ベトナム北部レアメタル含有ナ ボップ、ロン ホアイ、ナ ソン、シン クエン卑金属鉱床の鉱物学的・地球化学的特徴

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要旨

ナボップ、ロン ホアイ、ナ ソン、シン クエン鉱床などのベトナム北部の卑金属鉱床は、銅鉱石と鉛亜鉛鉱石についてベトナムの鉱物資源賦存量の90％（銅）と70％（鉛亜鉛）を占めている。ナ ボップとロン ホアイ鉱床は亜鉛に富む鉱床である。一方、ナ ソン鉱床は鉛に、シン クエン鉱床は銅に富む鉱床である。ナ ボップ、ロン ホアイ、ナ ソン、シン クエン鉱床のインジウム含有量は、それぞれ1.08～83.0、2.29～5.38、0.20～5.31、0.92～1.59 ppmの範囲を持つ。ナボップ、ロン ホアイ、ナ ソン鉱床の鉱石のIn/Zn比は、17×10^{-4}～23×10^{-4}、0.2×10^{-4}～0.6×10^{-4}、0.1×10^{-4}～0.7×10^{-4}の範囲を持ち、ナ ボップで高く、ロン ホアイ、ナ ソンで低い。これらの特徴は、これらの鉱床の閃亜鉛鉱のインジウム含有量の変化と調和的である。今回検討したシン クエン鉱床の鉱石には閃亜鉛鉱は認められなかったが、シン クエン鉱床の鉱石のIn/Zn比は、16×10^{-4}～87×10^{-4}の範囲を持つ。 この比は、ナ ボップ、ロン ホアイ、ナ ソン鉱床の鉱石のIn/Zn比よりも高い。シン クエン鉱床の鉱石のインジウムは、銅鉱物に含まれる可能性がある。

Mineralogical and geochemical characteristics of rare metals-bearing Na Bop, Lung Hoai, Na Son and Sin Quyen base metal deposits, Northern Vietnam

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Abstract

Base metal deposits in northern Vietnam such as Na Bop, Lung Hoai, Na Son and Sin Quyen deposits have reserve of 90% of Cu and 70% of Pb-Zn ore resources of Vietnam. The Na Bop and Lung Hoai ore deposits are Zn-rich ore deposits, while the Na Son and Sin Quyen deposit are Pb-rich and Cu-rich ore deposits, respectively. The Indium contents of the ores from the Na Bop, Lung Hoai, Na Son and Sin Quyen deposits range from 1.08 to 83.0, 2.29 to 5.38, 0.20 to 5.31, 0.92 to 1.59 ppm, respectively. The In/Zn ratios of ores from the Na Bop, Lung Hoai and Na Son deposits range from $17x10^{-4}$ to $23x10^{-4}$, $0.2x10^{-4}$ to $0.6x10^{-4}$ and $0.1x10^{-4}$ to $0.7x10^{-4}$, respectively. The In/Zn ratios of ores from the Na Bop deposit are higher than those of ores of the Lung Hoai and Na Son deposits. These characteristics are consistent with the variation of indium contents of sphalerite in these deposits. It suggests that indium in the ores from the Na Bop, Lung Hoai and Na Son deposits occur mostly in sphalerite. The In/Zn ratios of the ores from the Sin Quyen deposit range from $16x10^{-4}$ to $87x10^{-4}$. These ratios of the ores from the Sin Quyen deposit are higher than those of the ores from the Na Bop, Lung Hoai and Na Son deposits, although ores of the Sin Quyen deposit in this study does not contain sphalerite. Indium in the ores from the Sin Quyen deposit occurs in the Cu-bearing minerals.

1 Introduction

The Na Bop, Lung Hoai, Na Son and Sin Quyen deposits are important base metal resources of Northern Vietnam (Fig. 1). The Na Bop and Lung Hoai deposits are located in the Cho Don area and Cho Dien area, respectively, of the Cho Don district, Bac Kan Province. The Na Son and Sin Quyen deposits are located in the Vi Xuyen district of Ha Giang Province and Bat Xat district of Lao Cai Province, respectively. The Na Bop, Lung Hoai and Na Son deposits are located in Lo Gam zone, which is dominated by Cambrian-Devonian strata and Permo-Triassic granitoids (Tran et al., 2012), while Sin Quyen deposit is located in the Phan Si Pan Uplift and composed of Pre-Cambrian strata and Pre-Cambrian to Cenozoic alkaline granitoids (Gaskov et al., 2012). The products of

the Na Bop and Lung Hoai deposits are a large amount of zinc concentrate containing indium, cadmium and gallium, and a small amount of lead concentrate. The major products of the Na Son deposit is a large amount of lead concentrate with a small amount of Zinc concentrate containing cadmium and silver. The concentrates of Sin Quyen deposit are copper and iron concentrates containing gold and silver (Tran et al., 2012, Gaskov et al., 2012). The Na Son and Sin Quyen deposits also have high potential of REE resources. The aim of this study is to clarify the characteristics of ores from the Na Bop, Lung Hoai, Na Son and Sin Quyen deposits, which have a high potential for rear metal resouces.

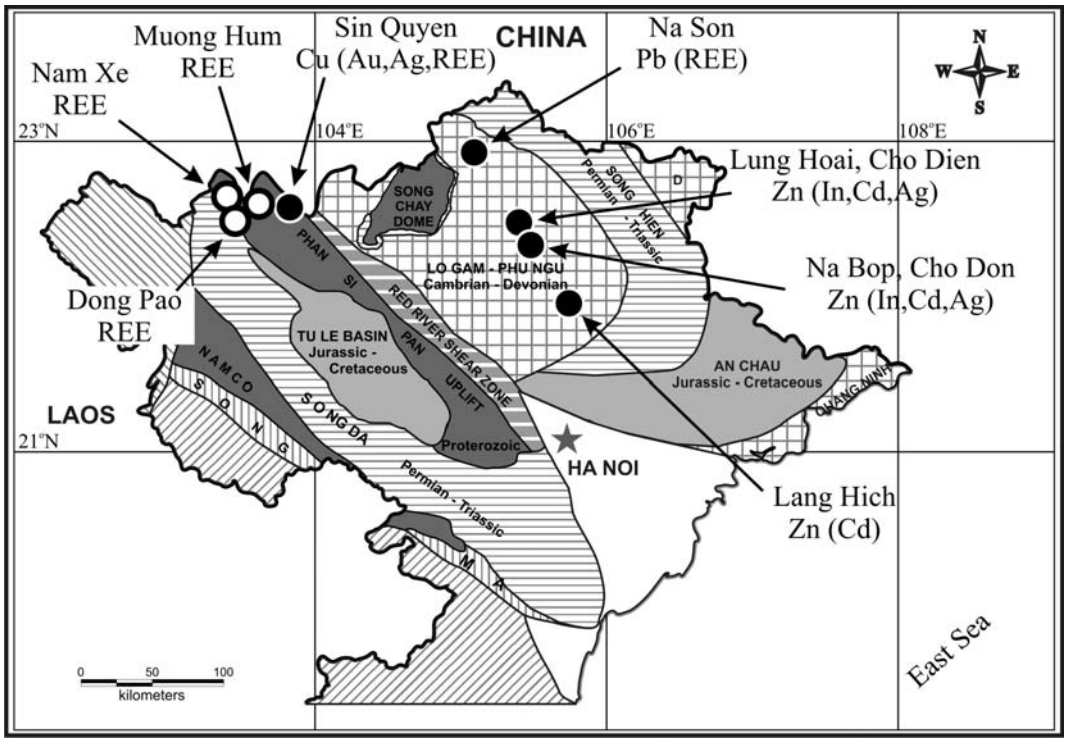

Fig. 1 Distribution of ore deposits in Northern Vietnam.

2 Outline of geology of studied deposits

The geology of northern Vietnam is divided into Indochina Terrane and South China Craton by the Ailao Shan–Red River Shear Zone. The Na Bop, Lung Hoai and Na Son deposits occur in South China Craton while the Sin Quyen deposit occurs in Indochina Terrane. The geology of Cho Don area is composed of Mia Le and Pia Phuong Devonian terrigenous-carbonate strata (D_1ml-D_1pp) including quartz-sericite schist, shale and clayish limestone. These strata were folded and cut by faults. Cho Dien area occurs about 20 km in the north of Cho Don area (Fig. 1). The geology of Cho Dien area is also composed by early Devonian strata (D_1ml-D_1pp) including shale, black argillite, clayish limestone, recrystallized limestone and marble. The Na Son deposit located in the northern part of Lo Gam zone and is hosted by trachydacite, rhyolite and and Devonian terrigenous-carbonate strata (D_1ml-D_1tb) consisting of cherty shale and limestone (Tran et al., 2012). The Sin Quyen deposit is located in the northeast of the Phan Si Pan uplift and situates very close to Red River Shear Zone (Fig. 1). Host rocks of the deposit consist of melanocratic gneiss, foliated biotite-quartz-amphibole and quartz-feldspar-amphibole rocks (PP-MPsq). These rocks are cut by leucocratic biotite-plagioclase-K-feldspar-quartz dykes (PP-MPsq) (Gaskov et al., 2012). The intrusive rocks near the Sin Quyen deposit are Paleo-Proterozoic Po Sen biotite granite and granodiorite.

3 Classification of ore and mineral assemblage

Base on the observation of hand specimens, observation of the thin sections and polish sections under the microscope and results determined by XRD and EPMA, the mineral assemblages of these deposits were estimated (Table 1). Ore deposits in the Cho Don area consist of the Na Bop, Ba Bo, Lung Vang, Na Tum, Pu Sap deposits. Ore deposits in the Cho Dien area consist of the Lung Hoai, Binh Chai, Bo Luong, Dam Van, Deo An and Po Sen deposits. The ore deposits examined in this study are the Na Bop and Lung Hoai deposits. The ores of the Na Bop deposit are classified into sphalerite-rich and pyrrhotite-rich parts. The pyrrhotite-rich part occurs as clots in sphalerite-rich part. There is a possibility that the pyrrhotite-rich part was formed prior to the formation of sphalerite-rich part. The sphalerite-rich part consists of a large amount of sphalerite and small amounts of pyrrhotite and

Table 1 The mineral assemblages of the studied deposits

Deposits	Na Bop		Lung Hoai		Na Son		Sin Quyen
Minera-lization / Minerals	pyrrhotite mineralization	sphalerite mineralization	arsenopyrite-sphalerite mineralization	sphalerite mineralization	galena mineralization	chalcopyrite mineralization	chalcopyrite-pyrrhotite mineralization
Magnetite					+		+
Galena	+	+	+		++		
Sphalerite		++	++	+	+		
Pyrite		+	+	+	+	+	
Chalcopyrite	+	+	+	+	+	+++	++
Cubanite							+
Arsenopyrite	++		+				
Pyrrhotite	++	+					++
Tetrahedrite						+	
Quartz				+	+	+	+
Amphibole							++
Allanite					+		+
K-feldspar					+++		
Carbonate	+	+++	++	+++	+		
Graphite	+	+					

+++: very abundant, ++: abundant, +: few.

arsenopyrite, while pyrrhotite-rich part consists of pyrrhotite, arsenopyrite, sphalerite, galena, pyrite and chalcopyrite. The pyrrhotite and pyrite coexist together. Chalcopyrite fills into interstices between pyrrhotite and pyrite. Arsenopyrite shows euhedral shape but was dissolved by pyrrhotite, chalcopyrite, sphalerite and pyrite. There are anhedral and euhedral carbonates. The anhedral carbonates are calcite, dolomite and ankerite. They were formed by the recrystallization. The Euhedral carbonate is calcite. It was formed in the same time with the early stage of the pyrrhotite mineralization, which is and partially dissolved by pyrrhotite. Graphite is included in the anhedral carbonate and sometime is surrounded by arsenopyrite.

The ores of the Lung Hoai deposit are classified into massive sphalerite part and arsenopyrite-sphalerite bended part. The mineral assemblage of massive sphalerite part is a large amount of sphalerite and small amount of pyrite and chalcopyrite. Pyrite and chalcopyrite occur as inclusion inside large grain of sphalerite. The arsenopyrite-sphalerite bended part is composed of large amounts of sphalerite and arsenopyrite and small amounts of galena, pyrite and chalcopyrite. Arsenopyrite is euhedral and cut by sphalerite. Pyrite and chalcopyrite also occur as inclusions in sphalerite.

Ores of the Na Son deposit are characterized by galena-rich ores. Galena-rich ores consists of a large amount of galena and small amounts of sphalerite, magnetite. These ores are cut by a network of chalcopyrite-tetrahedrite-pyrite. Magnetite is replaced by galena, sphalerite, tetrahedrite and silicate minerals. Sphalerite is replaced by galena and chalcopyrite. Galena is replaced by tetrahedrite and chalcopyrite. Gangue minerals are K-feldspar, quartz, allanite, calcite and dolomite.

Ores of the Sin Quyen deposit are mainly disseminated ores in foliated biotite-quartz-amphibole rocks and melanocratic gneiss. Mineral assemblage of ores of the Sin Quyen deposit is composed of chalcopyrite, cubanite, pyrrhotite, magnetite, quartz, amphibole, allanite and epidote. Chalcopyrite-pyrrhotite-quartz veins are partly present in the quartz-feldspar-amphibole rocks.

4 Analytical procedure

The chemical compositions of ores were determined by the combination of PIXE method at NMCC(Nishina Memorial Cyclotron Center) and AAS at Akita University. Fine-grained powder samples were prepared for PIXE analyses. Powder samples of 1 mg were mounted on polycarbonate filter of 0.4 □m pore size. The samples were measured using PIXE at NMCC. The analytical procedure and conditions are described by Sera et al. (1999). Pb, Cu, Zn contents in samples were estimated by the combination with PIXE data and Fe content determined as an internal standard by AAS. In and Cd concentrations were determined by ICP-MS at Akita University. ICP-MS analysis of ore samples were carried out according to the procedure by Satoh et al. (1999).

Table 2 Chemical compositions of ore samples from the Na Bop, Lung Hoai, Na Son and Sin Quyen deposits

Sample	Deposit	Pb	Zn	Cu	Fe	As	In	Cd	Ag
		wt %	wt %	wt %	wt %	wt %	ppm	ppm	ppm
No.7	Na Bop	0.11	4.89	0.04	3.83	-	83.0	150	4.4
No.33		5.43	0.05	0.23	40.30	0.42	1.08	1.42	-
No.40	Lung Hoai	0.03	12.08	0.08	19.43	4.79	2.29	585	61.3
No.50		0.36	9.69	0.01	2.18	-	5.38	491	-
NS.08.45	Na Son	29.58	7.52	0.32	5.26	-	5.31	243	66.6
NS.08.49		31.14	1.59	0.14	1.10	-	0.86	144	492
KC.526		61.78	2.94	0.22	0.45	-	0.20	189	-
KC.538		56.11	4.69	4.65	4.11	-	1.61	473	-
KC.569		13.94	6.71	0.99	4.02	-	0.56	273	193
KC.602		75.10	1.97	2.20	0.78	-	0.37	195	608
RF-4	Sin Quyen	0.31	0.01	8.94	26.38	-	1.0	0.97	-
SQ.7		0.09	0.03	6.20	15.14	-	1.59	3.95	6.69
SQ.31		0.11	0.06	10.20	18.30	-	0.92	1.48	2.13

-: Below detection limit.

5 Geochemistry of ore samples

5.1 Variation in major components of the ores

Ores of the Na Bop and Lung Hoai deposits are characterized by high Zn content, while ores of the Na Son and Sin Quyen deposits are characterized by high Pb and Cu contents, respectively. Pyrrhotite-rich samples of the Na Bop deposit and arsenopyrite-rich samples of the Lung Hoai deposit are characterized by higher Pb/Zn ratio compared with Pb/Zn ratio of sphalerite-rich ores of the Na Bop and Lung Hoai deposits. The fact that some ores from Cho Don and Cho Dien areas have higher Pb/Zn ratio with high Fe and As contents was also reported by Ishihara et al. (2010). Based on the mineral assemblage and composition of ores of Cho Don and Cho Dien areas, there is a possibility that two types of mineralization (early Fe-As mineralization and late Zn mineralization) were present in ore deposits in Cho Don and Cho Dien areas.

Ores of the Na Son deposit are characterized by Pb dominant signature (Zn/Pb <1). Zn and Fe contents of ores from the Na Son deposit are also lower than those of ores from the Na Bop and Lung Hoai deposits. Pb and Fe contents have weak negative correlations with Zn content. Some ores of the Na Son deposit show slightly higher Cu content compared with Cu content of ores of the Na Bop and Lung Hoai deposits (Fig. 2, Table 2).

The Sin Quyen deposit has high Fe concentration based on the occurrence of abundant pyrrhotite in the ores. Concentration of Pb and Zn in the ores range from 0.09 to 0.31 and 0.01 to 0.06 ppm, respectively, and are lower than that of pyrrhotite-rich samples from the Na Bop deposit and arsenopyrite-rich samples from the Lung Hoai deposit (Fig. 2, Table 2).

5.2 Characteristics of rare metals in the ores.

Indium contents in the ores examined are range from 1.08 to 83.0 ppm for the Na Bop deposit, 2.29 to 5.38 ppm for the Lung Hoai deposit, 0.20 to 5.31 ppm for the Na Son deposit and 0.92 to 1.59 ppm for the Sin Quyen (Fig. 3a, Table 2). These analytical results are similar to the data of Ishihara et al. (2010, 2011 and 2012). Sphalerite rich ores of the Na Bop deposit have higher In content (83.0 ppm), while sphalerite-rich ores of the Lung Hoai and Na Son deposits have moderate In contents (5.38 and 5.31 ppm, respectively). In contents of pyrrhotite-rich ore of the Na Bop, arsenopyrite-sphalerite ore of the Lung Hoai deposit, galena-rich ore of the Na Son deposit and chalcopyrite-rich ore of the Sin Quyen deposit are about 1 ppm.

Average In contents in sphalerite of the Na Bop, Lung Hoai and Na Son deposits determined by EPMA are 0.14, 0.02 and 0.01 wt %, respectively. The variation of In/Zn ratios of the ores from the Na Bop, Lung Hoai and Na Son deposits are consistent with the variation of In contents of sphalerite of these deposits. This suggests that host mineral of In is mainly sphalerite in the ores of Na Bop, Lung Hoai and Na Son deposits.

The abundance of sphalerite in the ores of the Sin Quyen deposit is very small. Sphalerite is not identified in studied samples from the Sin Quyen deposit. However, In content of the ores from the Sin Quyen deposit range from 0.9 to 1.6 ppm, which is within the range of In content of the ores containing 1 to 3 vol % of sphalerite from the Na Son deposit (Fig. 3a, Table 2). The ratios of In/Zn of the ores from the Sin Quyen deposit are higher than those of the ores from the Na Bop, Lung Hoai and Na Son deposits, although, the In contents in the ores from the Sin Quyen deposit are low. Based on the data of In and Zn contents, host mineral containing In in the ores of the Sin Quyen deposit is different from sphalerite. On the other hand, Cu minerals such as sakuraiite and roquesite also have high content of In. Thus, host mineral of In in the ores of the Sin Quyen deposit might be Cu-bearing minerals.

The positive correlation between Cd and Zn contents are recognized in the ores from the Na Bop, Lung Hoai and Na Son deposits (Fig. 3b, Table 2). The Cd contents of the ores from these deposits range from 1.4 to 150, 585-590 and 140-470 ppm, respectively. The average Cd contents of sphalerite determined by EMPA of the Na Bop, Lung Hoai and Na Son deposits are 0.34, 0.54 and 0.86 wt%, respectively. The EPMA data suggest that if the ores of those deposits have similar concentration of Zn, the Cd concentration of the ores of the Na Son deposit should be higher than that of the ores of the Lung Hoai and Na Bop deposits. The abundance of sphalerite in the ores from the Na Bop and Lung Hoai are very high compared with Na Son deposit. Therefore, it is suggested that the low Cd content of the ores from the Na Son deposit is caused by the dilution of sphalerite-bearing ores with galena.

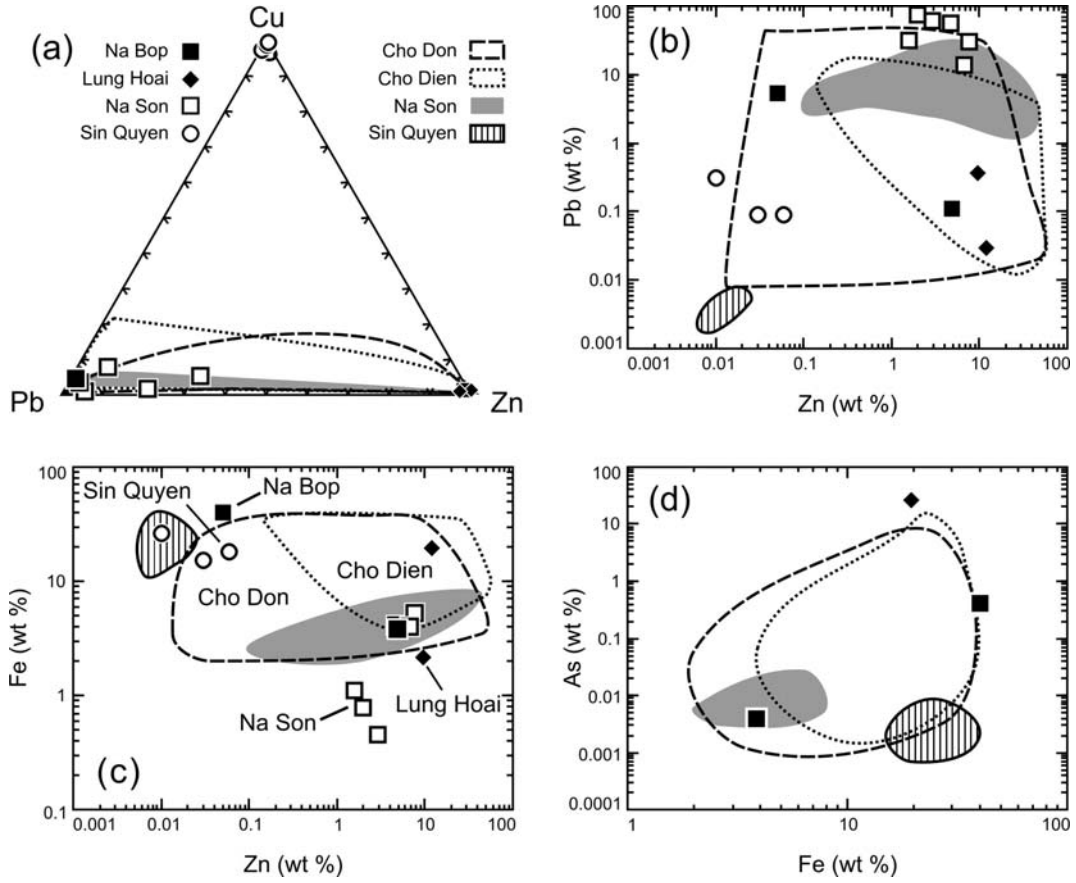

Fig. 2 Diagrams showing major chemical compositions of the ores from the Na Bop, Lung Hoai, Na Son and Sin Quyen deposit. (a) Pb-Zn-Cu ternary diagram, (b) Zn-Pb binary diagram, (c) Zn-Fe binary diagram, (d) Fe-As binary diagram. Data reported by Ishihara et al. (2010, 2011 and 2012) for the Cho Don, Cho Dien, Na Son and Sin Quyen deposits are shown as areas.

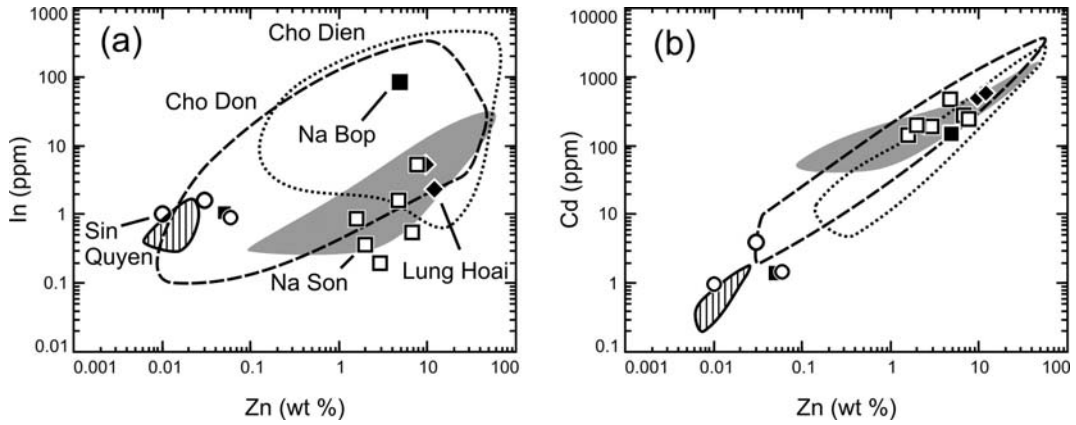

Fig. 3 Diagrams showing the relations between In (a) and Cd (b) with Zn contents in the ores from the Na Bop, Lung Hoai, Na Son and Sin Quyen deposits. The legends of these figures are same as the legends of Fig. 2.

6 Summary

Base on the mineral assemblage and characteristics of major components, the studied deposits are classified into three groups: Zn-rich ores (Na Bop and Lung Hoai deposits), Pb-rich ores (Na Son deposit) and Cu-rich ores (Sin Quyen deposit). The mineralization of the Na Bop and Lung Hoai is thought to be divided into the earlier arsenopyrite and pyrrhotite mineralization and late sphalerite mineralization. The sulfide mineralization of the Na Son deposit is divided into earlier Pb mineralization and later Cu mineralization. Indium occurs mostly in sphalerite in the ores from the Na Bop, Lung Hoai and Na Son deposits while Cu-bearing minerals in ores from the Sin Quyen deposit.

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