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Article

Indium concentration in zinc ores in plutonic and volcanic environments: examples at the Dulong and Dachang mines, South China

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Abstract: Two largest indium ore deposits of 5,000 tons In class in China, Dulong and Dachang mines, were studied geochemically. The Dulong deposits have 1000In/Zn value of 4.1 in the average, which is similar to 2.6 of the Changpo-Tongkeng orebody and 3.1 of the Longtaoshan orebody of the Dachang mine. Yet the Dulong ores are depleted in silver and antimony, and enriched in tungsten among the ore metals, while the Dachang ores are rich in silver and antimony similarly to the Toyoha ores occurring in the volcanogenic Green Tuff belt in Japan. Concentration of indium in sphalerites is homogeneous in the Dulong ores but is strongly banded in the Toyoha ores. It is suggested that the Dulong ore deposits were formed in a plutonic environment related to S-type ilmenite-series granite, while the Dachang deposits were formed at shallower level, related to subvolcanic intrusions. A volcanogenic environment is necessary to concentrate indium in tin-polymetallic ore deposits.

Keywords: Dulong, Dachang, base metal, indium, two-mica granite

1. Introduction

Indium of industrial level is mostly extracted from zinc concentrates of base metal deposits formed under volcanogenic vein-type ore deposits in Japan (Ishihara *et al*., 2006) and Bolivia (Ishihara *et al*., 2011), which occur mostly in volcanic lavas and tuffs intruded by felsic dikes. In China, however, a variety of economic trace components is concentrated in various ore deposits (Zhang *et al*., 2005). Two of the largest In-bearing deposits, Dulong and Dachang (Zhang *et al*., 1998), appear to be formed in a plutonic environment, because the ore bodies occur in metamorphic and sedimentary rocks associated with granitic intrusions.

In autumn of 2008, a short visit was made to the Dulong mine of Yunnan Province and the Dachang mine of Guangxi Province, and we observed small parts of their geologic constituents and the ore deposits (Murakami and Ishihara, 2008). This short paper is a preliminary result of the field observation and chemical analyses on these ore deposits. The visited mines, together with other small indium-rich mines, are shown in Figure 1.

2. Geological background

The studied region of Yunnan and Guangxi Provinces is underlain by the Precambrian basement rocks composed of various metamorphic rocks called Jiannan old-land, and overlying younger sedimentary rocks of mostly Devonian to Permian in age. The Jiangnan old-land is widely distributed in the northwestern part of South China and sporadically in the other southeastern parts (Fan *et al*., 2004, see also Fig. 2). Mesozoic granitic rocks of the Yanshanian stage intrude into these sedimentary rocks widely in South China, but their exposure is generally rare in the studied region. The Dulong deposits occur in the metamorphic rocks, and the Dachang deposits are seen in the sedimentary rocks, intruded by small granitic intrusions.

2.1 Dulong ore deposits

The ore deposits were once mined by underground method for the high-grade parts, but now bulk mining by open pit elongated along NNW-SSE direction (Plate I A), which follows major tectonic elements. Late Yanshanian S-type granite (Plate II F) intrudes into the northern part of the orebodies, which terminate at the Maguan-Dulong giant fault of NW-NNW direction. The

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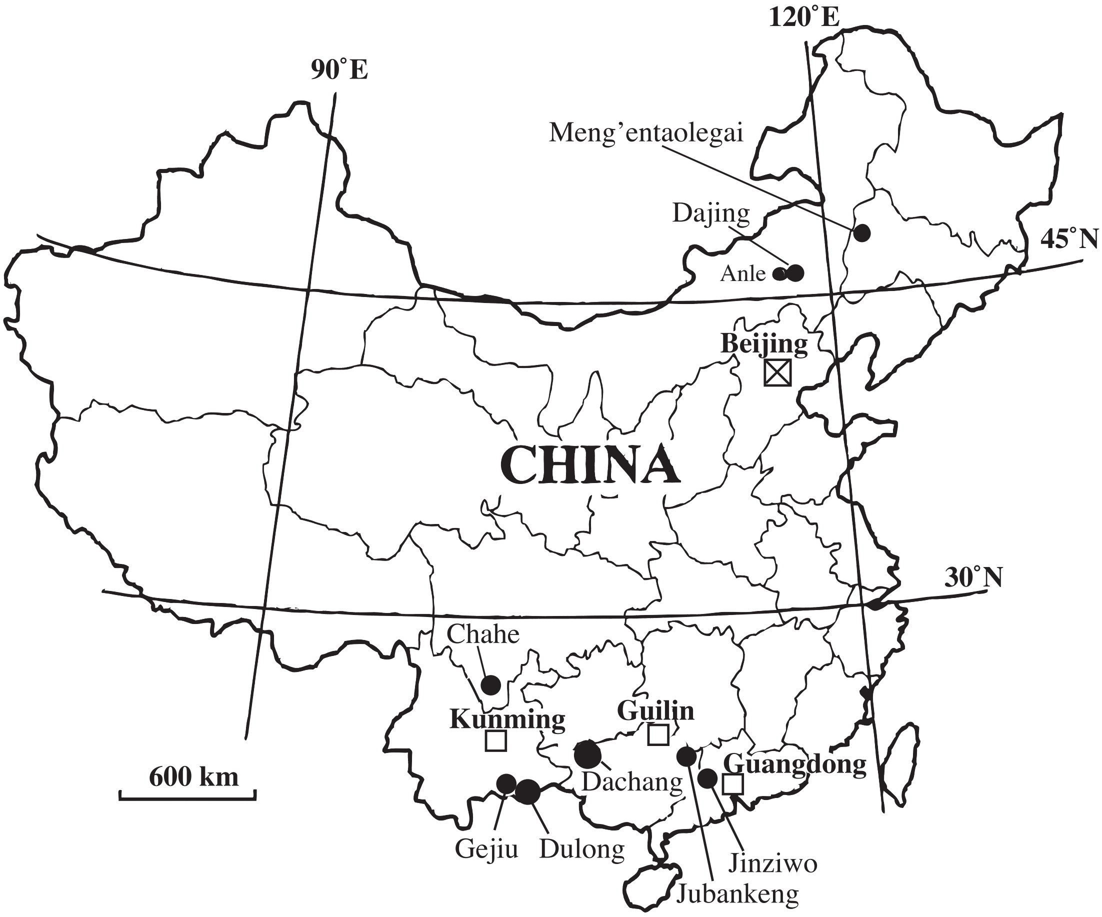

Fig. 1 Distribution of major indium-bearing base metal deposits in China. Size of solid circle implying relative amounts of indium (see Table 4; revised from Ishihara and Murakami, 2008).

orebodies are divided into the main indium-bearing tin-zinc orebody called Zone I and subsidiary silver-lead-zinc orebody called Zone II. The rock constituents of the pit are composed of Cambrian chlorite-muscovite schists and marble. Their metamorphic age is considered as the Indosinian stage, which is Permo-Triassic in age (Liu *et al*., 1999). We visited a few places at 1170 mL of the main open pit.

Major ore constituents are composed of magnetite, cassiterite, sphalerite, pyrrhotite, actinolite, chlorite, sericite, quartz and calcite. Magnetite is locally abundant in the ore zone; we obtained the highest magnetic susceptibility of 600 x 10^{-3} SI unit by KT-5 magnetic meter, which is equivalent to about 20 vol. % of magnetite. The main ore minerals of sphalerite, magnetite and pyrrhotite (Plate I B, C, D) occur as massive lens with minute layering and veining (Plate I B, C). Black-colored sphalerite occurs together with mafic silicates (Plate I E), magnetite and carbonates, and contains many chalcopyrite dots under the microscope (Plate I F). Indium is contained homogeneously in sphalerite (Murakami and Ishihara, 2008), and its content seems higher in cassiterite (Plate I F, G) than in sphalerite.

Liu *et al*. (1999) tried Rb-Sr isotopic dating using quartz and sphalerite from the ore deposits, and obtained an isochron age of 79.08±9.11 Ma and initial $^{87}Sr/^{86}Sr$ ratio ($^{87}Sr/^{86}Sr_i$) of 0.716771 with correlation coefficient of 0.9991. The metamorphosed marble has the $^{87}Sr/^{86}Sr_i$ ratio of 0.709922, which is almost the same as that of Cambrian sea water. The altered two-mica granite has an isochron age of 68.03±7.23 Ma with the Sr*i* ratio of 0.730132. Therefore, they considered that the mineralization occurred in the late Yanshanian stage (Liu *et al*., 1999).

2.2 Dachang deposits

The Dachang ore deposits consist of seven main orebodies (Fig. 3) with three kinds of the mode of occurrence of the ore minerals (Peng *et al*., 1999), as (1) veins including veinlets and networks (e.g., upper part of the Changpo-Tongkeng, Longtaoshan and Dafulou orebodies), (2) stratiform ores (e.g., Nos. 91 and 92 orebodies of the Changpo-Tongkeng orebody, and (3) skarn ores (e.g., Lamo). They occur in Devonian to Permian sedimentary area of 40 km^2, which is rich in carbonates (Plate II A), and marginal parts of the gra-

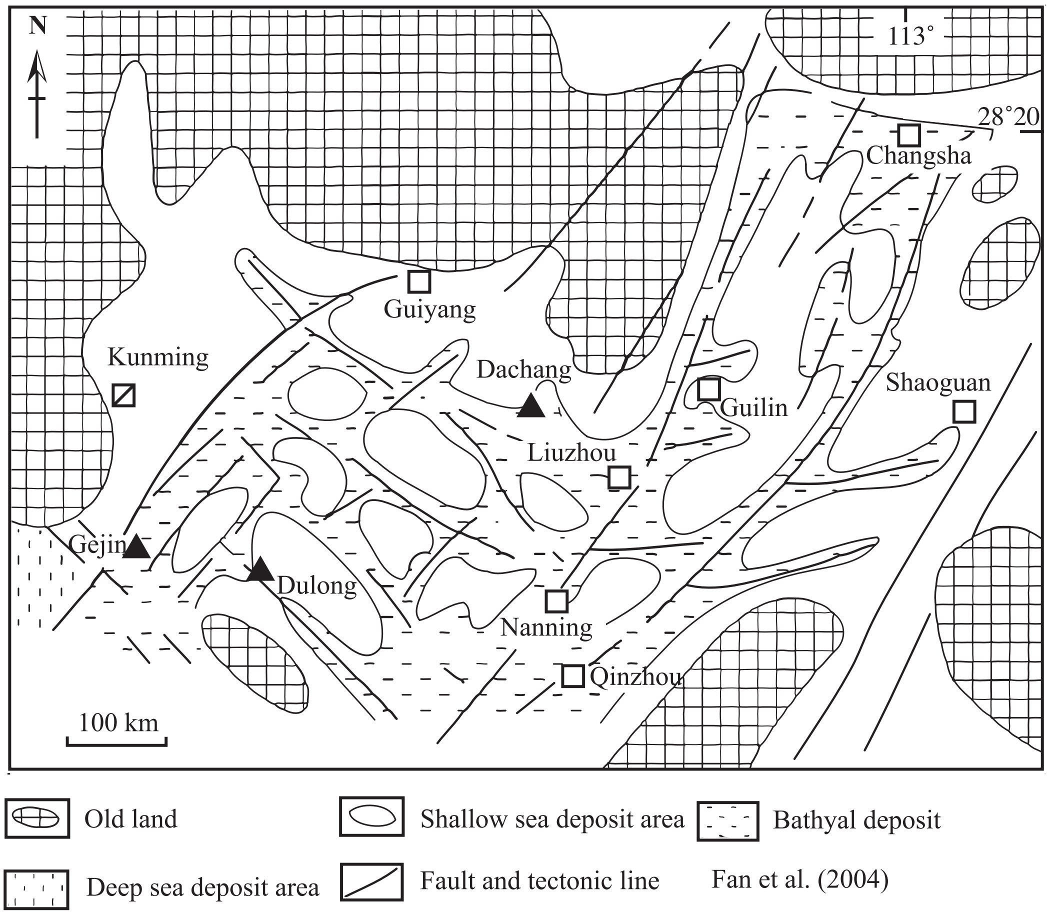

Fig. 2 Sedimentary facies map of South China (Fan *et al*., 2004) and location of the studied mines.

nitic intrusions.

The total ore reserves discovered in the Dachang mine is said about 80 million tons, in which 70 percent occurs in the largest Changpo-Tongkeng orebody. Averaged ore grades of the orebody are Sn 1%, Cu 2%, Zn 3.5%, Pb 5 %, Sb 4 % and Ag 100 ppm. It means that the Changpo-Tongkeng orebody contains ore metals of 560,000 tons Sn, 1,120,000 tons Cu, 2,800,000 tons Pb, 1,760,000 tons Zn, 2,240,000 tons Sb and 8,000 tons Ag. These ores are mined by underground truck-less mining method (Plate II B). The total indium content is estimated as 4,000 tons, in which 2,000 tons occurred in the Longtaoshan (or No. 100) orebody (Zhang *et al*., 1998). We visited only the Changpo-Tongkeng orebody, No. 92, at 445 mL.

The sedimentary rocks of the mine area consist of the lower Devonian to Permian sequence of impure carbonates and intercalated sandstone, shale and chert. The mineralizations are seen mostly along bedding plane of the sedimentary rocks (Plate II C, D), which were intruded by small bodies of the Yanshanian diorites and granitic rocks (Fig. 3). The Yanshanian granitic rocks occur widely below the Changpo-Tongkeng and Longxianggai orebodies, and are considered to be genetically related (Peng *et al*., 1997). The granitic rocks are subvolcanic looking at margins of the intrusive bodies (Plate II E).

Both epigenetic and syngenetic sources of the ore solutions were examined by strontium and neodymium isotopic ratios on tourmalines of Type I occurring in stratiform ores and their host siliceous rocks, and those of Type II from quartz-tourmaline veins in or near the granites by Jiang *et al*. (1999). Type-I tourmalines have $^{87}Sr/^{86}Sr$ ratios of 0.71339-0.71818 and $^{143}Nd/^{144}Nd$ ratios of 0.51201-0.51210, yet Type-II tourmalines have more variable $^{87}Sr/^{86}Sr$ ratios of 0.71187-0.72735 and slightly higher $^{143}Nd/^{144}Nd$ ratios of 0.51210-0.51224. They interpreted that the Type-I tourmaline formed by deeply circulating submarine hydrothermal fluids during the Devonian time, and the Type-II one formed by the Yanshanian magmatic-hydrothermal fluids mixed with Sr and Nd from the host Devonian rocks.

3. Chemical compositions

Seven Zn-rich ores (8112202, 6, 9, 14, A1, A2, A3, Table 1), two Cu-rich ores (8112211, 17) and magne-

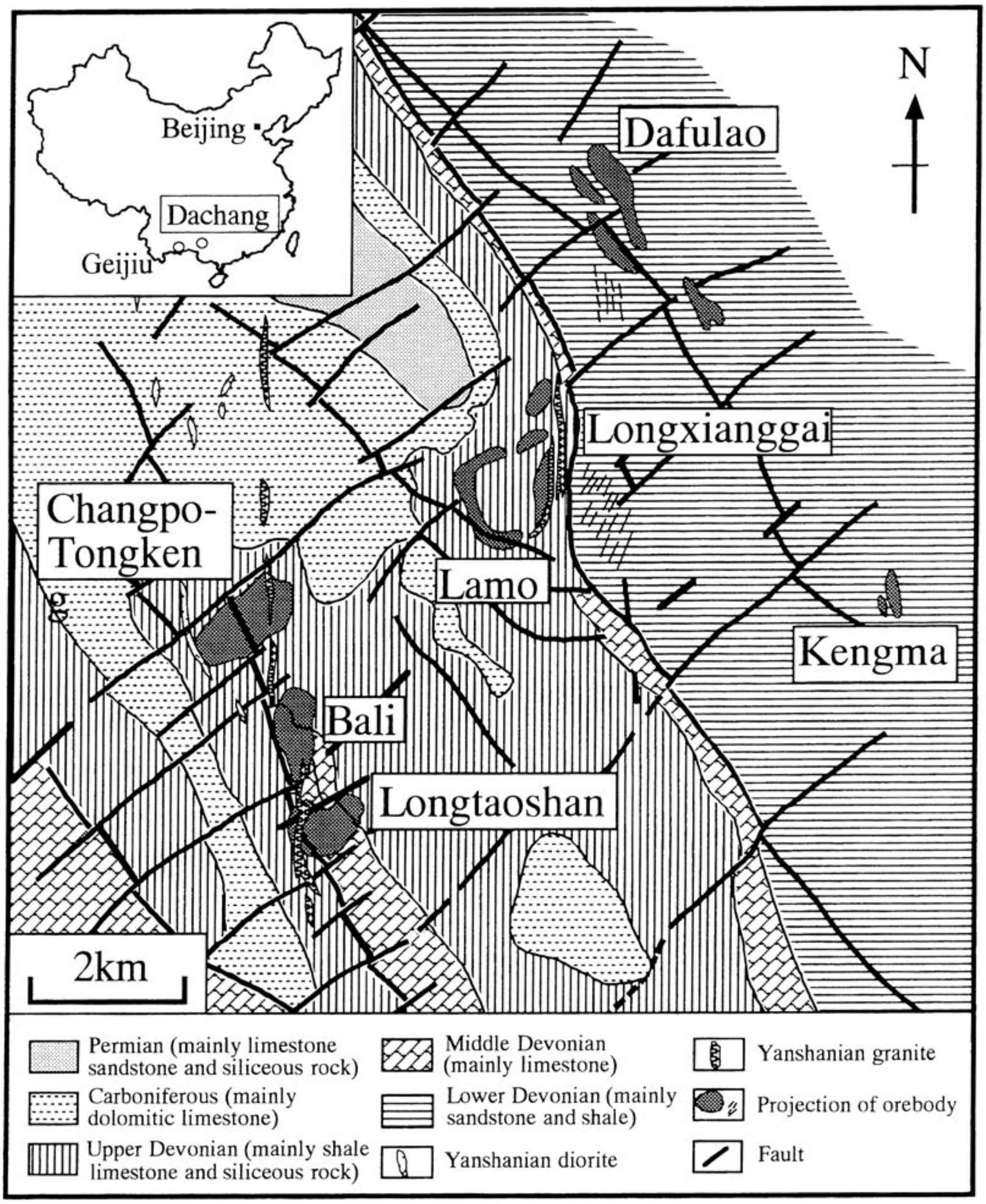

Fig. 3 Geologic map and seven orebodies at the Dachang ore deposits (Peng *et al*., 1999).

tite-rich ores (8112208, 10) were taken from the high-grade parts of the 1170 mL and analyzed for major ore components at the Dulong mine. From the Dachang mine, representative two high-grade and two moderate-grade ores were selected from underground level of the Changpo-Tongkeng orebody.

The ore samples were powdered at the Geological Survey of Japan and analyzed at Actlabs, Canada, by ICP/MS method after total digestion (TD). The results are listed in Table 1. Although number of the samples is very limited, there are distinct differences on the two ore deposits, as seen in the average contents of the table. The Dulong ores are higher in the Fe contents (31.0 % vs. 19.3 %), Mg contents (4.7 vs. 0.2 %) and Li (97 ppm vs. 4 ppm), which may substitute Mg position. That is, ferromagnesian components are richer in the Dulong ores, possibly reflecting relatively mafic host rocks of this mine. The sedimentary components of manganese, 1,211 ppm vs. 1,975 ppm and vanadium 5 vs.41 ppm, are somewhat dominant in the Changpo-Tonkeng ores.

On the contrary, granitic components are richer in the Dulong ores, as averaged as 0.68 % vs. 0.26 % K, 139 ppm vs. 59 ppm Rb, 24 ppm vs. 6 ppm Cs, 17.6 ppm vs. 0.3 ppm Ge and 10.3 vs. 0.2 ppm Be. Yet, zirconium 6 vs. 31 ppm, tungsten 55 ppm vs. 238 ppm and

Table 1 Analytical results of zinc ores from the Dulong and Dachang mines.

Analyt. Sym.	1000	In	Sn	Cd	Zn	Pb	Cu	As	Co	Ni	Bi	Sb	Ag	Se	Fe %	Mn	Mg %	Li	V	Cr	Al %
Unit Symbol	In / Zn	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	%	ppm	ppm	ppm	%
Detect. Lmt.		0.1	1	0.1	0.2	0.5	0.2	0.1	0.1	0.5	0.02	0.1	0.05	0.1	0.01	1	0.01	0.5	1	0.5	0.01
Dulong deposits																					
8112202	0.8	21	55	111	25300	236	71	66	1	5	7	22.8	7.5	1.3	15.4	2200	11.5	4	5	6	0.31
8112206	8.4	527	13	470	62600	33	3460	22	1	3	131	1.2	5.0	2.8	27.9	237	5.3	454	6	10	0.69
8112208	3.5	11	106	17	3120	59	343	23	1	3	136	7.3	2.8	0.4	56.0	323	2.7	58	4	7	0.19
8112209	1.4	99	18	313	69700	86	614	12	5	4	90	4.4	6.5	2.8	49.1	687	0.8	1	< 1	4	0.02
8112210	1.1	1	189	5	1160	59	12	70	1	3	5	14.2	2.7	0.2	51.2	319	4.2	8	4	7	0.06
8112211	24.5	296	547	116	12100	289	96900	533	308	119	465	4.1	149.0	5.2	18.9	426	0.3	102	2	1	1.65
8112214	0.7	89	55	552	131000	140	374	19	3	3	85	1.9	5.2	5.9	22.9	2460	5.4	6	2	4	0.11
8112217	18.2	248	439	117	13600	265	51000	228	141	99	371	4.7	148.0	6.3	14.8	729	0.7	357	13	7	4.59
81122A1	2.7	234	123	349	88100	222	2010	60	25	3	41	2.1	13.3	3.7	41.5	644	4.3	19	3	11	0.23
81122A2	2.2	344	13	720	159000	14	2580	160	39	4	83	3.4	10.5	6.7	23.8	596	3.8	21	4	5	0.27
81122A3	2.3	24	87	42	10400	84	3680	21	16	3	10	2.3	13.2	1.5	19.6	4700	12.3	42	4	7	0.52
Average	6.0	172	150	256	52371	135	14640	110	49	23	129	6.2	33.1	3.3	31.0	1211	4.7	97	5	6	0.79
Dachang deposits																					
8111904A	0.9	94	416	862	107000	5050	2760	2250	84	200	194	33.9	157.0	60.5	31.8	1890	0.2	5	106	27	2.75
8111905	2.5	50	270	227	20200	6670	615	639	109	46	5	431.0	31.9	5.0	7.3	149	0.1	6	42	9	0.67
8111907	3.3	1370	2380	3670	413000	261	5060	12000	104	5	49	229.0	89.1	18.0	17.0	3140	0.2	3	10	7	0.80
8111908	3.6	126	126	352	35300	1830	2360	94	43	12	26	27.7	62.8	3.1	21.2	2720	0.5	4	7	8	0.75
Average	2.6	410	798	1278	143875	3453	2699	3746	85	66	69	180.4	85.2	21.7	19.3	1975	0.2	4	41	13	1.24

Analyt. Sym.	Ca %	Na %	K %	Rb	Cs	Sr	Ba	Ga	Ge	Zr	Hf	Be	Nb	Ta	W	Mo	Th	U
Unit Symbol	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detect. Lmt.	0.01	0.001	0.01	0.2	0.05	0.2	1	0.1	0.1	1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Dulong deposit																		
8112202	12.20	0.01	< 0.01	1	1	211	1	1	0.4	7	0.1	1.7	0.3	< 0.1	1.3	0.2	0.6	0.9
8112206	0.15	0.04	1.04	304	52	3	21	7.2	1.3	6	0.2	3.6	1.8	0.1	11.4	< 0.1	2.6	1.4
8112208	0.04	0.01	0.24	103	15	2	1	21.1	9.1	2	< 0.1	8.2	0.4	< 0.1	2.8	0.4	0.4	0.3
8112209	1.45	0.01	< 0.01	2	0	24	< 1	0.3	1.4	1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.2	0.1	< 0.1
8112210	0.07	0.02	< 0.01	3	1	3	1	11.2	141.0	3	< 0.1	39.4	0.4	< 0.1	136.0	0.2	0.5	0.3
8112211	15.60	0.01	0.76	264	40	28	9	1.6	0.2	2	< 0.1	5.4	0.1	< 0.1	6.1	0.5	0.1	0.2
8112214	4.73	0.01	< 0.01	3	6	47	< 1	1.3	2.4	1	< 0.1	1.7	< 0.1	< 0.1	116.0	0.2	0.3	0.2
8112217	12.40	0.01	2.47	813	105	10	13	7.3	0.1	< 1	< 0.1	18.3	0.2	< 0.1	1.9	3.1	< 0.1	< 0.1
81122A1	0.27	0.01	0.03	7	17	5	2	10	17.3	13	< 0.1	14.6	0.4	< 0.1	149.0	< 0.1	0.7	0.8
81122A2	0.68	0.01	0.17	25	8	9	6	11.9	13.9	10	< 0.1	2.0	1.2	< 0.1	107.0	< 0.1	0.9	1.1
81122A3	1.94	0.01	0.02	6	16	27	2	4.4	6.2	11	0.2	8.1	0.6	< 0.1	67.9	0.1	1.1	0.9
Average	4.50	0.01	0.68	139	24	33	6	7	17.6	6	0.2	10.3	0.6	0.1	54.5	0.6	0.7	0.7
Dachang depo.																		
8111904A	0.25	0.05	0.69	151	13	20	3	7.6	0.7	54	1.4	0.4	5.8	0.2	386.0	0.3	5.3	2.2
8111905	0.77	0.01	0.14	22	3	12	38	4.4	0.2	11	0.2	0.1	<0.1	<0.1	324.0	<0.1	1.3	1.1
8111907	0.22	0.01	0.09	28	5	5	31	44.3	0.2	39	0.4	<0.1	0.6	<0.1	114.0	1.0	4.0	0.5
8111908	14.10	0.03	0.12	33	4	87	27	7.6	0.2	20	0.5	0.1	0.5	<0.1	129.0	0.3	2.9	0.4
Average	3.84	0.02	0.26	59	6	31	25	16	0.3	31	0.6	0.2	2.3	0.2	238.3	0.5	3.4	1.1

uranium plus thorium 1.4 ppm vs. 4.5 ppm predominate in the Changpo-Tongkeng ores.

About chalcophile components (Table 1), the zinc grades were much lower in the studied Dulong ores, as 5.2 % vs. 14.4 %. Therefore, related elements of cadmium and indium are also lower as 256 ppm vs. 1,278 ppm Cd, and 172 ppm vs. 410 ppm In. Yet, 1000In/Zn ratios are 6.0 vs. 2.6, indicating the Dulong ores are twice as much as the indium of the Changpo-Tongkeng sphalerites. Cadmium contents as shown by the 1000Cd/Zn ratios are 4.9 vs. 8.9, and higher in the Changpo-Tongkeng sphalerites.

Copper is definitely rich in the Dulong ores as 14,640 ppm vs. 2,699 ppm. The other ore elements are generally poor in the Dulong ores, as 150 ppm vs. 798 ppm Sn, 110 ppm vs. 3,746 ppm As, 49 ppm vs. 85 ppm Co, 23 ppm vs. 66 ppm Ni, 6 ppm vs. 180 ppm Sb, 33 ppm vs. 85 ppm Ag, 3 ppm vs. 22 ppm Se. However, bismuth 129 ppm vs. 69 ppm, is richer in the Dulong ores.

3.1 Correlation coefficient

Among the major ore components of the Dulong ores (Table 2), high correlation coefficients are obtained from Cd-Zn (0.97), Cu-Co (0.95), Cu-Ag (0.95), Cu-Bi (0.92) and Cu-Ni (0.91). High values are also observed on some minor elements; e.g., Cr-V (0.98), Bi-Ag (0.93), Ni-Ag (0.92), Co-Ni (0.89), Co-Ag (0.86), Bi-Co (0.82) and Sn-Ag (0.80). These high correlation coefficients are quite distinct among the previously studied ore deposits, such as those of the Toyoha mine and Bolivia.

Indium is best correlated with selenium (In-Se 0.59) and cadmium (In-Cd=0.52) in the correlation coefficient. Tin is the best correlated with not indium but silver (Sn-Ag=0.80) and copper (Sn-Cu=0.79).

3.2 Binary diagrams

In Figure 4, indium of the Dulong ores is plotted against commonly related elements such as tin and zinc, and also so-called low temperature components of silver and antimony. Their correlation coefficients are very low as follows: In-Sn (0.08), In-Zn (0.34), In-Ag (0.37), and In-Sb (-0.32). However, indium looks fairly well correlated with zinc (see solid triangle of Fig. 4B). For comparison, four samples from the Changpo-Tongkeng orebody of the Dachang mine and data from the Shinano Vein of the Toyoha mine (Ishihara and Matsueda, 2011), are also plotted.

In the In-Sn diagram, the Shinano ores are plotted toward the highest indium and tin area, and the Changpo-Tongkeng ores are plotted in similar area. The Dulong ores are, however, plotted toward a low tin (and indium) area (Fig. 4A). In the indium vs. zinc diagram (Fig. 4B), the Dulong ores are plotted to follow the In/Zn =0.001 at the low-grade side, but the Toyoha ores

Table 2 Correlation coefficients of the zinc ores from the Dulong mine.

	In	Sn	Cd	Zn	Pb	Cu	Fe	Mn	V	Cr	Ni	Co	Ga	Mo	As	Bi	Ag	Sb	Se
In	1.00																		
Sn	0.08	1.00																	
Cd	0.52	-0.26	1.00																
Zn	0.34	-0.30	0.97	1.00															
Pb	0.20	0.56	-0.20	-0.21	1.00														
Cu	0.37	0.79	-0.19	-0.26	0.67	1.00													
Fe	-0.01	-0.13	0.12	0.17	-0.07	-0.20	1.00												
Mn	-0.39	0.23	-0.07	-0.03	-0.12	-0.20	-0.32	1.00											
V	-0.22	0.02	-0.28	-0.28	-0.30	-0.12	-0.42	0.27	1.00										
Cr	-0.22	-0.11	-0.27	-0.26	-0.34	-0.21	-0.35	0.22	0.98	1.00									
Ni	0.26	0.75	-0.31	-0.38	0.59	0.91	-0.36	-0.16	0.25	0.15	1.00								
Co	0.33	0.72	-0.16	-0.21	0.49	0.95	-0.29	-0.18	0.03	-0.04	0.89	1.00							
Ga	-0.25	-0.27	-0.29	-0.28	-0.53	-0.31	-0.16	-0.22	0.36	0.40	-0.15	-0.16	1.00						
Mo	0.08	0.43	-0.30	-0.33	0.43	0.46	-0.26	-0.21	-0.07	-0.21	0.55	0.36	0.07	1.00					
As	-0.15	0.01	0.22	0.33	-0.26	0.00	0.16	-0.05	-0.05	-0.10	-0.06	0.11	-0.03	0.00	1.00				
Bi	0.49	0.71	-0.02	-0.12	0.64	0.92	-0.04	-0.32	-0.24	-0.33	0.83	0.82	-0.31	0.54	-0.02	1.00			
Ag	0.37	0.80	-0.19	-0.26	0.73	0.95	-0.21	-0.19	-0.11	-0.23	0.92	0.86	-0.32	0.67	-0.04	0.93	1.00		
Sb	-0.32	0.00	-0.39	-0.36	0.36	-0.04	0.08	-0.11	-0.31	-0.32	-0.11	-0.17	-0.14	0.10	-0.17	-0.10	-0.01	1.00	
Se	0.59	0.30	0.70	0.67	0.34	0.45	-0.08	-0.12	-0.28	-0.35	0.36	0.44	-0.47	0.26	0.16	0.57	0.51	-0.36	1.00

tend to have higher ratio around In/Zn =0.01. Absolute amounts of indium are much higher in the Shinano ores than the Dulong ores.

The Dulong ores are depleted in silver and antimony. A weak positive correlation is observed on the In-Ag

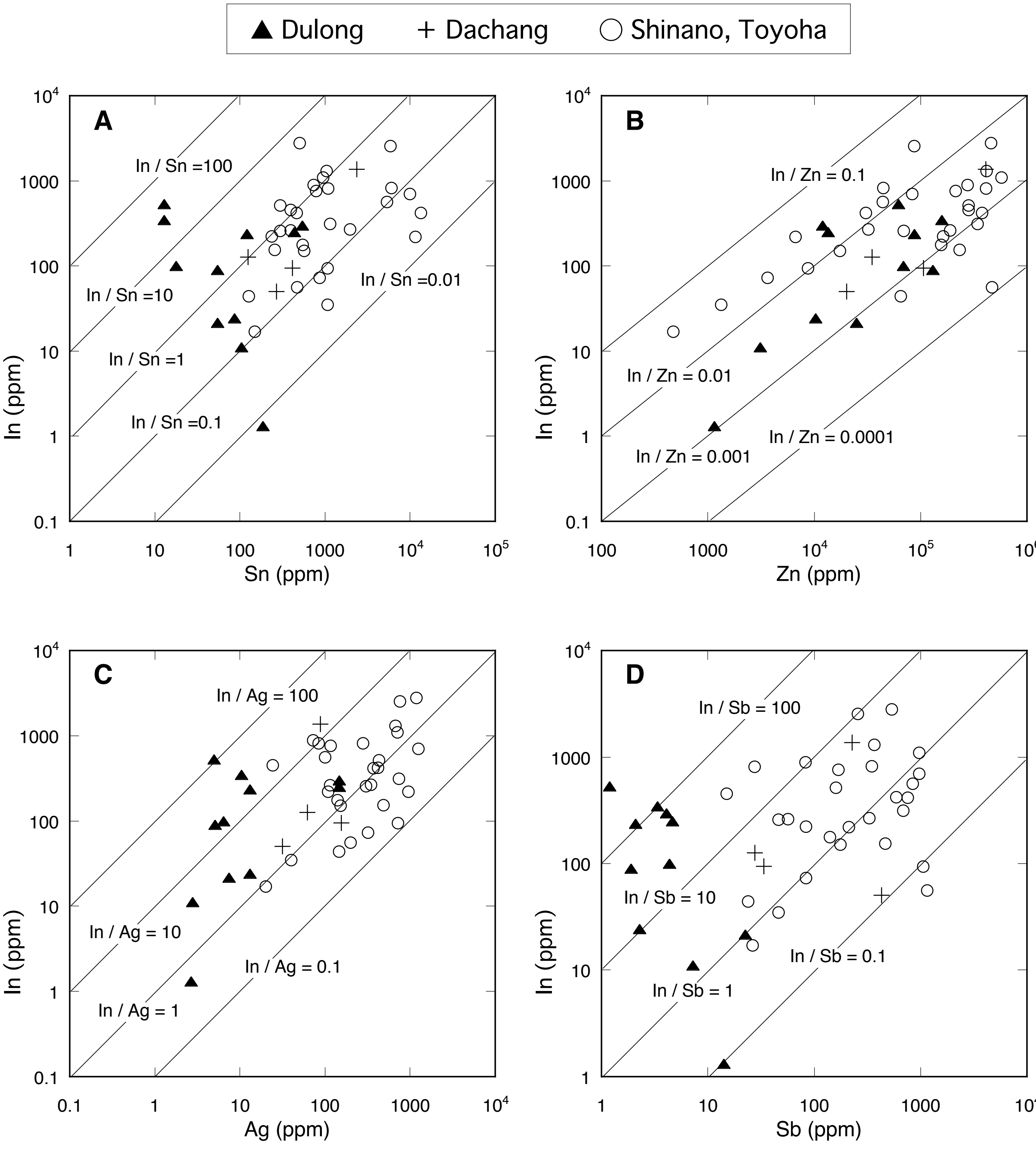

Fig. 4 Binary diagrams of indium and selected ore components of the Dulong, Dachang and Toyoha deposits.

diagram of the Dulong ores, while the Changpo-Tongkeng ores are plotted together with the Shinano ores (Fig. 4C). Antimony contents of the Dulong ores are clearly separated toward the low content area, less than 10 ppm, against the Toyoha ores (Fig. 4 D), while those of the Changpo-Tongkeng ores are plotted in similar area to those of the Shinano ores.

Among the other ore components, cadmium is always well correlated with zinc. Here, with this condition, the Dulong ores seem to have lower Cd/Zn ratios than the Changpo-Tongkeng and Shinano ores (Fig. 5A). Arsenopyrite occurs often in tin-bearing ore deposits, and cobalt can be contained in this mineral by its chemical affinity. The Dulong ores have higher Co/As ratio (Fig. 5B) than the Shinano ores, which has correlation coefficient of 0.93. Arsenic is low among the Dulong ores, relative to the Dachang and Shinano ores (Fig. 5C). Tungsten is much dominant in the Changpo-Tongkeng

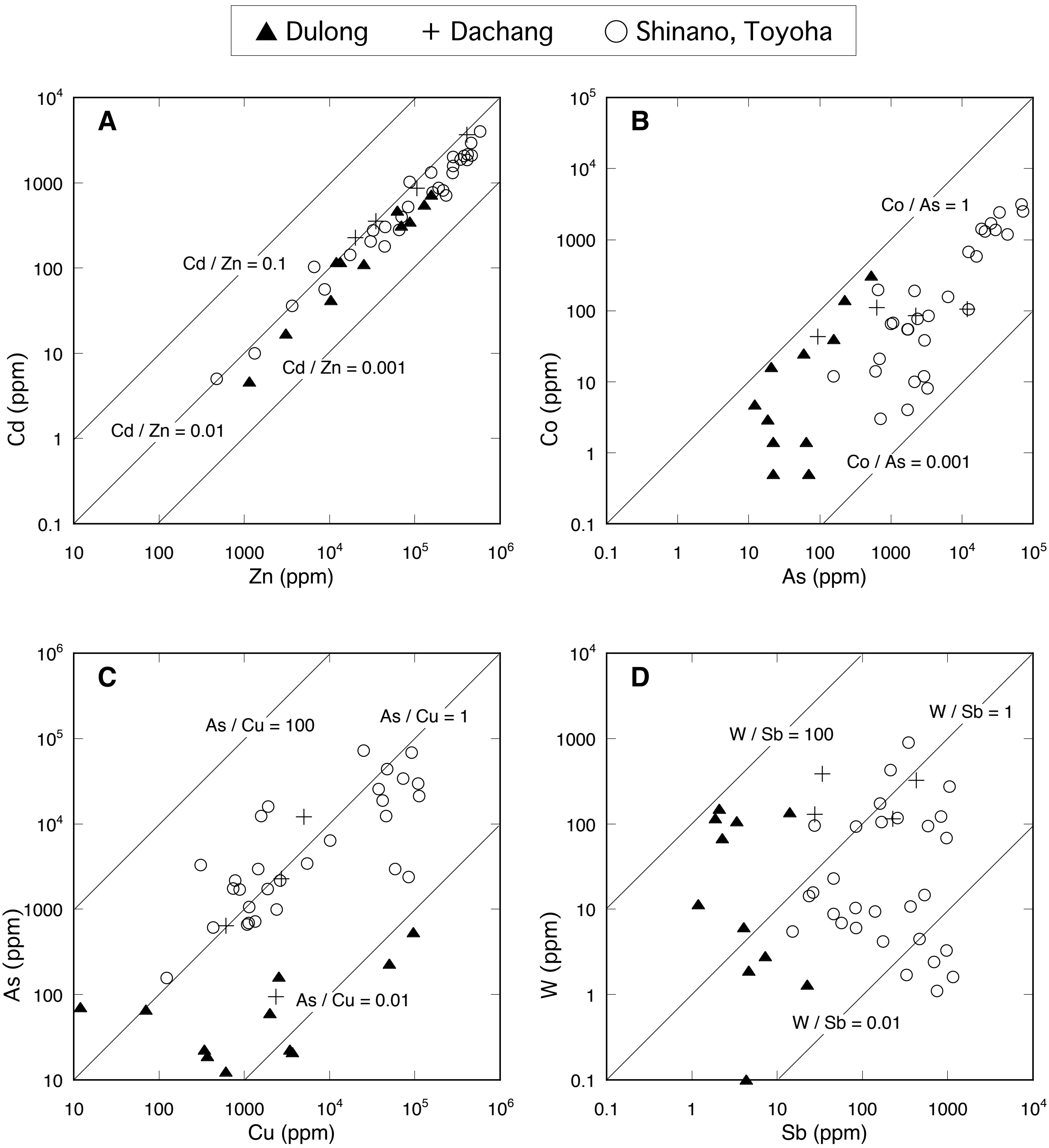

Fig. 5 Binary diagrams of selected ore components of the Dulong, Dachang and Toyoha deposits.

ores than the Dulong ores (Table 1). In the tungsten-antimony diagram, the Dulong ores are plotted in an area below 10 ppm Sb, while the Changpo-Tongkeng and Shinano ores above 10 ppm Sb (Fig. 5D).

4. Indium concentration and genetic problems

Zhang *et al*. (1998, 2003) reported an averaged indium content of 139 ppm (n=35) and 1000In/Zn ratio of 0.8 for the Dulong ores (Table 4). Our average is 172 ppm In (n=11) but its 1000In/Zn value is 6.0, much higher than their value in the In/Zn ratio. At the famous Toyoha mine, the whole average of 62 samples is 854 ppm In (n=62) and the 1000In/Zn ratio is 14.2 (Ishihara and Matsueda, 2011). It means that many indium minerals are contained in the Toyoha ores. Ohta (1989) considered economically most important minerals are Zn-In mineral which has an intermediate composition of sphalerite and roquesite, and indium-bearing sphalerites

Table 3 Indium contents of ores from the lead-zinc ore deposits in South China.

Locality	No. sample	In (ppm)	Zn(%)	Sn(ppm)	1000In/Zn	Tot.In
Dulong	35	139	18.2	n.d.	0.8	>3,500
Our study	11	172	5.2	150	6.0	n.d.
Dachang, Changpo-Tonkeng	16	95	15.0	960	1.6	>4,000
Our study	4	410	14.4	798	2.6	n.d.
Ditto, Dafulou	9	105	19.0	1,050	0.6	n.d.
Ditto, Longtaoshan	n.d.	310	10.1	17,900	3.1	2,000
Gejiu	n.d.	n.d.	n.d.	n.d.	n.d.	>500
Jinziwo, Guangdong	8	92	17	900	0.5	400
Jubankeng, ditto	5	87	7	910	1.2	n.d.

n.d.: Not studied, Tot. In: Estimated total In tonnages by Zhang *et al.* (1998).

whose In-contents go up to a few percent. A complete solid solution was observed between the Zn-In mineral and sphalerite. The other important indium carriers are kesterite, stannite, and anisotropic chalcopyrite.

4.1 Indium contents of zinc concentrates and sphalerites

For industry purpose, indium content of sphalerite concentrates is most significant. At the Toyoha mine, zinc concentrates of 2005 contained 1,030 ppm In for 48.3 % Zn, 6.2% Fe and 1.3% Pb (Ishihara *et al.*, 2006), thus the 1000In/Zn ratio is 2.1. This decreasing of 1000In/Zn of 14.2 to 2.1 indicates removal of indium minerals from the zinc concentrates. In South China, zinc concentrates were not available, but mineralogical data on sphalerites are given by Zhang *et al.* (2003), as follows: Changpo-Tongkeng orebody (n=16): 1,010 ppm In for 59.4 % Zn and 6.2% Fe, 1000In/Zn=1.7, and Dafulou orebody (n=2): 1,300 ppm In for 57.8 % Zn and 7.9 % Fe. 1000In/Zn=2.3.

Sphalerites are black by naked eyes and reddish under microscope at the Dulong deposits (Plate I E). The mineral occurs filling host silicates and magnetite crystals. Electron-micro-probe analyses indicate that indium in the Dulong ores is highly concentrated in cassiterite, other than sphalerite, and its distribution is homogeneous, unlike most of the sphalerites in the Toyoha ore deposits (Ohta, 1989).

The ore data are given in Table 3, together with total indium tonnages of major ore deposits estimated by Zhang *et al*. (1998).

Table 4 Chemical composition of two-mica granite at north of the Dulong mine.

Elements	%	Elements	ppm
SiO_2	72.93	Ge	1.3
Al_2O_3	14.01	Zr	113
Fe_2O_3	1.49	Hf	3.4
MnO	0.04	Nb	21.7
MgO	0.30	Ta	5.99
CaO	0.63	V	9
Na_2O	3.09	Cr	<20
K_2O	5.44	Co	15
TiO_2	0.20	Ni	< 20
P_2O_5	0.25	Cu	< 10
F	0.18	Pb	81
LOI	1.10	Zn	70
Total	99.49	Tl	3.79
Rb(ppm)	403	As	< 5
Cs	25.5	Sc	3
Sr	86	Be	7
Ba	336	Mo	< 2
Ga	24	W	108
A/CNK	1.16	Sn	26
NK/A	0.78	Bi	1
Fe_2O_3 / MgO	4.97	In	< 0.1
Ga*10000/A	3.24	Sb	7.6
Rb/Sr	4.69	Th	31
Zr-T(˚C)	769	U	11

4.2 Volcanic vs. plutonic environment

All the major indium deposits in Japan, such as the Toyoha, Ashio and Ikuno-Akenobe deposits, are hosted

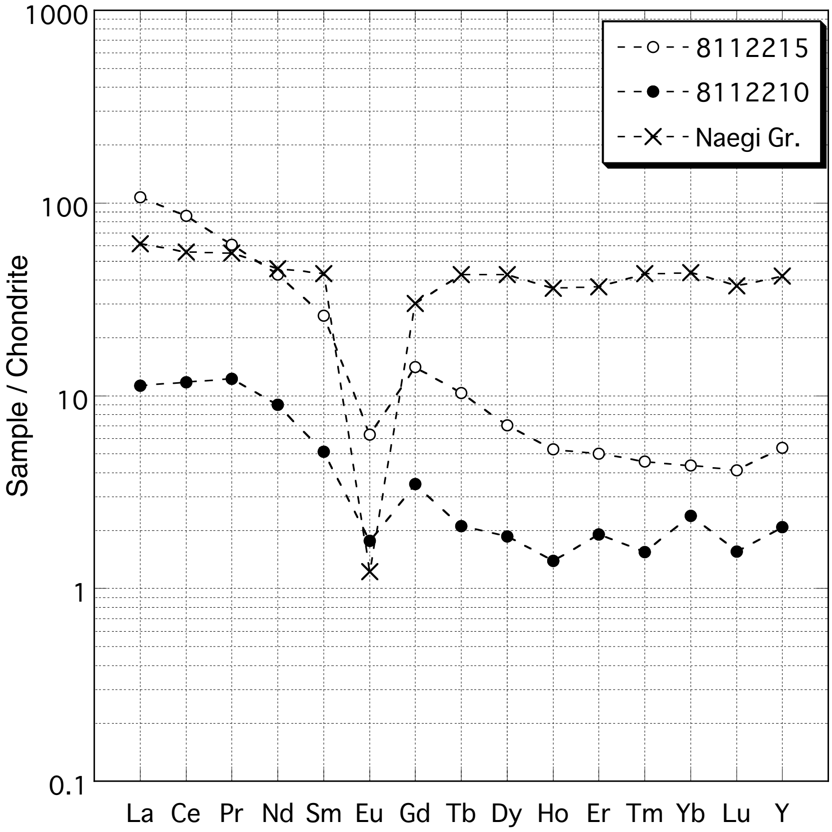

Fig. 6 REE patterns of the two-mica granite (8112215) and nearly barren zinc ore (8112210) from the Dulong mine.

in coeval volcanic rocks and occur with subvolcanic dikes (Ishihara *et al*., 2006). Here at the Dulong mine, holocrystalline muscovite-bearing biotite granite (Plate II F) intrudes metamorphic rocks at north of the Dulong ore deposit. The granite has A/CNK higher than 1.1, rich in K_2O (5.44%), F (1,800 ppm), Rb (403 ppm), W (108 ppm) and tin (26 ppm, Table 4); thus considered as S type. Cassiterites are mined by small-scale mining within the granites. Therefore, tin is enriched in the late stage of granitic magmatism, which may have caused tin-rich character of the Dulong ore deposits.

Granitic rocks also occur in the Dachang mine area. They are often subvolcanic in texture (Plate II E) and seem to have been crystallized in shallower level than the granite in the Dulong mine area. Moreover, many ore components of the Changpo-Tongkeng orebody in the binary diagrams are similar to those of the Toyoha deposits, which have been formed under a volcanic environment because only a few quartz porphyry dikes are seen in the volcano-sedimentary host rocks of Miocene age. The Dulong ores are, however, poor in so-called volcanogenic ore components, such as antimony, silver and selenium, and plotted differently from the Changpo-Tongkeng and Toyoha ores. These facts suggest that the Dulong ores were formed under a plutonic environment.

4.3 Source of ore metals

Tin is typical recycling element in the continental crust through ilmenite-series magmatic activities (Ishihara, 1981). Indium may have similar genetic background since high In sphalerite tends to occur tin-rich base metal ore deposits.

(1) Dulong mine

Muscovite-biotite granite at Dulong mine has very low magnetic susceptibility less than 10 x 10^{-3} SI unit and belongs to ilmenite series. Its rare earth element (REE) content is 150 ppm and Y content is 12 ppm and its LREE/HREE ratio is 15.6 (La/Yb=36.6). A typical tin granite in the Japanese Islands is Naegi granite in central Japan. Its western body which hosts the largest Ebisu deposits has an average is 152 ppm REE (n=5), and Y content is 92 ppm and LREE/HREE ratio is 2.4 (La/Yb=2.1; Ishihara and Murakami, 2006). REE patterns of the Dulong granite and Naegi granite are similar each other, but the Dulong granite is less fractionated having shallow Eu negative anomaly and less amounts of HREE (Fig. 6).

REE contents of the altered wall rocks and ores are very low, 24 ppm at maximum. REE pattern of this highest REE content is similar to that of the Dulong granite, implying that the REE is derived from the granite. Thus, tin in the orebody must have come from the Dulong granite.

Strontium initial ratio of sphalerite and quartz at the Dulong mine, $^{87}Sr/^{86}Sr_i$= 0.716771, is high enough to think the source in the felsic crustal materials, as mentioned previously. The very high Sr*i* ratio indicates that the granite was generated by remelting of underlying old crustal rocks. The ore elements must have derived from the same source in the crust, and transported to the ore deposit site by ilmenite-series magmatism.

(2) Dachang mine

At the Dachang mine area, a variety of the mineralizations is observed (Peng *et al*., 1997). The largest Changpo-Tongkeng ore deposits occur at a margin of the granite porphyry intrusion (Plate II E) and in the overlying Devonian strata following the bedding plane (Plate II D). At the indium-rich Longtaoshan deposits, orebodies occur also in carbonate rocks intruded by felsic dikes. Therefore, the tin-zinc mineralizations are affected by both magmatic and sedimentary source rocks.

One of the most important ore components, sulfur, shows a big variety in the $\delta^{34}S$ ratio. Averaged $\delta^{34}S$ values are mostly negative down to -10 per mil. The Changpo ores show ca.-5 per mil and the Tongkeng ores are around -3 per mil. These negative values depend upon availability of sulfur from black shale of the host rocks. On the contrary, the indium-rich Longtaoshan orebody has $\delta^{34}S$ values around +9 per mil. For the ^{34}S enrichment, both magmatic sulfur and sulfate sources from the carbonate beds (Ishihara *et al*., 2002) are possible.

About indium, there have been no sedimentary rocks containing anomalous amounts of the element by the reconnaissance study (Ishihara *et al*., 2009). We need further study for the provenance of these important ore components.

As mentioned previously, tourmalines in the ore deposits were studied for Sr and Nd isotopes (Liu *et al*., 1999), and Type-I tourmaline was considered formed by deeply circulating submarine hydrothermal fluids during the Devonian time, and the Type-II tourmaline formed by the Yanshanian magmatic-hydrothermal fluids mixed with Sr and Nd from the host Devonian rocks. Thus, the mineralizations occurred having both syngenetic ore fluids in the Devonian sea bottom and magmatic fluids from the Yanshanian tin granites.

5. Conclusions

Reconnaissance geochemical studies were made on the ores from 1170 mL of the Dulong open pit, and 445 mL of the Changpo-Tongkeng orebody, No. 92, Dachang mine, and the following conclusions were obtained:

(1) Dulong ores contain a maximum of 527 ppm In and averaged 1000In/Zn ratio is 4.1, while the Changpo-Tonkeng deposit contain up to 1,370 ppm In, but an average 1000In/Zn ratio is 2.6. These values are much lower than 854 ppm In (n=62) and 7.1 1000In/Zn (n=61) of the Toyoha deposits.

(2) The Dulong ores are depleted in silver and antimony, and enriched in tungsten among the ore metals, while the Dachang ores are rich in silver and antimony similarly to the Toyoha ores occurring in the volcanogenic Green Tuff belt in Japan. Concentration of indium in sphalerites is homogeneous in the Dulong ores but is strongly banded in the Toyoha ores. The Dulong ore deposits were formed in a plutonic environment related to S-type ilmenite-series granite, while the Dachang deposits were formed at shallower level, related to subvolcanic intrusions. A volcanogenic environment appears to be better to concentrate indium.

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深成・火山性環境下の亜鉛鉱石におけるインジウム濃集：華南の都竜と大廠鉱床の場合

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要　旨

中国を代表する 5,000 トン In 級のインジウム鉱床，都龍と大廠の鉱石を分析し，その地球化学的な考察を行った．都龍鉱床の鉱石は，平均 1,000 In/Zn 比 =4.1 を持ち，大廠鉱床の鉱石は，2.6-3.1 と同程度である．しかし都龍鉱床の鉱石は銀とアンチモンに乏しく，タングステンに富んでいる．大廠鉱床の鉱石は銀とアンチモンに富んでおり，2 成分図上で豊羽鉱床の鉱石と類似した領域にプロットされる．これらの性質・母岩・貫入花崗岩類を考慮すると，都龍鉱床は S- タイプチタン鉄鉱系花崗岩の貫入により“深成環境”で，大廠鉱床はより浅い亜火山性環境で生成した可能性が大きく，インジウムの濃集には“深成岩”よりも，より浅成の火山性環境が適しているものと考えられる．

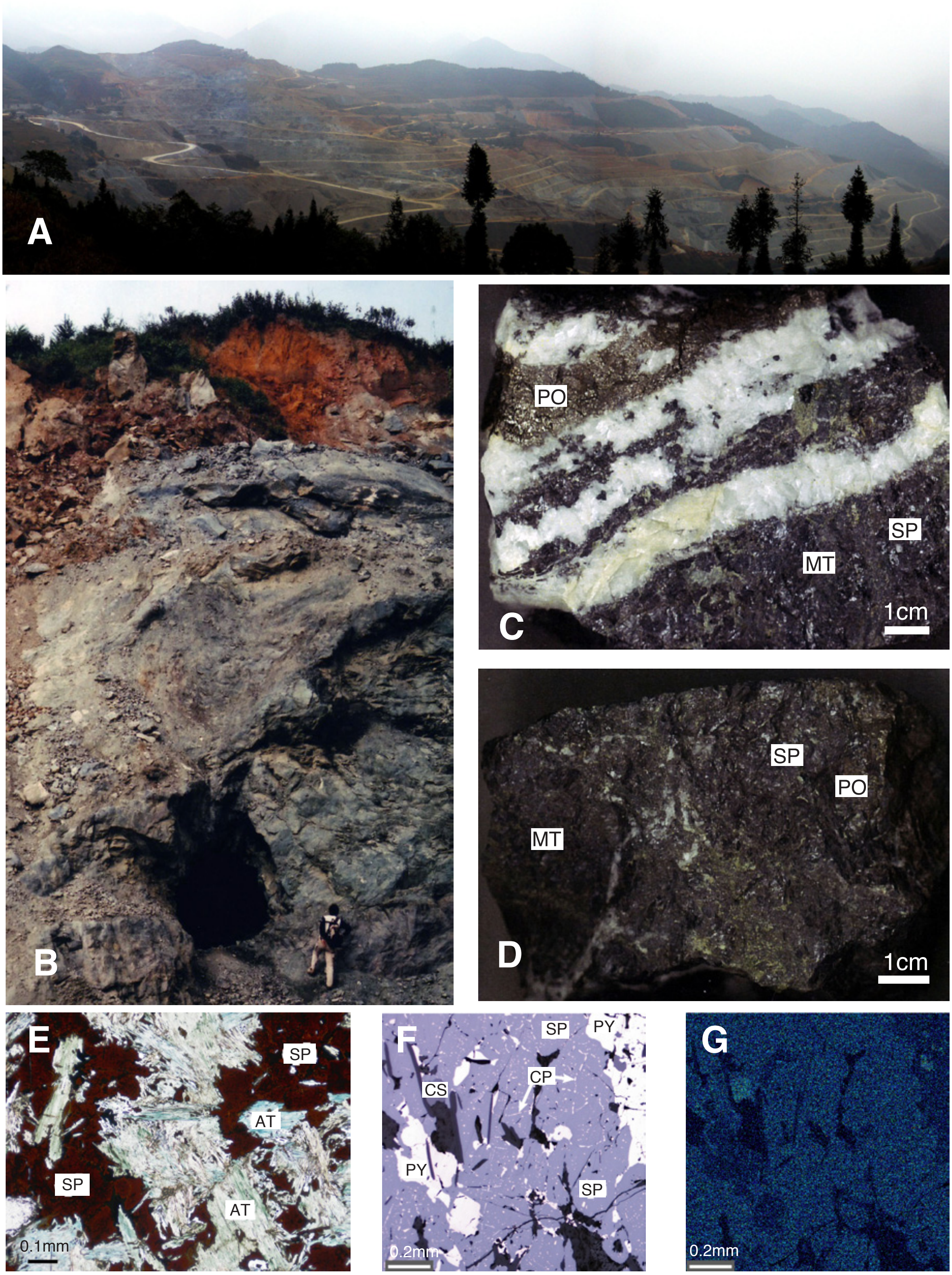

Plate I Selected photographs of the studied ore deposits at the Dulong open pit.
A: The northern part of the Dulong open pit. Flat and wide.
B: An old adit and mineralized sheared zone. See veinlets above the portal. No. 24 orebody, 1170 mL.
C: Magnetite (MT), pyrrhotite (PO) and sphalerite (SP) alternated with carbonates (white). Sample no.: 8112214.
D: High-grade sphalerite (SP)-pyrrhotite (PO)-magnetite (MT) ore. Sample no.: 8112209.
E: Euhedral actinolite (AT) replaced by reddish sphalerite (SP) under microscope. Single nicol.
F: Ore microscopy of sphalerite (SP) with chalcopyrite (CP) dots, and pyrite (PY) and cassiterite (CS).
G: Compositional image of indium (Lα). Note homogeneous In-distribution in sphalerite and cassiterite, and higher In-values on cassiterite.

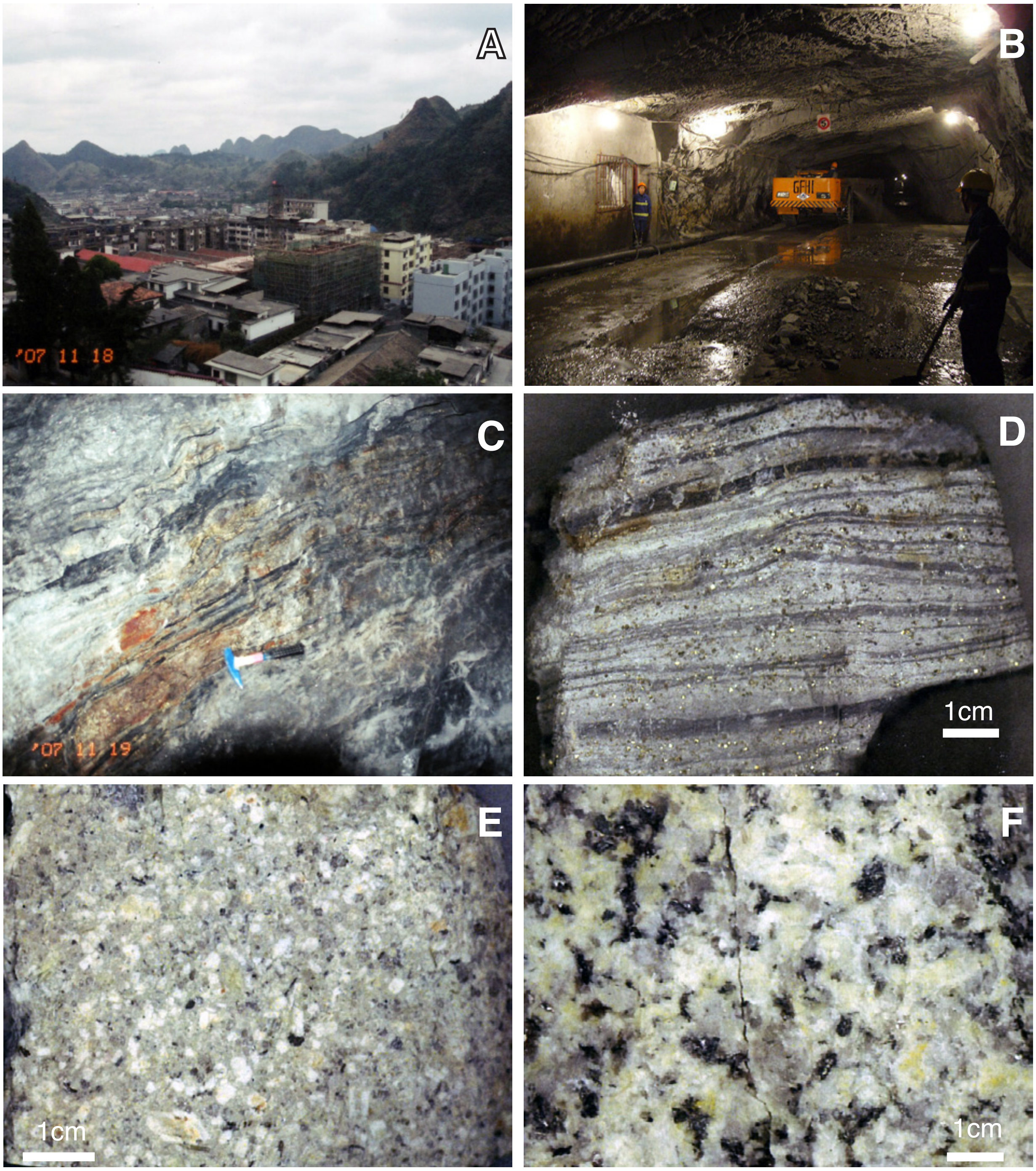

Plate II Photographs of the Dachang mine (A~E) and the Dulong mine (F).
A: Mining town, Dachang, with a unique limestone topography.
B: Modern underground mining of the Dachang mine at 445 mL.
C: Syn-sedimentary-looking ore beds of the Changpo-Tongkeng orebody, No. 92, 445 mL.
D: Close-up of the synsedimentary ore with euhedral pyrite disseminated.
E: Subvolcanic looking of the granite in the Dachang mine area.
F: Muscovite-bearing biotite granite to the north of the Dulong mine.