	8.5	156000	3200	1150	245000	345	< 1	3	1.4	67	90.4	9.4	2	1070	2.9	140.0	116	140	0.4	1.6
KO 3-8 do., -600 mL	73	19.9	868	36	9.8	3660	2370	84800	268000	33	3	6	10	77	7.1	6	2.1	2390	218.0	321.0	14.3	83.8	1.8	0.2
KO 4-1-1 do., do.	418	1.1	467	2060	5.4	378000	37700	1580	51800	101	1	8	4.1	104	58.8	1.1	5.3	12400	7.4	372.0	273	754	0.4	0.5
KO 4-14-' do., do.	760	3.6	785	812	3.8	214000	1220	1920	179000	200	3	8	10.9	586	24.5	106	9.4	16000	19.0	116.0	18.9	169	0.2	0.3
KO 4-21-' do., do.	1310	3.1	1050	2160	5.2	416000	9360	880	25500	7710	1	28	1	4	72.4	10.8	2	1710	2.9	671.0	15	367	91	111.0
KO 4-23 do., do.	268	8.3	1970	276	8.5	32300	26900	72800	184000	48	13	7	442	2420	43.8	1.7	2.9	34000	144.0	346.0	16.2	329	1.1	0.8
KO 5-14 do., do.	151	8.7	567	143	8.2	17400	580	41900	109000	27	8	4	254	1410	24.8	4.2	1.8	18800	83.3	153.0	5.1	176	0.6	0.5
KO 5-24 do., do.	703	8.4	10000	524	6.2	83900	4760	110000	182000	45	1	3	63	1370	57.6	68.3	1.9	29800	745.0	1260.0	2.8	969	9	0.3
KO 5-28 do., do.	56	0.1	472	2110	4.5	468000	12000	123	15200	180	1	10	< 0.5	12	6.8	1.6	1.8	157	1.0	199.0	4.9	1150	8	14.8
KO 6-9 do., do.	35	26.0	1080	10	7.6	1330	258	10200	209000	40	40	7	4.9	157	48.3	22.9	7.6	6370	17.6	40.3	15.7	46.2	0.5	0.4
KO 6-11 do., do.	17	36.4	149	5	10.8	472	135	5470	113000	21	22	3	2.5	84	25.7	15.7	4.3	3410	20.8	20.1	21.1	26.3	0.2	0.3
KO 6-14 do., do.	314	0.9	1150	1880	5.5	343000	217000	1460	38800	169	1	5	0.9	12	52.3	2.4	1.6	2950	6.4	739.0	10.6	691	3.2	2.2
KO 8-7 do., do.	1100	1.9	958	4000	6.9	581000	10100	1340	63400	206	1	4	< 0.5	3	68.7	3.3	1.7	714	2.6	715.0	26.7	975	92	24.3
KO 8-9 do., do.	422	13.8	13500	207	6.8	30600	2680	47300	265000	37	2	5	27.2	1190	23.4	95	2.2	43900	182.0	419.0	22.6	591	3.5	0.4
Average	568	9.0	2338	1033	5.6	184701	21251	26366	155793	409	8	10	58.9	603	44.8	90.5	5.44	13495	124.8	399.6	36.5	369	7.8	6.1
Izumo Vein (n=7)																								
KO 197-1 Izumo 150mL	110	0.2	540	3210	6.2	517000	8930	2380	55000	1100	1	4	0.6	40	57.9	38.4	8.2	1280	2.9	335.0	40.8	114	0.1	0.5
KO 92-3 do. -300mL	319	0.7	202	903	2.0	461000	27000	3640	97600	626	7	19	1.3	47	8.8	103	2.3	536	3.5	127.0	30.6	65.3	0.5	0.1
KO 98 do. -320 mL	2340	5.4	1270	2210	5.1	437000	1950	3990	84500	210	3	4	1.7	73	89.2	186	9	504	8.3	156.0	21.8	46.5	0.2	0.4
KO 120 do., -450 mL	122	0.4	187	1090	3.8	287000	689	71	124000	322	2	3	0.6	118	31.8	306	8.5	19000	0.9	226.0	29	414	0.3	0.8
KO 108-1 do. -550mL	651	2.5	574	1050	4.0	264000	3960	2150	232000	301	20	11	8.2	97	11.7	171	5.2	12900	9.4	119.0	10.5	85.8	0.5	0.3
KO 108-1 do., do.	248	1.1	739	870	3.8	230000	174000	1860	130000	289	12	8	9.1	106	13.1	48.5	63.4	40000	10.1	556.0	77	499	0.3	0.5
KO 108-2 do. Do.	287	3.3	151	373	4.4	85700	1250	447	343000	209	30	9	3.2	163	6.4	484	3.1	3180	2.4	25.6	14.7	46.3	0.2	0.4
Average	582	1.9	523	1387	4.3	325957	31111	2077	152000	437	11	8	3.5	92	31.3	191	14.2	11057	5.3	220.7	32.1	182	0.3	0.4

below 10 ppm.

Stage IV: Mainly massive sphalerite and pyrite with little gangue minerals. Associated minerals are pyrrhotite, arsenopyrite, marcasite, chalcopyrite, galena and wurtzite. Sphalerite of this stage is black to dark brown in color and contains 7-8 mole %FeS, which is much higher than that of the Stage I. The indium contents of this stage are very high, having generally 300~400 ppm In, and locally exceeding 1,000 ppm In. Almost all of indium-, tin- and tungsten-bearing minerals of the Toyoha mine occur associated with this stage of the sphalerites and other indium-bearing minerals from the Sorachi, Nemuro, Ishikari, Soya, Izumo and Shinano Veins of the southestern part.

Stage V: Chalcedonic quartz containing chalcopyrite and Ag-bearing tetrahedrite, associated with sphalerite, pyrite, arsenopyrite and stannite. The indium contents are below the detection limit (<10 ppm).

Stage VI: This is only seen in the Soya Vein, as an early quartz-chlorite vein and later galena-sphalerite-quartz-chlorite vein. The indium contents are below the detection limit (<10 ppm).

Stage VII: Mainly Mn carbonates, associated with quartz, pyrite and Mn-silicates. The latest stage is characterized by Sb-minerals such as jamsonite and stibnite (Narui *et al*., 1988). The indium contents are below the detection limit (<10 ppm).

3. Analyzed samples, method and results

The analyzed samples were taken from drill cores for the underground exploration. They belong to the stage IV ores of the E-W and/or WNW-ESE striking veins of Shinano Vein at -300 mL to -600 mL (n=29), Izumo

Table. 1 Continued.

Elements and ratio	In	1000	Sn	Cd	1000	Zn	Pb	Cu	Fe	Mn	V	Cr	Ni	Co	Ga	W	Mo	As	Bi	Ag	Se	Sb	Ge	Tl
Detection Limit (ppm)	0.1	In/Zn	1	0	Cd/Zn	0.2	0.5	0.2	10.0	1	1.0	0.5	0.5	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1
Iwami Vein (n=17)																								
KO 184 Iwami, -150mL	125	0.3	449	1550	4.2	373000	88300	4820	105000	592	1	4	1.3	5	5.6	1.2	1.7	461	1.3	254.0	92.5	56.4	0.1	0.2
KO 176-3 do. -300mL	1400	2.7	1260	6760	13.1	517000	2310	3760	81700	297	1	6	6	31	38.2	40.6	1.7	233	3.7	93.0	10.2	38.4	0.5	0.1
KO 178-2 do., do.	11	0.2	181	204	3.2	62900	25600	1240	387000	390	2	9	1.2	1	0.9	5.6	2.4	2170	1.2	47.5	22.3	32.5	0.2	0.1
KO 179-1 do., -320mL	208	1.2	522	998	5.9	169000	407000	799	20400	978	< 1	5	0.6	8	16.4	2.5	2.8	42	0.5	1260.0	6.2	250	0.1	0.9
KO 179-2 do, do.	1	0.1	78	3	0.6	5010	1670	39	412000	241	2	6	2.1	1	0.5	2.1	1.8	277	0.4	21.8	9.6	111	8.5	2.9
KO 179-3 do., do.	312	0.8	436	1530	4.0	379000	3040	1690	184000	702	8	13	2.9	34	13.9	6	6.7	723	1.8	84.9	4.3	21.7	0.2	0.3
KO 180 do.,-335mL	243	0.7	593	2120	5.9	358000	106000	1340	108000	633	1	7	0.6	61	33.5	67.5	3.3	440	17.6	330.0	15.5	157	1	1.9
KO 181 do., 350 mL	954	2.2	590	1940	4.5	431000	856	2100	125000	355	1	4	1.8	28	14.9	3.7	2	608	4.4	54.8	96.6	17	0.5	0.1
KO 189-2 do., -400 mL	1070	2.2	580	1920	3.9	493000	397	3740	48400	344	1	11	1.2	8	6.5	14.4	1.8	205	1.6	65.9	23.5	38.4	0.1	< 0.05
KO 182-1 do., -450 mL	151	0.8	154	1050	5.3	198000	4430	486	289000	269	2	5	1	7	5.3	10.3	2	1080	5.9	26.5	16	10.6	0.2	< 0.05
KO 182-4 do., do.	203	0.4	458	1990	4.3	461000	5660	1440	87500	320	1	4	5.9	146	13.7	19.2	2.2	28300	1.6	269.0	8.6	750	1.2	< 0.05
KO 194-2 do.,-500 mL	369	2.4	409	842	5.5	152000	1730	642	305000	126	23	18	11	159	51.4	230	40.5	6820	3.8	128.0	18	288	0.3	0.7
KO 194-2 do., do.	471	2.7	450	1100	6.3	174000	1510	1620	198000	106	< 1	1	2	129	59.1	122	46.5	25700	1.9	>100	14.2	731	1.3	0.5
KO 193 do. -600mL	195	1.5	1900	599	4.7	127000	7970	23500	329000	184	11	14	4.6	17	9.4	10.7	4.4	682	16.6	137.0	24.4	39	0.3	0.1
KO 195 do., do.	285	444.6	871	22	34.0	641	122	208000	238000	10	2	3	2.2	67	3.7	164	1.7	219	28.9	407.0	13.5	6.8	0.2	< 0.05
KO 196-1 do., do.	173	0.8	1040	1010	4.9	208000	1130	3330	246000	182	27	15	6.7	106	59.5	244	4	16000	13.9	58.3	19	219	0.5	0.1
KO 196-2 do., do.	140	82.8	765	20	12.1	1690	1230	49700	374000	52	1	14	3.6	17	1.1	10.5	1.9	488	111.0	158.0	69.9	10	0.4	< 0.05
Average	371	32.2	632	1392	5.8	241779	38762	18132	208118	340	5.6	8	3.2	48	19.6	56.1	7.49	4968	12.7	212.2	27.3	163	0.9	0.7
Soya Vein (n=4)																								
KO 132 -400 mL	155	0.9	563	668	3.7	182000	452000	1280	11000	85	< 1	3	< 0.5	7	6.3	0.8	4.2	51	11.5	1250.0	4.8	59.4	0.1	0.2
KO 135a -450 mL	143	0.3	1520	2200	4.4	498000	4680	7580	55000	601	1	3	0.6	26	11.1	3	5.9	3840	4.8	157.0	9.9	101	0.3	0.1
KO 135b do.	220	0.4	1580	3360	6.5	516000	16300	3810	59000	278	< 1	3	< 0.5	55	18.3	2.3	3.1	540	4.4	268.0	25.8	264	1.4	< 0.05
KO 138 do. -500 mL	5350	11.0	1420	3020	6.2	488000	2970	7520	47800	347	3	6	0.8	75	9.7	3.2	3.6	53	12.3	147.0	55.6	11.3	0.5	< 0.05
Average	1467	3.1	1271	2312	5.5	421000	118988	5048	43200	328	2	4	0.7	41	11.4	2.33	4.2	1121	8.3	455.5	24	109	0.6	0.1
Nemuro & Sorachi Veins (n=5)																								
KO 131 Nemuro-150mL	86	0.4	466	839	3.9	217000	204000	735	175000	339	1	4	< 0.5	40	5.6	57.3	1.9	1880	2.5	353.0	179	183	0.2	0.3
KO 126 Sorachi-365mL	8230	17.5	2590	3500	7.5	469000	660	14000	70700	237	1	5	1.2	80	17.5	33.1	7.2	173	3.4	174.0	23.9	53	1.2	< 0.05
KO 112-2 do. -430mL	803	1.9	420	1990	4.6	428000	3520	1130	113000	727	2	13	4	48	88.6	53.7	20.2	766	9.5	256.0	33.9	54	0.2	0.2
KO 112-3 do., do.	10400	23.4	1950	6390	14.4	445000	6120	12600	60100	932	2	5	7.2	102	> 500	4.3	3.4	1240	26.5	15000.0	23.4	6640	27	3.4
KO 113 do., -450mL	731	2.5	474	1230	4.2	292000	1050	2380	214000	1700	6	10	2.4	68	9.1	83.3	4.1	1120	4.3	43.6	55.9	40.1	0.2	0.1
Average	4050	9.1	1180	2790	7.5	370200	43070	6169	126560	787	2.4	7	3.7	68	30.2	46.3	7.36	1036	9.2	3165.3	63.2	1394	5.7	1.0
Whole average	854	14.2	1503	1396	5.7	246505	35231	18362	160124	418	7	9	30	314	33	83	7	9079	63.7	563.0	34.8	357	4	3.5
Zn concentrates	1030	2.1	1650	2740	5.7	483000	12800	4540	61900	607	5	12	4	32	133	18	13	1930	38.0	471.0	31.7	417	0.3	2.2
Pb concentrates	270	n.c.	5740	211	8.5	24900	648000	19800	53000	235	5	45	7	37	18	22	67	2670	557.0	2730.0	75.1	621	0.6	2.2
Cu concentrates	817	n.c.	13500	305	13.9	21900	35100	205000	246000	97	4	4	32	237	71	22	62	3700	2500.0	3820.0	50.3	1240	3.1	1.0
Tailing-1	57	2.2	274	134	5.1	26300	4290	733	307000	3780	61	58	43.2	114	17.7	109	7.8	18100	23.5	76.9	9.0	78.5	0.5	0.9
Tailing-2	68	4.1	991	87	5.2	16700	1220	3320	195000	3610	71	52	49.2	273	24.1	66.8	6.0	12200	216.0	78.1	12.7	134	0.5	0.7

Analyst：ActLabs by ICP/MS. N.c., not calculated

Vein at -150 mL to -550 mL (n=7), Iwami Vein at -150 mL to -600 mL (n=17), and Soya Vein at -400 mL to -500 mL (n=4) from the east to west. From N-S series veins, the analyzed samples are obtained from Sorachi Vein at -365 mL to -450 mL (n=4) and Nemuro Vein at -150 mL (n=1). These veins are shown in Fig. 1 and depth of the sample location is shown in Table 1.

3.1 Results on the ores and tailings

The chemical analyses were performed at Actlabs (Ancaster, Canada) and all by TD-MS (Total Digestion-Mass Spectrometry). High-grade Pb ores (>5000 ppm Pb) are, however, analyzed separately by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). High-grade Ag values (>100 ppm) are also re-examined by chemical method after dissolving only sulfide elements. Their detection limits and obtained values are shown in Table 1. Averaged chemical compositions of all the analyses are shown at the bottom of Table 1. Chemical composition of two tailing samples from the Oshidori-sawa second covering point in the center and north margin is also supplemented.

The whole averaged value of our study is compared with the average composition of the produced ores in 2004, which was provided by the Toyoha mine and given in parenthesis as follows: In 854 ppm (309 g/t), Ag 563 ppm (305g/t), Cu 1.84 % (0.61 %), Pb 3.52% (2.17%), and Zn 24.65% (11.24%). Comparing with the mine's data, the average of our studied samples are higher in all economic elements, such as In (x 2.8), Ag (x1.9), Cu (x 3.0), Pb (x 1.6) and Zn (x 2.2), implying that we selected higher grade ores than the produced ores. The iron content of our studied ores is

16.0%. These results agree to the fact that the studied ores were mostly selected from the later-stage high-grade veins containing much pyrrhotite and Fe-rich sphalerites, besides pyrite.

Indium contents of the studied ores vary from 11 ppm to 10,400 ppm, except for one (1 ppm) with very low content of the ore minerals but iron sulfides. Averaged values for major E-W veins are as follows: 568 ppm In for the Shinano Vein (n=29), 582 ppm In for the Izumo Vein (n=7), and 371 ppm In for the Iwami Vein (n=17). The whole samples (n=62) are 854 ppm in the average. The Soya and Nemuro-Sorachi Veins are very high, 1,467 ppm In (n=4) and 4,050 ppm In (n=5), respectively. Another way to evaluate indium anomaly of one given

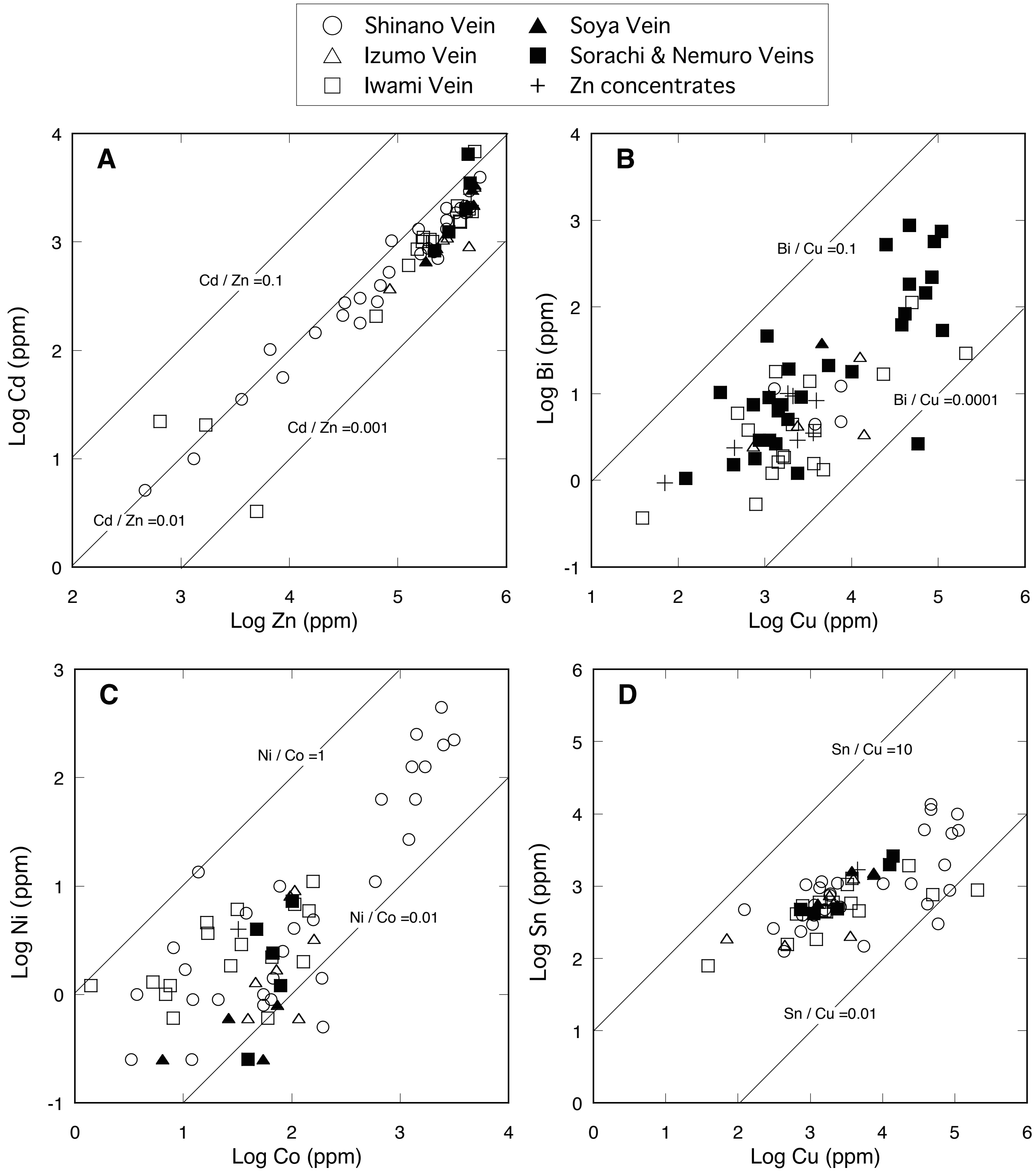

Fig. 3 Binary diagrams for four pairs with the high correlation coefficients in the log-scale, as Cd-Zn 0.95, Bi-Cu 0.75, Ni-Co 0.73 and Sn-Cu 0.71.

Table. 2 Distribution coefficient among the analyzed ores from the Toyoha mine (n=62), excluding Zn concentrates and tailings, and ores from Hosin Inclined Shaft.

	In	Sn	Cd	Zn	Pb	Cu	Fe	Mn	Cr	Ni	Co	Ga	W	As	Bi	Ag	Se	Sb
In	1.00																	
Sn	0.48	1.00																
Cd	0.66	0.08	1.00															
Zn	0.51	-0.06	0.95	1.00														
Pb	-0.08	-0.07	0.32	0.37	1.00													
Cu	0.30	0.71	-0.28	-0.45	-0.28	1.00												
Fe	-0.27	0.00	-0.50	-0.47	-0.43	0.25	1.00											
Mn	0.18	-0.23	0.60	0.69	0.33	-0.52	-0.34	1.00										
Cr	0.01	0.17	-0.16	-0.13	0.05	0.14	0.20	0.13	1.00									
Ni	0.06	0.49	-0.38	-0.43	-0.23	0.62	0.44	-0.44	0.43	1.00								
Co	0.34	0.58	-0.10	-0.22	-0.24	0.59	0.28	-0.46	0.16	0.73	1.00							
Ga	0.56	0.36	0.42	0.28	0.00	0.16	-0.25	0.00	-0.05	0.20	0.47	1.00						
W	0.20	0.22	-0.09	-0.13	-0.35	0.17	0.47	-0.14	0.31	0.33	0.55	0.22	1.00					
As	-0.04	0.33	-0.21	-0.22	-0.15	0.31	0.43	-0.35	0.19	0.70	0.69	0.33	0.43	1.00				
Bi	0.17	0.65	-0.36	-0.48	-0.09	0.75	0.28	-0.60	0.27	0.70	0.72	0.27	0.30	0.49	1.00			
Ag	0.37	0.45	0.27	0.14	0.47	0.29	-0.44	-0.01	0.01	0.14	0.22	0.53	-0.07	0.09	0.33	1.00		
Se	0.17	0.02	0.11	0.08	0.05	0.09	0.06	0.13	0.03	-0.04	0.06	0.11	0.05	0.03	-0.05	0.07	1.00	
Sb	0.13	0.33	0.21	0.20	0.33	-0.01	-0.26	0.00	0.05	0.26	0.35	0.57	0.05	0.52	0.21	0.64	-0.03	1.00

deposit is 1000In/Zn ratio, which is also shown in Table 1. At the Toyoha mine, the 1000In/Zn of the whole measurement is 7.1, excluding unusually low zinc and high copper ore of KO195.

The 1000In/Zn of zinc concentrates is 2.1, but that of the whole average of our studied result is 7.1. These figures imply that indium occurs not only in the sphalerites but also in many other minerals, such as tin, copper, silver and antimony sulfides and sulphosalts, in the Toyoha ore deposits. There is an extremely high 1000In/Zn ratio of 445 in the ores of the Iwami Vein, which is a local massive chalcopyrite ore containing only 641 ppm Zn and gives the highest value of 445 (KO195, Table 1). This value was excluded in the average calculation. Copper-indium mineral, such as roquesite ($CuInS_2$) may be expected to occur in this sample. The other trace elements rich in the studied veins are arsenic 9,079 ppm, tin 1,503 ppm, cadmium 1,396 ppm, manganese 418 ppm, antimony 357 ppm, cobalt 314 ppm, tungsten 83 ppm, bithmuth 64 ppm, gallium 33 ppm and selenium 35 ppm.

Tailings of possibly 2004 production, which are now completely covered by a synthetic sheet, are rather high in zinc (2.63 and 1.67 %) and are also high in indium (57 and 68 ppm) and tin (274 and 991 ppm), reflecting the ores mined out in the last stage of the mining. Tailings are also high in arsenic (1.2~1.8%), which is 1.7 times of the whole average of the studied ores, implying that the element as arsenopyrite tends to move to the tailings after flotation, which is clearly observed in lead-zinc ores of North Vietnam by Ishihara *et al*. (2010a). As far as increasing ratio is concerned, vanadium (11 times), manganese (9 times), and chromium (6 times) increased in the tailings. There are not much differences on the other ore components, such as Ni (1.7 times), Bi (1.7 times), Fe (1.6 times) and Mo (1 time). All the other elements, which are mostly ore metals, are decreased in the amounts (Table 1), because they were taken out by the flotation.

3.2 Correlation coefficient among ore metals

Correlation coefficient among the selected analyzed components of the ores, excluding those from the Hosin Inclined Shaft and zinc concentrates and tailings, are shown by log unit in Table 2. The total number is 62. The highest five values are obtained on the following pairs: Cd-Zn=0.95, Bi-Cu=0.75, Co-Ni=0.73, Bi-Co=0.72 and Cu-Sn=0.71; which are shown also in their binary diagrams, except for the Bi-Co pair (Fig. 3 A~D). Cd and Zn relationship is usually most beautiful in all the studied sphalerite-bearing ore deposits (e.g., Ishihara *et al*., 2006). The highest correlation coefficient on the Cd-Zn indicates cadmium substituting Fe and Zn in sphalerite. Co-As pair has also high value of 0.69, because cobalt is often substituted in arsenopyrite (Ishihara, 2011). Related to In, high values are obtained with Cd(0.66), Ga(0.56), Zn(0.51) and Sn(0.48).

On the individual veins, which are not shown here, the Shinano and Iwami Veins are mentioned here, because large numbers of the chemical analyses and the Shinano Vein formed closest to the supposed feeder of the ore solution (Fig. 1), while the Iwami Vein representing its western margin. Shinano Vein (n=29) has only seven pairs with the correlation coefficients higher than 0.80, such as Cd-Zn=0.98, As-Ni (0.87), As-Co (0.84), Co-Ni (0.84), Bi-Co (0.82), Cu-Ni (0.81) and Cd-V (0.80). On the other hand, the Iwami Vein (n=17) has only two pairs higher than 0.80, as Cd-Zn (0.92) and Co-Ga (0.80), implying that the Shinano ores were precipitated close to the conduit of the ore solutions.

3.3 Variation diagrams including indium

Indium was first found in stannite and Ag-bearing tin-sulfides by Yajima (1977). Binary diagram of indium vs. tin is given in Fig. 4A. The studied ores are plotted in the In/Sn ratio varying from 0.01 to 10, and there is a weak positive correlation between two elements as a whole, although the correlation coefficient in the log scale is 0.48. The ores from the Shinano Vein are widely scattered, while those of the Izumo Vein tend to have high In/Sn ratio. Indium contents of the Soya, Sorachi and Nemuro Veins show larger vertical variation than those of tin.

Indium is positively correlated with zinc in the In-Zn diagram, especially on the Shinano ores (Fig. 4B). The ores of the Iwami Vein are widely scattered, particularly to the low indium side. Correlation coefficient of the whole analyses is 0.51. In/Zn ratio varies from 0.0001 to 0.05, but two of the Iwami Vein exceed 0.05, in which indium minerals may be expected (KO195 and KO196-2). Again, ores of the Soya, Sorachi and Nemuro Veins, have large variation of indium in the high-grade sphalerite ores. Thus, mode of occurrence of

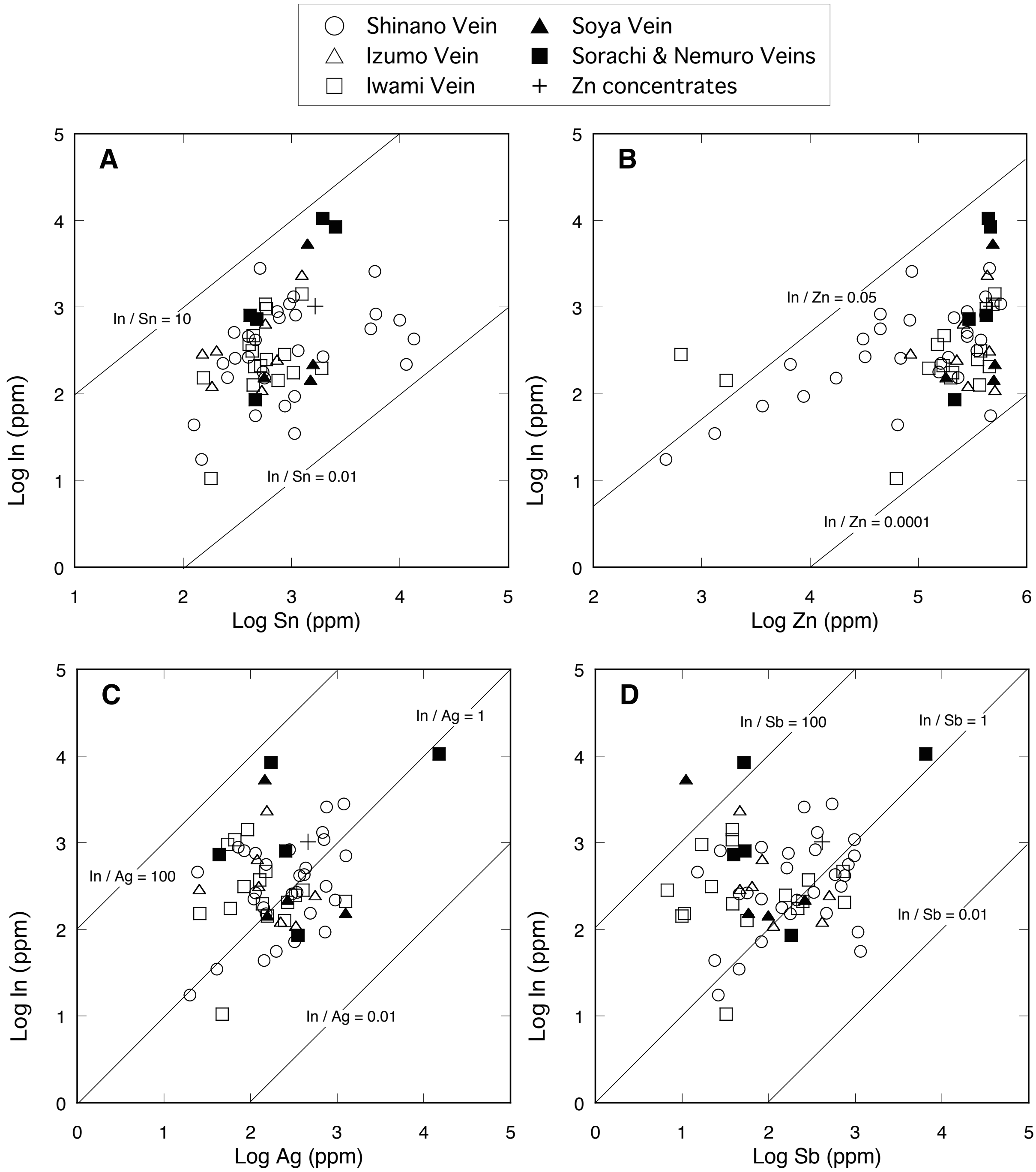

Fig. 4 Binary diagrams for In-Sn, In-Zn, In-Ag and In-Sb of the studied ores from the Toyoha mine.

indium in these N-S veins would be different from that of the E-W veins.

Indium is most positively correlated with silver around the In/Ag =1 (Fig. 4C). Their correlation coefficient is 0.37 (Table 2), which is lower than that of In-Zn. Indium is similarly distributed with antimony (Fig. 4D) but their correlation coefficient is only 0.13 (Table 2).

3.4 Vertical variation of the ore components

Fig. 5 is vertical plotting of average contents of each vein width for In, Zn, Sn, As and In/Zn used for ore reserve calculation at the Toyoha mine (T. Yoshie, personal communication), which is channel sampling done at mining face in the 1990s. For In (Fig. 5A), the content increases with depth on the Izumo-Shinano ores, except for one plotting. Similar interpretation may be said on the Sorachi ores, except for two plottings. In/Zn pattern is similar to the In plotting (Fig. 5B). However, the Zn contents are completely different, in decreasing with the depth (Fig. 5C). On the other hand, the Sn and As contents increase with the depth or highest around 500 mL (Figs 5D, E).

4. Comparison with Bolivian deposits

Both the Toyoha and Bolivian indium-bearing base metal regions are volcanogenic. Yet there are similarities and unsimilarities between the two regions. Basement terrains of the two regions are essentially accreted marine sediments of Cretaceous age in the Toyoha mine area, and of the middle Paleozoic in the

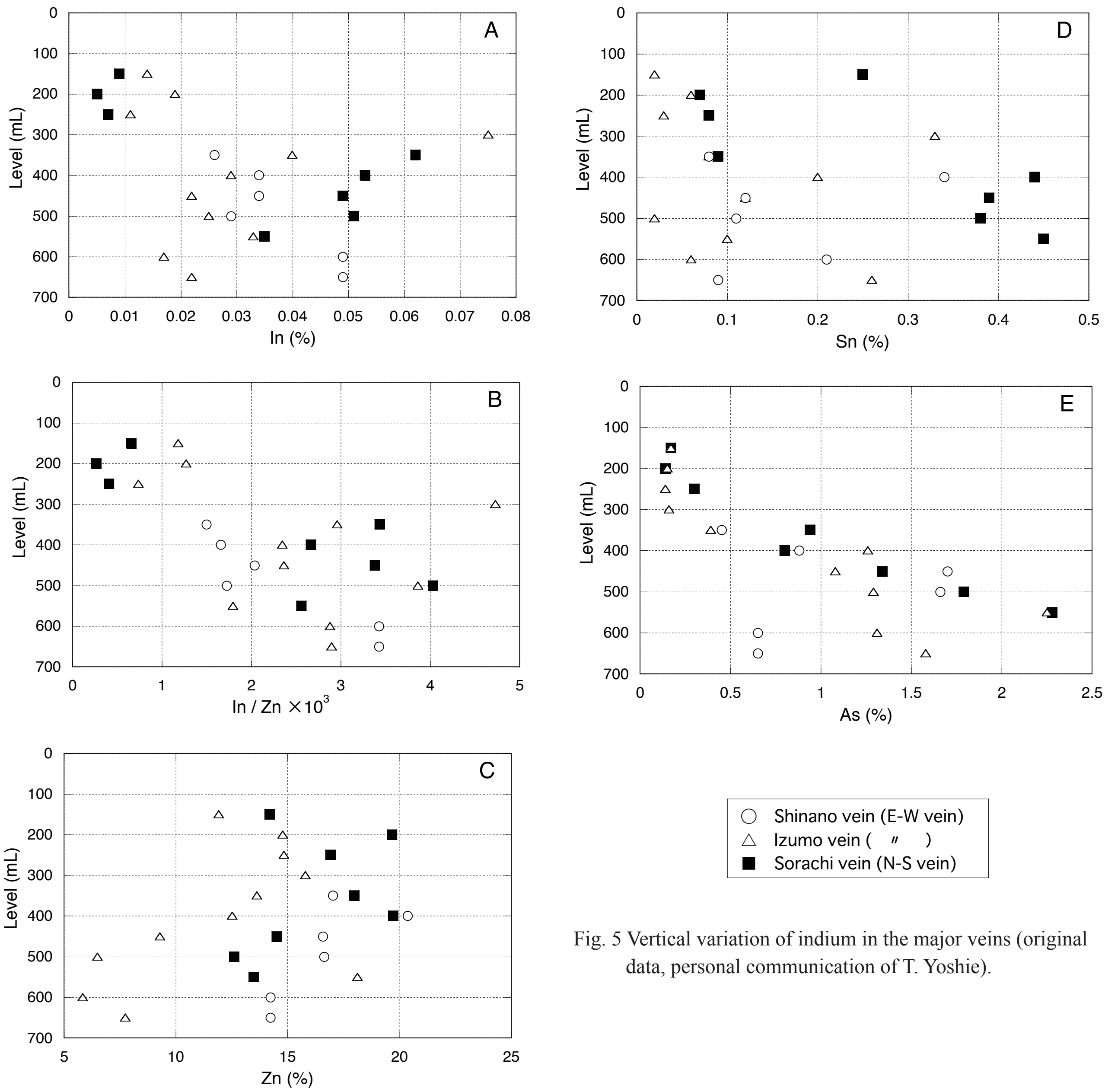

Fig. 5 Vertical variation of indium in the major veins (original data, personal communication of T. Yoshie).

Table. 3 Comparison between averaged ores and concentrates of the Toyoha and some Bolivian ore deposits. The Bolivian data from Ishihara *et al*. (2010c).

	1,000 In/Zn	1,000 Cd/Zn	In ppm	Sn ppm	Cd ppm	Zn ppm	Pb ppm	Cu ppm	Fe %	Mn ppm	Ni ppm	Co ppm	Ga ppm	W ppm	Mo ppm	As ppm	Bi ppm	Ag ppm	Sb ppm	Se ppm
Average ores																				
Toyoha mine (n=	3.5	7.1	854	1503	1396	246505	35231	18362	16.01	418	30	314	45	83.2	7.1	9079	64	563	357	35
Bolivia (n=46)	5.3	5.7	768	2284	1490	262296	15941	5193	12.50	734	10	61	82	13.0	0.3	3989	134	144	4024	11
Zinc concentrates																				
Toyoha mine	2.1	5.7	1030	1650	2740	483000	12800	4540	6.19	607	4	32	133	17.6	13.0	1930	38	471	417	32
Bolivar mine	1.7	7.7	584	2650	2640	343000	29500	3300	8.88	355	11	11	199	0.6	0.7	1360	474	188	1030	8
Porco mine	1.2	3.9	498	1320	1600	406000	9630	2020	9.73	809	2	3	41	2.8	1.0	1110	77	211	171	9

Bolivian tin belt. Both the regions were involved in Miocene volcanism but with the mafic magnetite series of juvenile type (e.g., low Sr_0) in the Toyoha mine area, and ilmenite-series rhyo-dacitic volcanism of recycled type in the Bolivian tin belt (Sugaki *et al*., 1988), as best observed at the Porco mine and Potosi mine.

In Table 3, an average composition of all the samples from the Toyoha deposit (n=62) is compared with an average composition of all the studied deposits in Bolivia (n=46, Ishihara *et al*., 2010b). Zinc concentrates from three representative mines are also supplemented. Indium contents are slightly higher in the Toyoha deposits (854 ppm) than in the Bolivian deposits (768 ppm), and the 1000In/Zn ratio is also higher in the Toyoha deposit (7.1, n=61) than in Bolivian deposits (5.3, n=46). The tin contents are lower in the Toyoha deposits than in the Bolivian deposits as 1503 vs. 2284 ppm. The Toyoha ores are higher in silver (3.9 times), copper (3.5 times), nickel (3 times), cobalt (5.3 times), arsenic (2.3 times), lead (2.2 times) and iron (1.3 times) than the Bolivian averages among the major ore components. Antimony is distinctly higher in the Bolivian ores (11.3 times), which appear to be related to antimony mineralization occurring often around the indium-polymetallic deposits in Bolivia. Manganese and bismuth are higher in the Bolivian side, whose reasoning has not been known.

Zinc concentrates from these mines are also listed in Table 3. Both indium-content and 1000 In/Zn ratio are higher in the Toyoha mine than those of the Porco and Bolivar mines in Bolivia; the Toyoha concentrates seem to contain the highest indium in this world. Cadmium contents are similar having the 1000 Cd/Zn ratio of 5.7 for the Toyoha mine, 7.7 for the Bolivar mine and 3.9 for the Porco mine. Arsenic contents are higher in the Toyoha concentrates than the Bolivar and Porco concentrates. Both antimony and bismuth are much dominant in the Bolivar concentrates than the other concentrates.

The chemical characteristics between Toyoha and Bolivian deposits reflect general difference of the host rocks between the two regions as described before. If the iron is all contained within sphalerites in the zinc concentrates, iron percentage replacing zinc in sphalerites are calculated to be 11.8 wt.% for the Toyoha mine, 25.9 wt % for the Boliver mine, and 24.0 wt.% for the Porco mine. The iron content in sphalerite is largely a function of oxygen fugacity during the crystallization (Tsukimura *et al*., 1987), implying that the Bolivian sphalerites were crystallized under much lower oxygen fugacity than the Toyoha sphalerites.

5. Conclusions

1) Chemical analyses of indium-polymetallic ores of the Toyoha deposits, which mainly belong to the stage IV mineralization, show variable indium contents among the ore veins: E-W trending Shinano-Izumo-Iwami Veins, WNW-ESE trending Soya Vein, and N-S trending Sorachi-Nemuro Veins. High-grade indium ores tend to occur southeast of the ore deposits; indium contents are locally high as 1.0 wt.% at Sorachi Vein. Average indium contents and 1000In/Zn ratio are 568 ppm and 9.0 (Shinano, n=29), 582 ppm and 1.9 (Izumo, n=7), 371 ppm and 6.4 (Iwami, n=16), 1,467 ppm and 3.1 (Soya, n=4), and 4,050 ppm and 9.1 (Nemuro-Sorachi, n=5). The whole average is 854 ppm (n=62) and 7.1 (n=61).

2) Indium contents are positively correlated with zinc contents on the Shinano Vein. On the whole veins, indium contents are most positively correlated with cadmium and zinc with the correlation coefficient of 0.66 and 0.51, respectively, although the indium contents are correlated only locally with tin contents (0.48). Within available mine's level of 500 meters, zinc contents decrease but indium, tin and arsenic contents increase with the depth. These chemical characteristics suggest that indium was intimately associated with zinc, cadmium, tin and arsenic in the ore fluids.

3) Indium contents of the ores are similar between Toyoha and Bolivar ore deposits. The Toyoha ores, however, are richer in iron, copper, arsenic, nickel and cobalt, while the Bolivar ores are richer in manganese, antimony, bismuth and tin. These chemical characteristics are considered to reflect a juvenile igneous character for the Toyoha deposits, and terrestrial sedimentary and felsic igneous environment for the Bolivar deposit.

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北海道，豊羽鉱床産インジウム多金属鉱石の化学的特徴

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要　旨

豊羽鉱床の第 IV ステージに属するインジウム高品位多金属鉱石の化学的性質を，東西系の信濃－出雲－石見脈，西北西系の宗谷脈，南 - 北系の空知－根室脈について検討した．インジウム含有量は最高 1 ％（空知脈，-430　m L）に達するほど多く含まれるが，平均値では分析例が少ない根室 - 空知脈 (4,050 ppm，1000In/Zn=9.1，n=5)，宗谷 (1,467 ppm，1000In/Zn=3.1，n=4) では少し高く，分析例が多い出雲脈 (582 ppm，1000In/Zn=1.9 ppm，n=7)，信濃脈 (568 ppm，1000In/Zn=9.0，n=29)，石見脈 (371 ppm，n=17; 1000In/Zn=6.4 (n=16，異常に高い 1 個を除く，n=16) では一桁低下する．全平均値は 854 ppm(n=62)，1000In/Zn=7.1(n=61) である．これらのインジウム多金属鉱石は鉱液の供給口と考えられている南東部で多く見られる．

インジウム含有量は鉱石の亜鉛含有量と信濃脈では正相関 (相関係数 0.65）するが, この相関係数は全体としては 0.51 に低下する．インジウムと錫との正相関性は，石見脈 (0.71) などで局部的に高い．上下 500m 間の垂直変化では，深部へ向けて亜鉛含有量は減少するが，錫と砒素，インジウム含有量は増加の傾向を示す．これらの化学的特徴は熱水鉱液中でインジウムが錫および砒素を親密に伴っていたことを示唆する．ボリビアの堆積岩地域に産出する同様なインジウム含有鉱石と比較すると，豊羽鉱床はインジウム含有量では類似するが，鉄・銅・砒素・ニッケル・コバルト・銀などに富んでいる傾向がある．他方，ボリビア産の鉱石はマンガン・アンチモン・ビスマス・錫などに富む傾向が見られる．これらの傾向はそれぞれの鉱床母岩が，豊羽鉱床で苦鉄質火山岩類，ボリビアで堆積岩・珪長質火成岩類が卓越することに関係していると考えられる．