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Article

Mineralogical and chemical characteristics of the allanite-rich copper and iron ores from the Sin Quyen mine, northern Vietnam

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Abstract: Selected ores from the Sin Quyen allanite-rich Au-bearing chalcopyrite-magnetite deposits were studied microscopically and chemically. The ore minerals tend to occur along the NW-SE-trending sheared zone of altered host rocks; yet the ore minerals show no stress effect, implying the mineralization later than the regional shearing. The ore minerals occur associated with the metasomatic minerals consisting mainly of clinopyroxene, hastingsite, allanite, epidote, biotite, titanite, carbonate minerals and rarely quartz. Allanites containing almost all of the rare earth element (REE) components of the ores occur in disseminated manner and are euhedral to subhedral. The mineral is an early crystallized mineral replaced by magnetite and chalcopyrite. The allanite contains around 16 wt.% REE and is low in mafic components having chemical composition of Mn-poor type, which tends to occur in the magnetite-series granitic rocks in Japan. The REE components could have been derived from an oxidized alkaline granitic activity of mid-Tertiary. Both chalcopyrite and magnetite are well separated by the mineral dressing, and all the allanites moved to the tailings. Therefore, the tailing pond turns out to be an excellent LREE reservoir in future.

Keywords: Sin Quyen, allanite, chalcopyrite, hastingsite, magnetite series

1. Introduction

Au-bearing chalcopyrite-magnetite deposits of the Sin Quyen mine in North Vietnam are a new modern mine open-pitted since 2006. The ore deposits, hosted by altered amphibolite and biotite gneisses within highly deformed and metamorphosed sediments of the Proterozoic Sin Quyen Formation, were formed in a wide fault zone of the Song Hong (Red River) Fault (Figs. 1 and 2), which acted as a channel for pre-mineralization magmatic and post-mineralization hydrothermal activities (McLean, 2001).

Au-bearing chalcopyrite-magnetite deposits occur in lens shape with clinopyroxene, hastingsite, allanite, epidote, biotite, titanite and some quartz in altered parts of the amphibolite intrusion and gneisses of the Sin Quyen Formation with some granitic dikes (Fig. 3). Similar mineralizations are observed in and around the Sin Quyen Formation along the NW-SE fault zone; namely the major ones of Vi Kem, Nam Chac, Suoi Thau and Ban Vuoc (Fig. 2), and more than 10 mineral localities, besides Sin Quyen mine (Bui *et al*., 2004).

The Sin Quyen mine is composed of the largest base-metal deposits rich in allanite of hydrothermal origin in North Vietnam (Fig. 1). For the confirmed ore reserves, two sources are available: one by ESCAP (1990), while the other by McLean (2001), as follows:

ESCAP (1990): 551,000 tons Cu, with the cut-off grade of 0.3% Cu and the minimum width of the ore bodies 1 m. Besides, the following economic components are contained: 334,000 tons REE_2O_3, 843,000 tons S, 34.7 tons Au and 25.3 tons Ag.

McLean (2001): 480,000 tons Cu from 52,800,000 tons ore with the average grade of 0.91 % Cu and the cut-off grade of 0.5% Cu. Besides, REE ores (Ce, La, Pr, Nd) of 370,000 tons containing an average of 0.7 % REE; magnetite ores of 2,850,000 tons with the average Fe_3O_4 grade of 5.4%, and 23.2 tons gold from the average grade of 0.44 g/t Au.

The ore deposits are unique containing abundantly REE, which is rather unusual in base metal ore deposits (Giere, 1996). REE-rich lead-zinc deposit is also

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known at the Na Son mine near Ha Giang of the northernmost Vietnam (Fig. 1, Ishihara *et al*., 2009). Therefore, it is a common feature of the North Vietnam to have REE minerals in the base metal ore deposits, and it is our interest to describe mode of occurrence of the REE-minerals in base metal deposits and it's migration during the ore processing.

The senior author had an opportunity to visit the Sin Quyen mine and collected representative ores from the open pit in 2009. This paper describes briefly petrography and chemistry of these interesting base metal ores, and the ore geneses are considered. The tailings of these ores were also analyzed chemically, in order to know migration of the REE minerals during the ore dressing.

2. Geological background

Geological background of North Vietnam is briefly given in RIGMR (2006) and Ishihara *et al*. (2009). The Sin Quyen ore deposits occur along the NW-SE trending Sin Quyen Fault, which is a part of the Red River Fault zone. The rock constituents around the ore deposits are divided into, from the southwest to the northeast, the Proterozoic Lung Po Formation and Sin Quyen Formation, and Phanerozoic (Cambro-Ordovician) sediments (Fig. 2). These rocks are intruded by two large granitic units of the Po Sen (751-760 Ma U-Pb, SHRIMP) and Muong Hum intrusive bodies (Bui *et al*., 2004), and small unit of the Dien Bien Phu intrusion (McLean, 2001).

The Proterozoic metamorphic rocks with an amphibolite metamorphic grade are divided into the oldest unit of the Lung Po formation and conformable upper unit of the Sin Quyen Formation (Fig. 2). The Sin Quyen Formation consists of biotite-muscovite-graphite-quartz gneisses in the lower unit and graphite-poor felsic gneisses in the upper unit. The schistosity tends to trend in NW-SE direction and dip generally toward NE direction. Many mafic and felsic dikes or sheets, called amphibolite or leucogranite, both have unknown ages in the strict sense, are intruded into the Sin Quyen Formation (Fig. 3). The Sin Quyen Formation is conformably overlain by the Cambro-Ordovician sediments around its northeastern margin (Fig. 2).

Intrusive rocks of the Sin Quyen mine area vary in age from Proterozoic (1,700 Ma, Bui *et al*., 2004) to Phanerozoic. The Proterozoic rocks are composed of small bodies of altered amphibolites, with amphibole (66 vol.%), plagioclase (19 vol.%), biotite (6 vol.%) and accessory titanite, epidote, apatite, chlorite, calcite and sericite. These altered amphibolites are intimately associated with the chalcopyrite-magnetite mineralization of especially high-grade ore zones (Fig. 3). The granites also occur as dikes or lenses, which contain enclaves of amphibolite and biotite gneiss. The granites are said rich in plagioclase (McLean, 2001); therefore, these Proterozoic mafic and granitic rocks turn out to belong to a juvenile-type of magmatism, although the Proterozoic age has to be reconfirmed by precise age dating.

Younger granitoids, called Dien Bien Phu Complex,

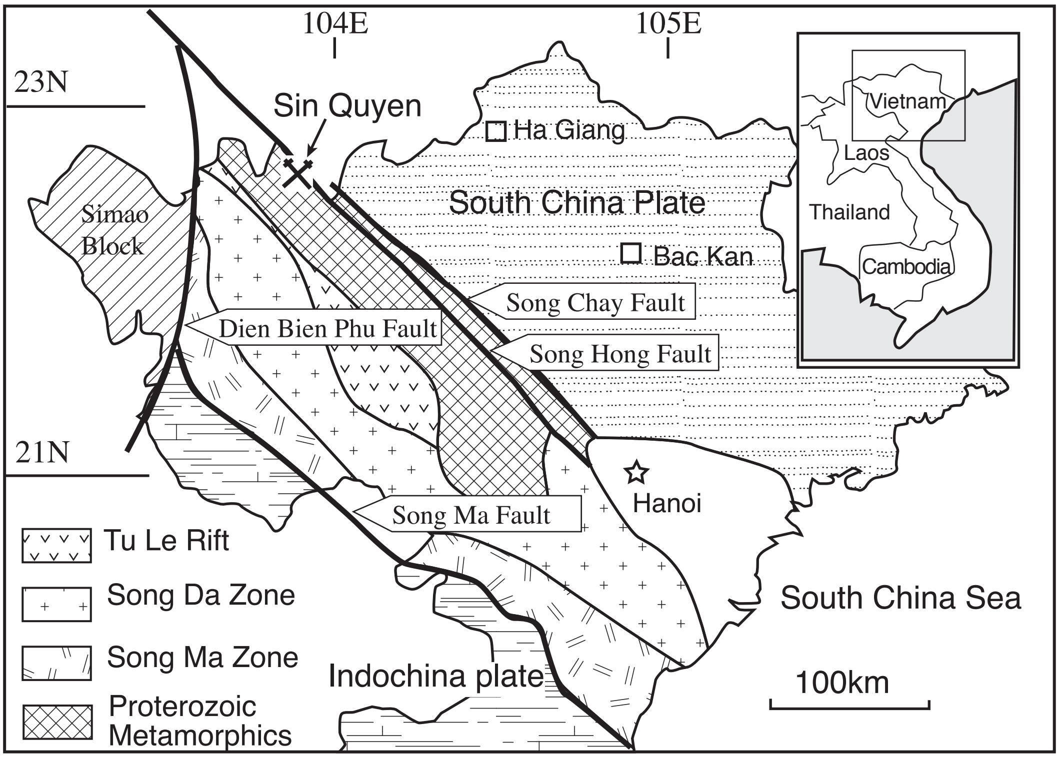

Fig. 1 Tectonic setting of the northernmost Vietnam and location of the Sin Quyen deposit. Modified from Ishihara *et al.* (2009).

which occur in small stock-size bodies in NW-SE direction (Fig. 2), have been assigned to Permian in age. McLean (2001) reported a petrographic character of plagiogranite containing much plagioclase (63 vol.%), besides quartz (26 vol.%) and biotite (6 vol.%). Therefore, all the intrusive rocks of the Sin Quyen mine area are said products of a juvenile-type of magmatism. Leucogranite we observed in the open pit, however, is a normal leucogranite containing abundant K-feldspar and the bulk contents of 4.09 % K, 2.32 % Na and 0.71 % Ca (Table 1). Age of the granitic rocks may be variable, and more age determination is needed on these intrusive rocks.

Toward west of the Sin Quyen mine, Bui *et al*. (2004) described two large intrusive bodies of the Po Sen calc-alkaline granitoids and Muong Hum alkaline granitoids, and Cambro-Ordovician ages are given for them (Fig. 2). However, the latest Precambrian age of 751 Ma (U-Pb, SHRIMP) was given to the Po Sen pluton, and Paleogene K-Ar ages of 30-36 Ma were given to mica minerals from the Muong Hum alkaline pluton (Hayashi *et al*., 2009). Therefore, systematic re-examination of their intrusion ages is necessary for the granitoids of the whole region.

3. Field and microscopic studies

Representative ores and granitic dike were observed at 64 mL of the East pit of the Sin Quyen mine, and a part of the collected samples are shown in Plate I. The granite appears to be dike in form and seems of pre-mineralization stage, but is not generally mineralized (Plate IA). The main ore minerals of magnetite and chalcopyrite tend to occur with green silicates composed of pyroxene-amphibole and allanite-epidote group minerals, besides original felsic host gneisses (Plate IB, C, D). The magnetite and sulfides are locally very abundant (Plate IE, F).

3.1 Leucogranite

This leucogranite is fine to medium grained (Plate IA), but shows a heterogeneous recrystalline texture under the microscope (Plate IIA). This rock seems to be once crushed by regional shearing, then recrystallized. The leucogranite is weakly porphyritic having the phenocrysts of K-feldspar up to 5 mm and albite up to 1.5 mm in diameter, filled with fine aggregates of quartz, albite, K-feldspar and biotite. The phenocrystic K-feldspar shows generally microcline texture, clean-looking

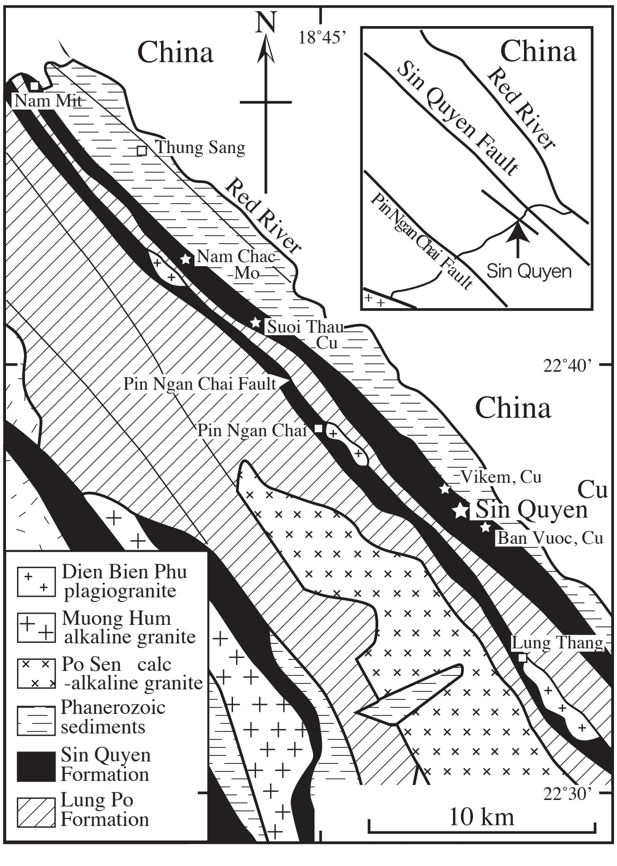

Fig. 2 Geological map of the Sin Quyen mine area. Modified from McLean (2001) and Bui *et al*. (2004). Star indicates copper deposits and occurrence.

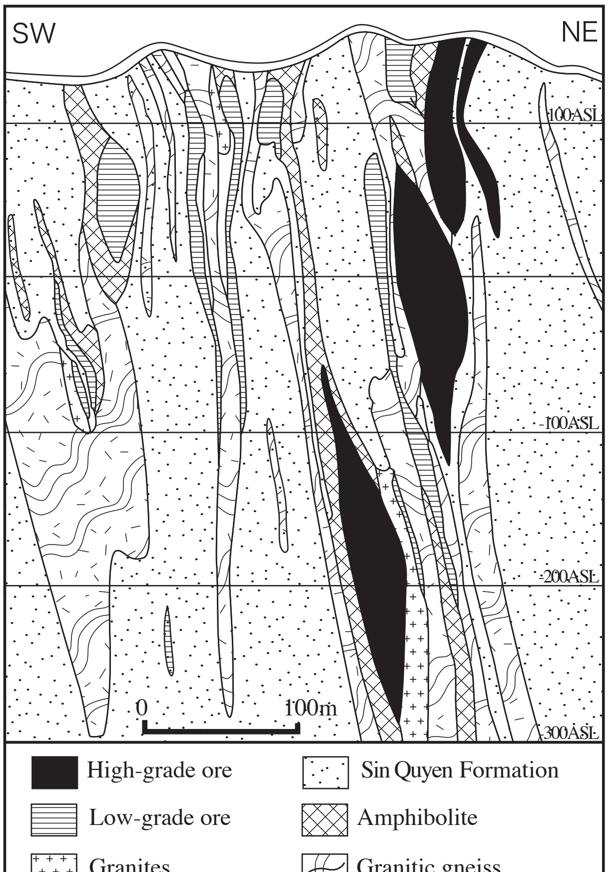

Fig. 3 Northeast-southwest profile of the Sin Quyen ore deposit (after McLean, 2001).

Table 1 Chemical compositions of the ores and tailings of the Sin Quyen mine, North Vietnam. Cpx: clinopyroxene, Mt: magnetite.

Analyte Symbol	LREE	HREE+Y	Fe	Mn	Mg	Cu	As	Zn	Ga	Cd	Co	Ni	Al	Ca	Na	K	Rb	Pb	Sr	Ba
Unit Symbol	ppm	ppm	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	%	%	%	ppm	ppm	ppm	ppm
Detection Limit	0	0	0.01	1	0.01	0.2	0.1	0.2	0.1	0.1	0.1	0.5	0.01	0.01	0.001	0.01	0.2	1	0.2	1
57 Cu concentrates	1587	28	28.9	201	0.17	209000	< 0.1	727	4	6.0	320	142	0.81	0.51	0.22	0.20	17	107	22.5	7
56 Fe concentrates	3887	40	67.7	311	0.14	476	3	33	32	0.2	33	21	1.05	0.49	0.29	0.23	19	66	29.8	52
3035 Fine granite	166	26	1.2	327	0.13	12.9	1	36	21	0.2	15	2	8.07	0.71	2.32	4.09	132	19	175	1100
20 Magnetite ore	17088	160	39.4	1020	0.70	3900	18	79	34	0.2	108	51	4.28	5.29	0.89	0.60	15	45	66.2	40
3031 Mt-cp ore	54978	484	29.5	338	0.26	27600	12	98	30	0.8	61	35	4.45	2.76	1.29	0.30	27	18	154	27
41 Cp-Mt ore	34410	284	25.2	1170	0.87	9110	88	247	36	1.8	71	32	6.84	6.07	1.58	1.24	102	48	143	217
19 High-grade Cu ores	8579	159	19.4	875	1.15	42300	7	235	35	1.3	141	35	5.68	3.98	1.35	1.72	118	69	125	35
42 Cp skarn ore	7869	177	21.8	1900	1.04	11300	< 0.1	154	23	0.7	120	69	4.33	11.50	1.00	0.28	7	52	106	25
21 Cp skarn ore	7158	119	15.0	1680	0.82	14900	24	164	39	0.8	45	15	9.08	11.80	2.51	0.41	9	50	218	56
39 Cp-Mt green ore	2833	65	20.1	927	1.85	17600	16	156	23	0.7	52	24	7.32	3.92	1.54	3.17	183	79	201	127
40 Cp-mt green rock ore	2650	78	17.1	628	0.99	13900	19	86	29	0.5	42	15	7.92	2.78	3.64	1.64	125	50	211	245
3034 Cp green rock ore	1764	111	11.6	1220	1.26	8160	< 0.1	63	21	0.4	76	31	5.77	7.02	0.24	0.23	6	20	238	23
55 Cp-epidote skarn	8463	149	13.1	921	1.41	1100	68	1950	27	17.8	49	32	8.11	4.32	2.80	1.70	117	328	213	380
3036 Epidote skarn	13	17	15.5	4360	2.49	113	< 0.1	139	14	0.4	17	14	1.82	9.13	0.30	0.38	11	59	11.6	86
Average of the ores	13255	164	21	1367	1	13635	32	306	28	2	71	32	6	6	2	1	65	74	153	115
83 Tailing	6664	113	12.2	872	1.38	235	11	49	23	< 0.1	35	22	6.51	3.60	2.43	1.71	110	15	180	308
84 Tailing	6971	118	11.3	834	1.24	234	10	59	23	< 0.1	28	17	6.70	3.56	2.54	1.38	75	16	174	266
85 Tailing	6955	117	11.2	879	1.28	194	3	46	22	< 0.1	31	19	6.85	3.71	2.46	1.71	98	12	178	296
86 Tailing	7333	118	11.1	856	1.24	207	4	45	22	< 0.1	31	19	6.63	3.82	2.56	1.68	98	16	183	305
87 Tailing	6471	114	11.8	899	1.36	202	7	53	24	< 0.1	34	21	7.02	3.48	2.42	1.81	106	18	169	304
88 Tailing	7636	125	12.2	901	1.29	233	< 0.1	47	22	< 0.1	33	20	6.91	4.01	2.60	1.81	103	13	193	314
89 Tailing	5505	91	11.1	878	1.05	203	7	42	22	< 0.1	31	19	4.17	3.66	2.23	1.43	55	11	169	259
90 Tailing	5012	91	10.3	840	1.09	191	5	64	22	< 0.1	26	15	5.28	3.38	2.40	1.50	63	11	167	270
91 Tailing	5957	97	10.8	837	1.25	170	6	55	24	< 0.1	31	20	6.12	3.38	2.38	1.73	112	11	171	312
92 Tailing	7077	116	12.3	843	1.27	235	2	44	22	< 0.1	33	20	6.49	3.77	2.37	1.73	102	11	176	296
93 Tailing	7114	120	11.7	851	1.25	267	3	64	21	< 0.1	30	18	6.68	3.81	2.47	1.68	92	14	177	285
94 Tailing	6692	116	11.7	865	1.27	238	5	56	22	0.2	31	18	6.76	3.67	2.37	1.70	91	19	168	281
95 Tailing	7114	121	13.1	943	1.34	275	< 0.1	59	23	0.2	35	21	7.04	3.86	2.53	1.75	99	19	181	301
96 Tailing	6396	110	11.9	882	1.29	187	3	54	23	< 0.1	33	22	7.23	3.72	2.48	1.92	114	17	181	321
97 Tailing	6708	114	12.8	894	1.41	290	4	53	25	< 0.1	33	21	7.30	3.72	2.87	1.83	109	21	194	313
98 Tailing	6955	119	13.1	913	1.42	230	6	62	23	< 0.1	32	20	7.29	3.73	2.63	1.71	97	24	176	298
99 Tailing	7090	120	12.9	900	1.39	250	4	52	23	< 0.1	31	20	6.85	3.99	2.61	1.73	99	24	188	288
100 Tailing	2509	45	10.8	785	0.99	200	3	48	21	< 0.1	27	17	2.70	2.99	2.31	1.46	26	18	146	268
Average of the tailings	6453	109	12	871	1	225	5	53	22	0	31	19	6	4	2	2	92	16	176	294

Table 1 Continued.

Analyte Symbol	S	In	Bi	Ag	Sb	Se	Li	Be	V	Cr	Cs	Ge	Zr	Hf	Nb	Ta	Te	Sn	W	Mo	Th	U
Unit Symbol	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	0.01	0.1	0.02	0.05	0.1	0.1	0.5	0.1	1	0.5	0.05	0.1	1	0.1	0.1	0.1	0.1	1	0.1	0.1	0.1	0.1
57 Cu concentrates	n.d.	3.8	8.0	10.1	2.3	10.3	2.6	0.9	18	25.2	1.52	0.5	8	0.2	8.9	< 0.1	10.3	61	< 0.1	11.3	5.8	26.4
56 Fe concentrates	n.d.	0.1	2.4	0.21	2.4	1.1	2.8	0.6	308	96.8	1.38	2	10	0.3	10.3	< 0.1	0.1	10	< 0.1	7.2	8.8	50.7
3035 Fine granite	n.d.	< 0.1	0.1	< 0.05	< 0.1	0.7	6.1	1.5	< 1	29.8	1.43	1.1	3	< 0.1	5.1	0.2	0.1	3	25.0	< 0.1	11.9	2.1
20 Magnetite ore	n.d.	0.6	1.1	0.19	0.5	2.3	6.4	6.1	242	70.3	1.83	3.5	7	0.4	15.8	< 0.1	2.1	52	20.5	0.4	58.0	36.3
3031 Mt-cp ore	3.39	0.4	2.6	0.95	0.2	5.9	5.5	1.3	218	29.2	2.14	13.3	22	0.6	12.1	0.2	2.8	25	8.0	0.7	90.0	28.5
41 Cp-Mt ore	n.d.	0.7	0.1	0.38	0.7	3.7	15.1	6.9	200	70.0	11.30	7.8	14	0.5	37.9	< 0.1	1.1	55	< 0.1	1.2	90.0	29.1
19 High-grade Cu ores	n.d.	1.6	1.8	2.10	0.7	3.4	17.9	7.7	142	119.0	5.72	2.5	8	0.3	10.4	< 0.1	0.2	75	28.1	1.1	46.7	70.1
42 Cp skarn ore	n.d.	1.1	0.4	0.34	0.5	3.6	3.7	5.2	113	47.8	0.22	1.9	16	0.8	42.7	< 0.1	0.5	62	< 0.1	1.5	26.8	55.4
21 Cp skarn ore	n.d.	1.4	0.1	0.37	0.6	2.1	4.0	5.8	91	19.8	0.26	2.3	17	0.7	58.7	1.4	1.1	124	16.4	0.9	26.9	39.6
39 Cp-Mt green ore	n.d.	0.3	0.9	0.98	4.3	1.6	38.2	4.0	137	101.0	6.24	1.5	27	0.6	10.7	< 0.1	0.3	20	< 0.1	54.8	14.7	35.6
40 Cp-mt green rock ore	n.d.	0.4	0.3	0.61	0.9	1.5	22.8	3.7	86	44.3	6.58	1.0	16	0.5	23.2	0.6	1.1	36	< 0.1	1.5	20.3	81.8
3034 Cp green rock ore	3.12	0.4	0.5	0.29	0.2	2.7	3.2	6.9	97	63.0	0.13	2.1	17	0.7	64.7	0.5	0.7	19	30.5	0.8	11.0	17.8
55 Cp-epidote skarn	n.d.	0.7	2.2	2.23	38.8	2.0	23.4	4.4	122	59.5	5.98	2.7	85	2.3	42.4	0.2	0.5	29	< 0.1	37.5	26.1	71.0
3036 Epidote skarn	0.03	0.4	1.5	0.14	< 0.1	1.1	3.9	9.0	63	13.3	1.00	0.7	15	0.5	9.1	0.2	0.3	87	14.1	0.3	2.2	2.9
Average of the ores	2	1	1	1	5	3	13	6	137	58	4	4	22	1	30	1	1	53	20	9	38	43
83 Tailing	0.79	0.2	1.0	< 0.05	0.1	1.8	18.7	4.0	78	48.0	5.07	2.0	11	0.3	52.0	1.0	0.6	32	1.5	0.2	17.2	65.1
84 Tailing	0.71	0.2	0.8	< 0.05	< 0.1	1.9	13.6	3.8	64	44.1	3.77	1.7	9	0.4	47.0	0.9	0.4	31	0.7	0.5	18.1	52.9
85 Tailing	0.71	0.2	0.6	< 0.05	< 0.1	1.8	16.0	3.8	69	41.5	4.68	1.7	9	0.4	49.2	1.0	0.5	32	0.9	0.1	18.8	63.6
86 Tailing	0.72	0.2	0.8	< 0.05	< 0.1	1.9	16.1	4.0	69	43.2	4.49	1.9	9	0.3	47.2	0.9	0.4	32	0.8	0.2	18.6	66.0
87 Tailing	0.79	0.2	0.7	< 0.05	< 0.1	1.7	17.4	3.5	67	47.6	5.34	1.8	10	0.3	51.3	1.0	0.4	32	1.2	0.3	18.0	63.4
88 Tailing	0.75	0.3	0.6	< 0.05	< 0.1	2.3	17.6	4.0	77	45.2	4.84	2.0	9	0.4	49.0	1.0	0.4	33	0.8	0.3	19.3	72.1
89 Tailing	0.71	0.2	0.5	< 0.05	< 0.1	2.2	14.4	3.5	71	38.0	3.52	2.8	10	0.3	48.8	1.0	0.3	34	0.7	0.2	11.3	58.6
90 Tailing	0.64	0.2	0.5	< 0.05	0.1	1.6	15.9	3.6	65	48.0	3.87	2.8	8	0.3	44.2	0.9	0.3	30	0.8	0.2	11.5	53.3
91 Tailing	n.d.	0.2	0.6	< 0.05	< 0.1	1.7	18.5	3.6	75	48.2	5.34	1.4	10	0.3	50.6	1.0	0.5	30	1.0	0.2	15.2	57.5
92 Tailing	n.d.	0.2	0.6	< 0.05	< 0.1	2.3	17.3	4.0	75	48.2	4.68	1.6	10	0.3	47.7	0.9	0.4	31	1.5	0.2	17.9	56.7
93 Tailing	0.63	0.2	1.6	< 0.05	< 0.1	2.6	15.6	3.6	72	42.2	4.15	1.8	9	0.3	47.3	1.0	0.4	30	0.8	0.2	18.4	54.9
94 Tailing	0.71	0.2	0.7	< 0.05	< 0.1	1.7	15.1	3.4	72	44.7	4.45	2.0	10	0.3	51.7	1.0	0.4	37	0.9	0.1	18.0	57.5
95 Tailing	0.70	0.3	0.8	< 0.05	< 0.1	2.1	16.9	3.9	74	45.8	4.54	2.1	9	0.3	56.2	1.1	0.4	32	1.2	0.9	19.0	59.8
96 Tailing	0.69	0.2	0.5	< 0.05	< 0.1	2.0	19.2	4.0	77	48.3	5.48	2.3	11	0.4	49.7	1.0	0.4	30	1.4	0.2	17.4	60.5
97 Tailing	0.67	0.2	0.5	< 0.05	< 0.1	2.0	18.7	4.1	79	48.7	4.81	2.0	10	0.3	53.8	1.0	0.3	32	1.0	0.2	17.2	56.6
98 Tailing	0.64	0.3	1.2	< 0.05	< 0.1	1.7	16.7	3.7	76	47.8	4.78	2.1	9	0.3	50.2	1.0	0.6	33	0.8	0.2	19.1	57.6
99 Tailing	0.69	0.2	0.5	< 0.05	< 0.1	2.6	17.0	4.0	74	47.5	4.50	2.1	9	0.3	48.3	0.9	0.4	33	0.8	0.2	17.9	63.4
100 Tailing	0.57	0.2	0.7	0.16	< 0.1	1.2	14.9	3.0	63	39.8	3.15	2.8	7	0.3	44.2	1.0	0.4	27	1.2	0.1	2.5	38.2
Average of the tailings	1	0	1	0	0	2	17	4	72	45	5	2	9	0	49	1	0	32	1	0	16	59

with no clay minerals, but contains inclusions of albite and quartz. Albite in the groundmass is not clean, containing minute sericite and clay minerals. Quartz shows a myrmekitic intergrowth with albite in some places.

Among minor minerals, garnet is subhedral to euhedral and surrounded by albite, biotite and quartz. The garnet contains grains of deformed biotite and quartz within the crystals. Therefore, the garnet is considered formed during the recrystallization stage after regional shearing. Few grains of allanite, 0.1 to 0.2 mm in length, occur as reddish brown columnar crystals. The other accessory minerals are apatite, monazite, rutile (?), iron sulfides, calcite and magnetite. Magnetite is very small amount occurring as a massive form or needle-shaped crystals along cracks, which could be formed in the later hydrothermal stage.

3.2 Banded ores

The ores are often banded by felsic zone composed of detrital and recrystallized quartz and feldspars, and dark greenish zone containing pyroxene, amphibole, biotite and allanite-epidote (e. g., Plate IIB). The color becomes blackish, when magnetite is abundant. Epidote without ore minerals shows clean yellowish green color (Plate IC). One of such rocks of No. 3034 is composed of alternation of epidote (50 vol.%) and quartz (30 vol.%), together with amphibole (10 vol.%), allanite (5 vol.%), titanite (5 vol.%), apatite (2 vol. %) and calcite (1 vol.%) under the microscope. Epidote is yellowish green and granular in shape having grain size of 0.05 to 0.1 mm. Titanite is wedge-shaped and less than 0.15 mm in size. Quartz is anhedral and less than 0.5 mm in size, showing wavy extinction weakly. Apatite tends to occur in quartz-rich part of the rock.

The sample No. 3036 is massive pyroxene rock, composed mainly of clinopyroxene, which is partly replaced by bluish green amphibole. The clinopyroxene is less than 5 mm in size and has distinct cleavages in three directions. The color is partly yellowish green along the cleavages. The optic angle is large as $2V(+)=70^{\circ}$, indicating possibility of aegirine-augite. Amphibole has needle to columnar shape of subhedral crystals with the color of bluish green (Z') and yellow (X'), which is supposed to be hastingsite. Secondary carbonate is fairly abundant, while quartz is minor mineral.

3.3 Massive ores

The massive ores are generally dark colored and high-grade compared with the banded ores, and occur in green banded rocks, composed of hastingsite (up to 50 vol.%), biotite (30 vol.%), allanite (10 vol.%), epidote (5 vol.%), magnetite (5 vol.%) and chalcopyrite (3 vol.%). Biotite occurs in fine grained platy crystals and has Z-color of greenish brown. Allanite is often twinned and zoned with distinct pleochroism (Plate IIB). The pleochroism is reddish brown to greenish yellow in the core but pale yellow at the rim. Biotite next to the allanite has a weak radioactive halo.

Magnetite is 0.5 to 2.0 mm in size and subhedral to anhedral and occurs associated with allanite (Plates IIB, E). Magnetite contains inclusions of biotite and allanite, so that it is crystallized later than these silicates. No later hematitization is observed over margin and cleavage of the magnetite crystals. Chalcopyrite is 0.2 to 1.0 mm in size and anhedral, filling among the earlier crystallized minerals of allanite, magnetite and pyrrhotite (Plate IIE, F).

4. Chemical characteristics

Eleven selected ores, two concentrates (Nos. 56, 57), eighteen tailings (Nos. 83-100) and one leucogranite (No. 3035) were analyzed by ICP-MS after a complete digestion with HF, $HClO_4$, HNO_3 and HCl, except for F, which was analyzed by SIE (Specific Ion Electrode) method. Sulfur was analyzed by infrared method. All the analyses were performed at the Activation Laboratories, Ancaster, Canada. The results are shown in Table 1. Both the ores and tailings are quite different from those of base metal deposits occurring in the sedimentary terrain of North Vietnam reported by Ishihara *et al*. (2010a, b), which are poor in copper, but rich in zinc and lead.

4.1 General remarks

The studied ores contain 11.6 to 39.4 wt.% Fe. Referring their magnetic susceptibility values measured by a portable device, the Fe contents higher than 15 wt.% Fe appear to have both oxide and silicate iron, which are typically shown by the high-grade Cu and REE ores in Table 1. The highest value of 39.4 wt.% Fe was obtained from magnetite-allanite (1.7 wt.% REE) ore (No. 20, Table 1). The Cu contents generally vary from 0.1 to 4.2 wt.%, and Pb-Zn contents are very low, less than a few hundreds ppm. Total REE+Y contents range from 0.2 to 6 wt.% (Table 1), and the LREE/HREE+Y ratios vary from 16 to 121, except for the epidote-dominant rock (No. 3036) of 0.8. The leucogranite is not high in the REE content and has 6.4 LREE/HREE+Y ratio.

Among minor elements, U contents are as high as18-82 ppm and Th contents are low relative to the U contents. Thus, the U/Th ratios are much higher than 0.25 of common granitoids (e.g., Ishihara *et al*., 1969). Tin and tungsten contents of the ores are relatively high in the chalcopyrite-magnetite ores, as 19-124 ppm Sn and <0.1-30.5 ppm W. Mo is sporadically high up to 55 ppm Mo. Indium contents are very low (<1.6 ppm In), unlike lead-zinc deposits of North Vietnam (Ishihara *et al*., 2010a, b).

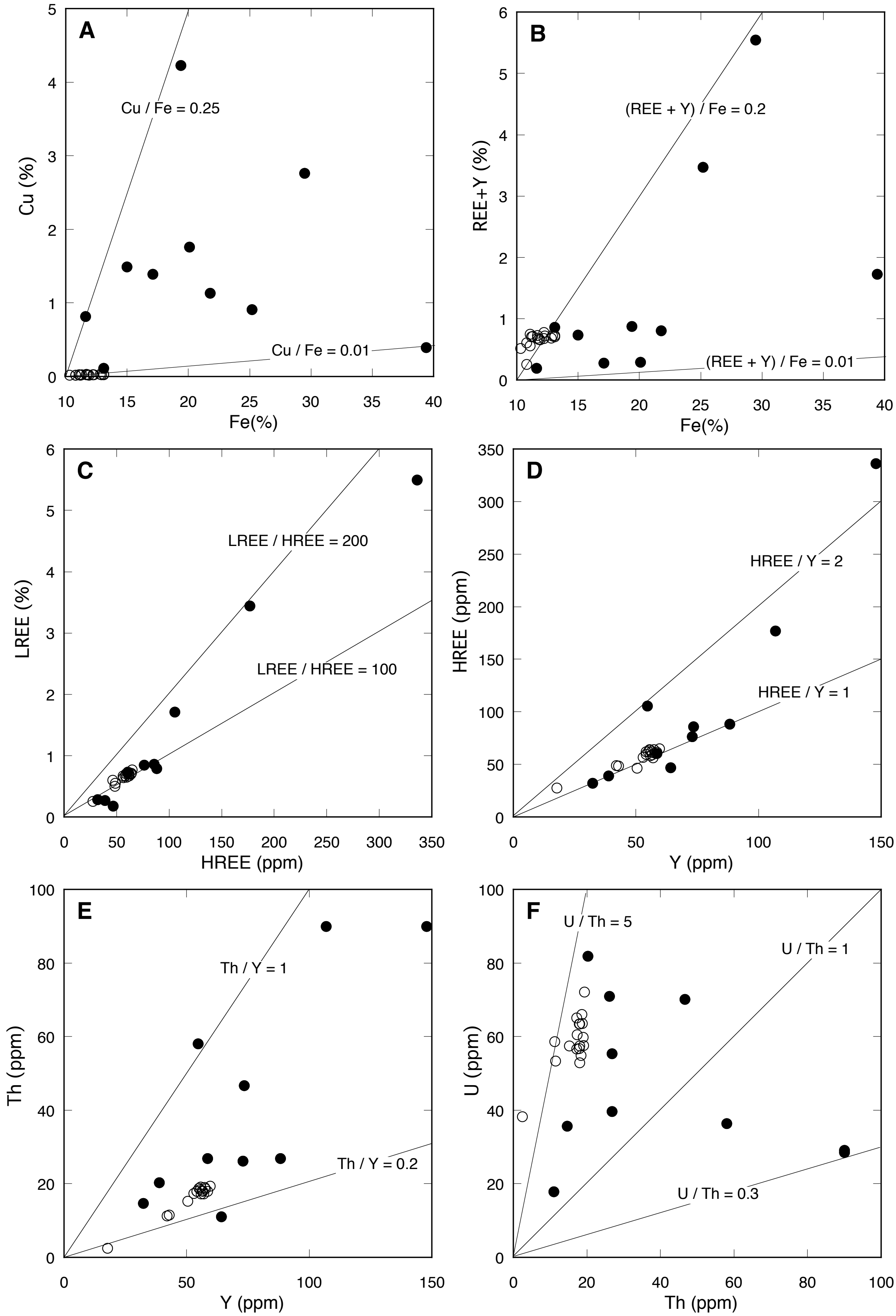

Fig. 4 Binary diagrams of selected components of the Sin Quyen ore deposits. ●: Ores, ○ Tailings.

4.2 Binary diagrams

Binary diagrams of the major ore components are shown in Fig. 4. Cu and Fe ratio varies from 0.01 to 0.25 in the ores, but very low in the tailing (Fig. 4A). The Cu contents of the tailings decrease to the 290 -170 ppm level (Table 1), implying that chalcopyrite was well separated out by the flotation into the copper concentrates. The other chalcophile elements, such as arsenic, zinc, cadmium, cobalt, indium, bismuth, silver, antimony and molybdenum (Table 1), are also moved together with the copper sulfides. Therefore, sulfur contents of the tailings are only around 0.57-0.79 % S (Table 1).

REE+Y contents are briefly correlated with Fe content in the ores, with the (REE+Y)/ratio from 0.01 to 0.2 (Fig. 4B), implying that both the components were derived from the same ore solution. A large difference of these two diagrams is seen on the tailings. The tailing samples decrease in Fe contents to around 10-13 wt.% Fe, implying the magnetite and chalcopyrite have been separated out (Fig. 4A). Yet, those of REE+Y contents, which are various amounts in the ores but being at 7,000-8,000 ppm level in the tailings (Fig. 4B), indicating that almost all of the REE-holding allanites have been moved to the tailings.

Good positive correlations have been observed between LREE and HREE with their ratio 200 or less (Fig. 4C). Positive correlation between HREE and Y is also good with their ratio around 1-2 (Fig. 4D), reflecting their geochemical affinities. A positive correlation is less distinct between Th vs. Y diagram (Fig. 4E). The Th/Y ratio varies between 0.2 and 1 (Fig. 4E). Uranium is enriched in the Sin Quyen ores and has U/Th ratio over 1 (Fig. 4F), which is much higher than the granitoid value of 0.25 (Ishihara *et al*., 1969). This high U/Th ratio implies that thorium was not but uranium was enriched in the ore deposits by the Cu-Fe mineralizations.

4.3 REE patterns

REE patterns of the chalcopyrite-magnetite ores with different REE contents of 5.5, 3.5, 1.7, 0.9 and 0.003 wt.% REE+Y are shown in Fig. 5. These patterns are similar each other, implying that the patterns reflect contents and compositions of the contained allanites. The whole patterns are similar to that of the leucogranite (No. 3035), which has a weak Eu anomaly. In details, the highest REE + Y grade ore of No.3031, shows a sudden increase of Lu, which is somewhat similar to the REE pattern of the epidote rock (No. 3036, not shown here).

Low REE+Y grade ores tend to have increased amounts of HREE (e.g., No. 19), which may be due to presence of epidote. REE contents of this mineral are very low, but within the lowest range, its REE contents increase toward the heaviest REE side. Epidote is known generally to have HREE-rich character and in the case of one occurring in the Vierkisest granodiorite, slight positive Eu-anomalies are observed (Giere and Sorensen, 2004).

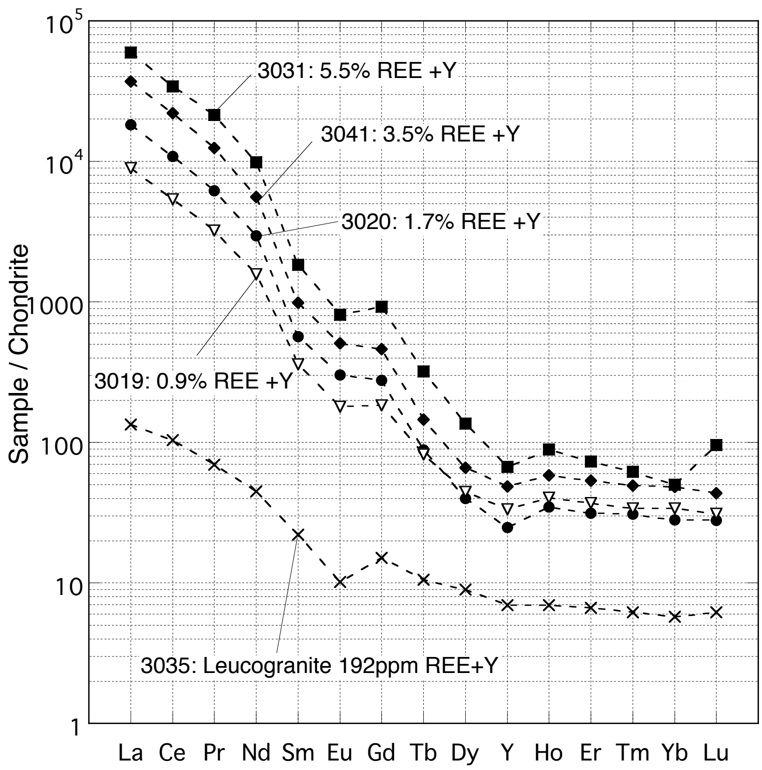

Fig. 5 REE patterns of the ores and leucogranite of the Sin Quyen deposits.

5. Chemical composition of allanite

Selected allanites were analyzed by a JEOL JXA-8900 electron microprobe equipped with five wave-length-dispersive spectroscopes (WDS), at AIST. Allanites and their epidote rims are analyzed on the two samples of Nos. 3034 and 3039, and the results are shown in Table 2. Epidote similar to the rim epidote occurs to fill allanite crystals as aggregates; thus these were formed later than the allanite crystallization by increasing of oxygen fugacity of the ore solution.

Compared with the allanites in granitoid from Nakano, a type locality of the magnetite-series granitoids in the eastern Shimane Pref. (Hoshino *et al*., 2007), the studied allanite of No. 3039 is higher in the contents of SiO_2, Al_2O_3 and CaO, but lower in those of TiO_2, MnO, MgO and ΣREE. Thus, the studied allanites are depleted in "mafic" components. Among the REE, the allanites are slightly enriched in LREE of La_2O_3 and Ce_2O_3, but depleted in the other REE of Pr_2O_3, Nd_2O_3, Sm_2O_3 and Gd_2O_3.

The epidote rim is very thin, less than 0.01 mm in width (Plate IIB, C). As compared with the host allanite, the rim epidotes are richer in SiO_2, Al_2O_3, CaO, MnO, and depleted in FeO, TiO_2, MgO and ΣREE_2O_3. This compositional change must have occurred just before the magnetite and chalcopyrite mineralizations for the mode of occurrence by change of the hydrothermal fluid composition.

Allanite with the idealized formula $(Ca^{2+}, REE^{3+})_2 (Al^{3+}, Fe^{3+}, Fe^{2+})_3Si_3O_{12}(OH)$, is related to epidote by the coupled substitution of $REE^{3+} + Fe^{2+} \Leftrightarrow Ca^{2+} + Fe^{3+}$. Therefore, the rim epidote decreases from 16.32 % to 0.72 % in the total REE contents and from 8.71 to 1.24 % in the FeO contents. On the other hand, the rim epidote increases from 15.37 % to 23.49 % in the CaO contents and 5.20 % to 11.28 % in the Fe_2O_3 content. Alumina content of the epidote increases from 18. 83 % to 23.63 % to compensate decreasing of Fe_2O_3 content.

Table 2 Average chemical compositions of allanites and associated epidotes occurring in chalcopyrite-magnetite ores (Nos. 3034, 3039).

	No.3039	No.3034	
	Allanite(n=21)	Allanite(n=30)	Epidote(n=4)
SiO2	34.99	35.22	39.03
TiO2	0.56	0.54	0.22
Al2O3	17.40	18.83	23.63
Fe2O3	4.76	5.20	11.28
FeO	10.81	8.71	1.24
MnO	0.12	0.08	0.22
MgO	0.66	0.22	0.02
CaO	13.48	15.37	23.49
La2O3	5.80	5.42	0.16
Ce2O3	9.16	8.70	0.38
Pr2O3	0.77	0.58	0.02
Nd2O3	1.46	1.47	0.13
Sm2O3	0.16	0.15	0.03
ΣREE	17.35	16.32	0.72
Total	100.13	100.49	99.85

Analyst: M. Hoshino.

*Fe2+/Fe3+ of the present allanite and epidote samples was calculated based on 8 cations and 12.5 atoms of oxygen.

Hoshino *et al*. (2007) studied allanites occurring in the main granitic bodies and related pegmatites in Japan, and found two groups of the allanite rich in manganese (more than 0.14 atoms per formula unit, apfu) or poor (less than 0.14 apfu) in manganese, which generally correspond to the ilmenite-series or magnetite-series granitic magmatism (Fig. 6). The magnetite-series allanites are also different in having higher TiO_2 and MgO contents, and LREE-dominant REE patterns. The granite classification is essentially made by difference of oxygen fugacity of the granitic magmas (Ishihara, 1977). The studied allanites have the magnetite-series characteristics, indicating that the mineralizations occurred with metasomatic fluids derived from an oxidized source magma. This character continued to the later hydrothermal stage and precipitated magnetite in the ore deposits.

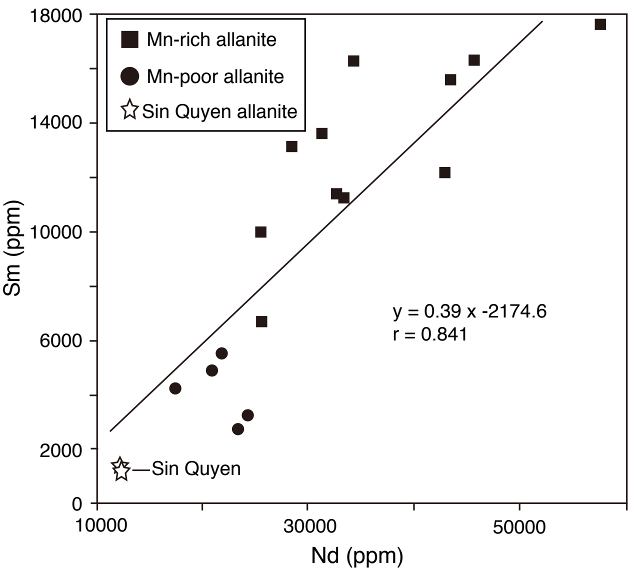

Fig. 6 The Sin Quyen allanite plotted against Sm vs. Nd diagram of the allanites from two types of granitoids in Japan (after Hoshino *et al*., 2007).

6. Some genetic consideration

From the alignment of many chalcopyrite-magnetite deposits along northwesterly metamorphic zones (Fig. 2), it is obvious that the mineralization is controlled by shearing related to the Red River Fault, which is the southeastern part of the Ailao Shan-Red River tectonic element (Tapponnier *et al*., 1990). The oldest host rocks are Proterozoic in age, but the youngest rocks may be mid-Tertiary in age, because monazite and xenotime of some leucogranites were reported to have U-Pb age of 22 and 24 Ma and that of zircon of 30 and 34 Ma (Tapponnier *et al*., 1990). The ore minerals observed in this study show no stress effect on the texture and seem to be crystallized after the regional shearing. Thus, the mineralization is considered to have occurred during a mid-Tertiary time.

REE-mineralizations are seen commonly with carbonatite and/or alkaline A-type granitoids. As mentioned previously, the Muong Hum intrusion is composed of alkaline granites of Paleogene age. If branch of similar granite intrudes along the Red River Fault, it could be one candidate of the source rock for the Sin Quyen deposit. We need further detailed study for petrology and age dating for the leucogranite dikes occurring in the Sin Quyen deposit area.

7. Conclusions

(1) The magnetite and chalcopyrite ores of the Sin Quyen deposits occur with metasomatite consisting of pyroxene, hastingsite, allanite, epidote, biotite, titanite and latest-stage carbonates.

(2) Both allanite and ore minerals show no stress effect; the mineralizations appear to be much later than the deformation of the host rocks, possibly related to magnetite-series granitic magmatism of alkaline affinity during a Paleogene time.

(3) The chalcopyrite-magnetite ores have LREE-enriched character, because allanite is the main REE mineral. Allanite is euhedral and epidotized at the rim, and is an early crystallized mineral replaced by magnetite and chalcopyrite.

(4) The studied allanites are depleted in "mafic" components, and could be compared with allanites in the magnetite-series granite.

(5) The allanites have chemical composition of Mn-poor type of Hoshino *et al*. (2007), indicating that the mineral crystallized from metasomatic fluids liberated from an oxidized magmatic activity.

(6) Both chalcopyrite and magnetite are well separated by the mineral dressing, and all the allanites moved to tailings. Therefore, the tailing pond turns out to be an excellent LREE reservoir in future.

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北部ベトナム，Sin Quyen 鉱山の褐簾石に富む銅 - 磁鉄鉱鉱床の予察的研究

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要　旨

Sin Quyen 鉱山の褐簾石に富む含金黄銅鉱 - 磁鉄鉱鉱床の代表的鉱石について顕微鏡観察と化学的性質を予察的に調べた．鉱床は母岩の北西 - 南東系片理面に規制されて胚胎する縞状鉱として産出するが，主鉱石鉱物である磁鉄鉱・黄銅鉱は塊状～鉱染状に産出し鉱物粒は変形を受けていない．鉱化作用は広域的な変形運動後の恐らく古第三紀に生成したものと考えられる．随伴変質鉱物は，輝石・角閃石類・褐簾石・緑簾石・黒雲母・チタン石・方解石・少量の石英からなり，褐簾石は軽希土類に富み 16 Wt.％に達する希土類元素を含む．褐簾石は自形，早期晶出相の一つで，磁鉄鉱と黄銅鉱に交代される．この褐簾石は化学組成上，Mn に乏しい性格を持ち，これは日本の花崗岩地帯では磁鉄鉱系花崗岩類の褐簾石に見出されるものであるから，Sin Quyen 鉱床も REE に富む酸化的なアルカリ花崗岩質マグマ活動で生成した可能性が高い．この点は鉱床が磁鉄鉱に富むこととも整合的である．磁鉄鉱と黄銅鉱とは磁力選鉱・浮遊選鉱で完全に回収されおり, 褐簾石は全てテーリング（選鉱廃石）に移動している．従ってテーリングの REE 含有量は高く, テーリング場は将来の軽希土類資源貯鉱場と考えることも可能である．

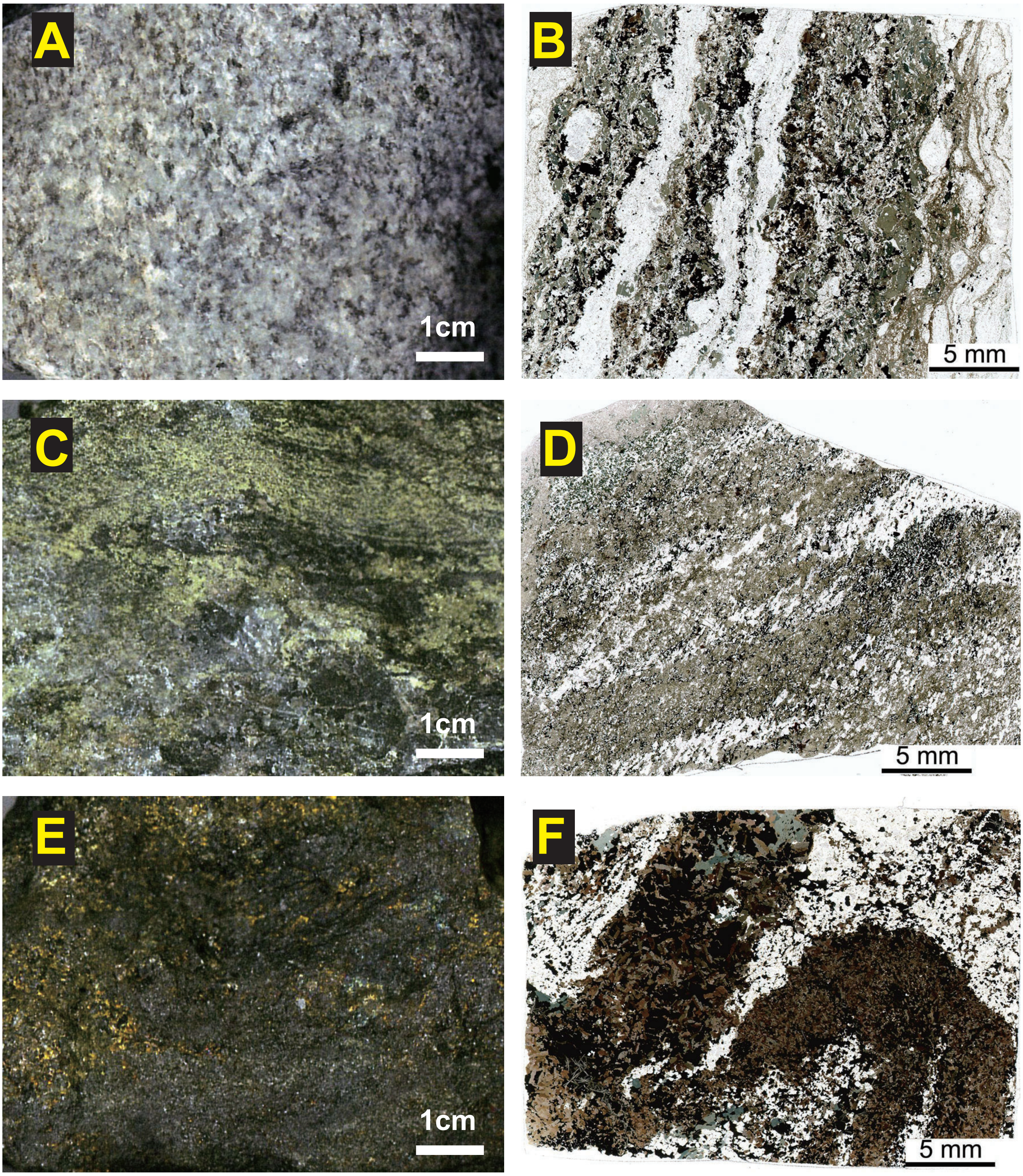

Plate I Studied granite and ores and their thin sections from the Sin Quyen ore deposits.
A: Outlook of the leucogranite, No. 3035.
B: Thin section of banded allanite-rich ore, No. 3039.
C: Epidote-rich ore of No. 3034.
D: Thin section of No. 3034.
E: Chalcopyrite-magnetite-rich ore of No. 3031.
F: Thin section of No. 3031.

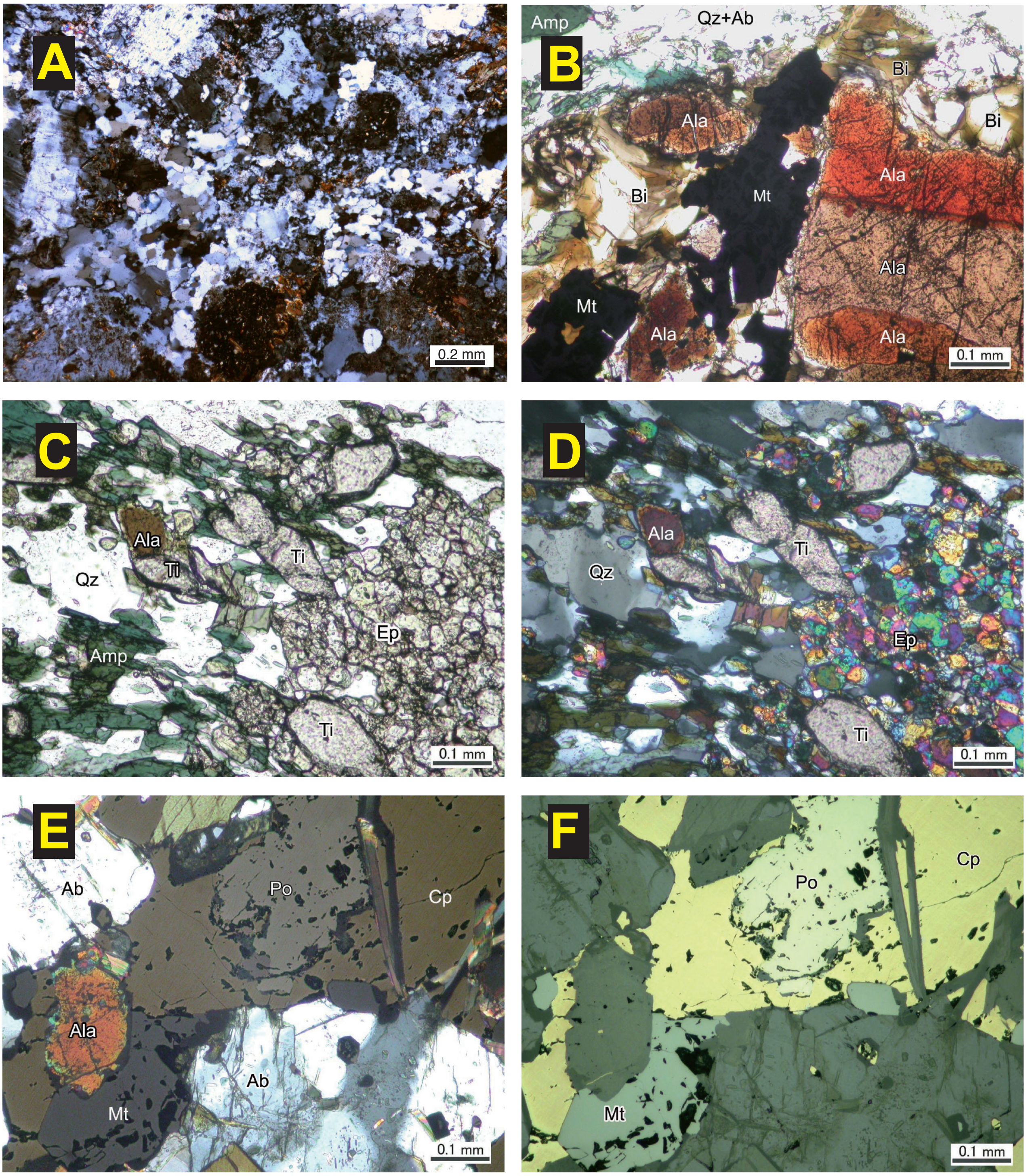

Plate II Thin and polished sections of rock and ores from the Sin Quyen ore deposits.

A: Recrystallized leucogranite, possibly after shearing. No. 3035. Crossed nicols.

B: Allanite (Ala) with different orientations occurring together with magnetite (Mt) biotite (Bi), amphibole (Amp), quartz (Qz) and albite (Ab). No. 3039. One nicol.

C: Epidote (Ep) occurring together with titanite (Ti), amphibole (Amp) and a little allanite (Ala). No. 3034 (one nicol).

D: Crossed nicols.

E: Pyrrhotite (Po), chalcopyrite (Cp) and magnetite (Mt) occurring with albite (Ab). Crossed nicols. No. 3031. Crossed nicols.

F: Polished surface under one nicol.

Abbreviation: Ab, albite; Ala, allanite; Amp, amphibole; Bi, biotite; Cp, chalcopyrite; Ep, epidote; Mt, magnetite; Qz, quartz; Po, pyrrhotite; Ti, titanite.