INŻYNIERIA MINERALNA
CZASOPISMO POLSKIEGO TOWARZYSTWA PRZERÓBKI KOPALIN

2 (47)
2021

http://doi.org/10.29227/IM-2021-02-24 Received: 15 Jul 2021, Accepted: 15 Sep 2021, Published: 10 Nov 2021

Mineralogical and Geochemical Characteristics of Lead-zinc Ore Deposits, and Potential Accompanying Components in the Cho Don - Cho Dien Area, Bac Kan Province, Vietnam

NGUYEN Tien Dung[1], NGUYEN Khac Du[1, 2, *], NGUYEN Ngoc Thom[2]

[1] Hanoi University of Mining and Geology, 18 Vien street, Hanoi, Vietnam

[2] Center for Excellence in Analysis and Experiment HUMG, Hanoi, Vietnam

Corresponding author: nguyenkhacdu@humg.edu.vn

Abstract. The Pb-Zn mineralization in the Cho Don - Cho Dien ore districts often occurs in 2 types: (1) oxidized ore near to the surface and (2) sulfide ore at deeper section. Based on microscopic observations, sulfide ores can be divided into sphalerite-galena-pyrite and/or galena-sphalerite mineralization types. To examine the geochemical features of the Pb-Zn ores, SEM-EDX and ICP-MS analytical methods were performed in this study. Previous $\delta^{34}S$ data of Pb-Zn concentrates, and sulfide minerals from various deposits suggest that the Pb-Zn ore-forming fluids might be related to the felsic-granitic magmatic activities rather than a genesis of stratiform type. Geochemical data show that the major, minor, and trace element compositions of lead-zinc ores have wide ranges of variation even in each deposit. The sulfide ores are generally higher in economic components than those in the oxidized ores. The positive correlations between Pb-Ag can be found in the entire dataset, whereas excellent Zn-Cd correlation can only be observed from Cho Don ore samples. Apart from the principal components (Pb and Zn), the ores also contain other accompanying elements that supply high-technological manufacturing industries. Of which As, Cu, Ag, Sb, and Cd could be potential by-products and can be extracted during smelting Pb/Zn concentrate processes, and need more detailed studies for every deposit.

Keywords: Cho Don-Cho Dien Pb-Zn ore deposits, Mineralogy and geochemistry, Accompanying components, By-products

1. Introduction

Bac Kan province, situated at about 200 km from Ha Noi to the north (Fig. 1a), is one of the most abundant lead-zinc ore resource localities in Viet Nam. Most of the ores, high in essential metal concentration, distribute in Cho Don, Cho Dien ore districts and scattered in other places such as Ngan Son, Pac Nam, Bach Thong, and Cho Moi. Many deposits have been exploiting from the 19th Century up to the present, resulting in a few hundred thousand tons of zinc, lead, silver, cadmium, and indium have been extracted.

Based on the occurrences, lead-zinc ores can be divided into two ore types: (1) sulfide and (2) oxidized ores, of which the latter often appear at a depth from a few tens to a few hundred meters below the surface. Both are primarily present in Paleozoic carbonate and/or terrigenous-carbonate formations in northern Vietnam [1-3]. Although the lead-zinc deposits are formed spatially in the carbonatic rocks, the ore-forming fluids could have derived from magmatic and/or metamorphic processes [4, 5]. In those deposits, apart from primary metals lead (Pb) and zinc (Zn), some trace elements could be considered as by-products such as silver (Ag), cadmium (Cd), indium (In) [1, 6-11]. Those components are often formed as accompanying elements and/or inclusions in other sulfide phases [12-18]. However, the relationship between each ore deposit type and its accompanying elements remains controversial.

In the presenting manuscript, on the basis of microscopic observations, geochemical data combined with isotopic data presented in previous studies, we will clarify the mineralogical, genesis, geochemical characteristics of Pb–Zn ores, and potential by-products from the various deposits in the Cho Don-Cho Dien ore district in the north of Viet Nam.

2. Outline of regional geology and analytical methods

2.1 Outline of Cho Don - Cho Dien geology

The Cho Don and Cho Dien ore districts are distributed in the Lo Gam structure, which is the southernmost part of the South China plate (Fig. 1a). The Pb–Zn deposits in Cho Don are located mainly-

http://doi.org/10.29227/IM-2021-02-24 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

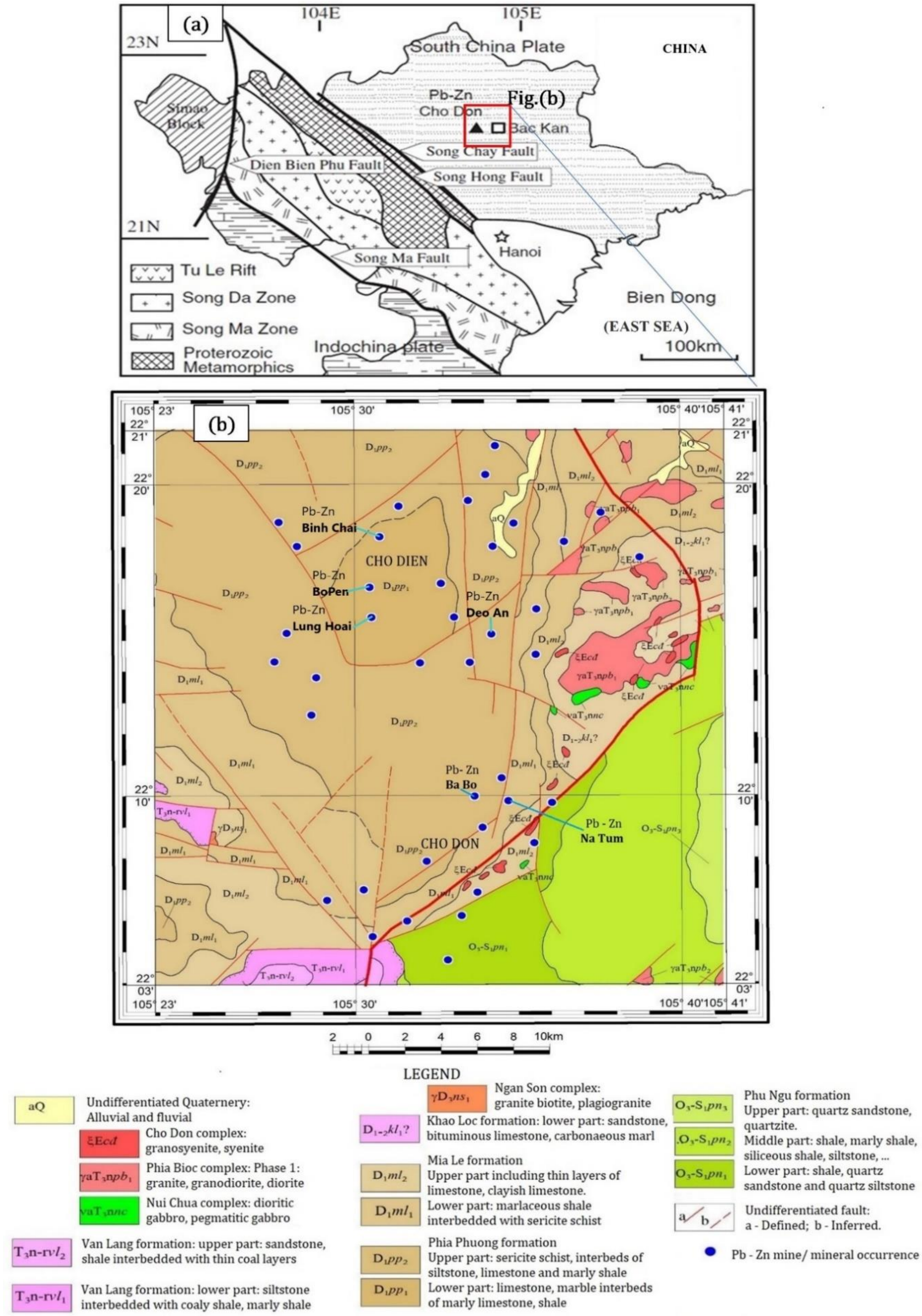


Fig. 1. (a) Tectonic sketch map of northern Vietnam and (b) Simplified geological map of the Cho Don-Cho Dien area, Bac Kan province showing the location of the studied Pb-Zn mines in highlight (modified from [1, 5]).

in Lower Devonian (D_1ml – D_1pp) sedimentary rocks of Mia Le and Phia Phuong formations, and a few occurrences are recorded in terrigenous sedimentary of Phu Ngu formation ($O_3 – S_1$*pn*) in Upper Ordovician and Lower Silurian. The hosted rocks comprise sericite–quartz schists, shales, interbedded with limestones, cherty limestones, quartzites, tuffs, and tuffaceous sandstones. Grayish limestone, siltstones, shales, and sandstones are commonly observed at the mineralization zones. Lead-zinc deposits in the Cho Don area consist of Ba Bo, Na Tum, Lung Vang, Na Bop - Pu Sap deposits. The main economic minerals are galena and sphalerite; however, the former is predominated. These minerals always associate with pyrrhotite, pyrite, arsenopyrite, and chalcopyrite. Their optical characteristics will be described in detail in a later section.

The Cho Dien ore district is located about 20 km to the north of the Cho Don district (Fig. 1b). The Pb–Zn deposits and occurrences comprise Lung Hoai, Binh Chai, Bo Luong, Dam Van, Deo An, Suoc, and Bo Pen. All of the deposits are distributed in Lower Devonian (D_1*pp* – D_1*ml*) sedimentary rocks. The host rocks contain shales, bituminous mudstones, dolomitic limestones, and marbles. Ores from all deposits are similar in primary mineral composition, including sphalerite, pyrite, arsenopyrite, and a lesser amount of galena. Pyrrhotite and chalcopyrite are commonly observed and are reported as secondary minerals. Oxidized ores are composed of smithsonite, cerussite, siderite, rhodochrosite, and iron hydroxides, limonite [3, 5, 19].

The Pb–Zn deposits in the Cho Don-Cho Dien ore districts are generally classified into the stratiform ore deposit type, which appears worldwide (i.e., Russia, Kazakhstan, Bulgaria, Poland, Austria, France, China, and other countries). It is notified recently that stratiform deposits are typified by the intimate association with carbonatic rocks of Paleozoic-Mesozoic is the stratigraphic control of mineralization without the appearance of igneous complexes ([3] and references therein). However, the felsic magmatic rocks appear widely in this area with various compositions, their relationship with ore-forming fluids remains controversial.

2.2 Samples and Analytical methods

We collected twenty-six samples from various deposits, occurrences (i.e., in a tunnel, outcrops, and drill cores) (Fig. 2), and ore types in the Cho Don and Cho Dien ore districts to examine the ore mineralogy and geochemistry (major, minor, traces including rare earth elements). Thin and polished sections were prepared from rock chips at Hanoi University of Mining and Geology. Microscope (Carl Zeiss – Axio Scop. A1**)** and Scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) (Quanta 450, FEI Company, Hillsboro, OR, USA) were initially applied to determine and estimate mineral modes qualitatively (Fig. 4).

Major, minor, and trace element compositions of twenty-two selected lead-zinc ore samples including fourteen sulfides and two oxidized ores, four Pb/Zn concentrates, and two ore tailing were obtained using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x) at Center for Radioactive and Rare Elements Analysis and Experiment, Geological Division for Radioactive and Rare Elements, Viet Nam. Sample preparation processes strictly follow the Standard Basis of Viet Nam (TCCS 01/XH: 2012). The detection limit for most of the elements is ten parts per billion (ppb). Results are presented in Tables 1, 2, and Figure 5.

http://doi.org/10.29227/IM-2021-02-24 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

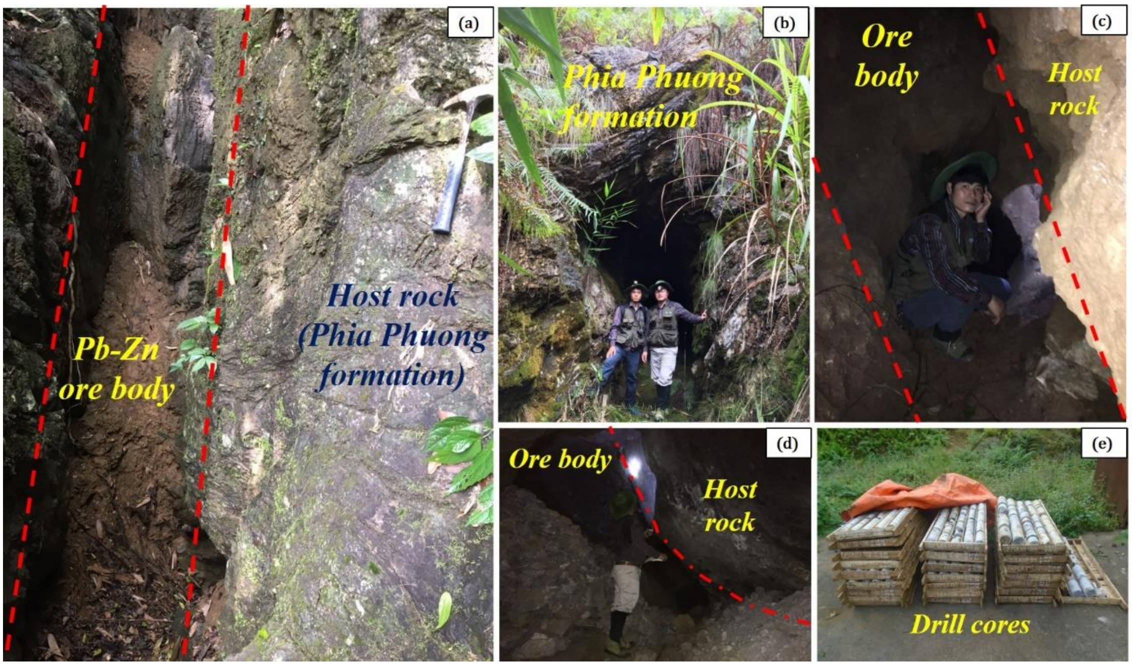


Fig. 2. Field survey and Sampling in Cho Don-Cho Dien ore districts: (a) outcrop showing the distribution of Pb-Zn ore body coincident with a fault plane; (b-d) Pb-Zn ore extraction by tunneling and relationship between ore body and host rock. (e): Drill cores from the Cho Dien mine group.

3. Results

3.1 Ore Mineralogy

As mentioned in the earlier section, the lead-zinc ores are formed spatially related to the carbonatic rocks of lower Devonian (D_1pp and D_1ml), rock-forming minerals are composed of calcite, dolomite, clay minerals group, quartz, barite, and organic material. Dissolution and embayment textures of rock-forming minerals are commonly observed in contact with opaque minerals (Fig. 3c). The abundances of quartz, barite, hydrothermal calcite, and dolomite in rocks and/or mineralization zone seem to be related to the occurrence of sulfide minerals.

In oxidized ore samples, minerals assemblage mainly comprises smithsonite, hydrozincite, calamine, cerussite, rhodochrosite, bornite, and limonite [5], making the dark brown color of the ores. The lead-zinc sulfide ores could be either massive sulfides or banded, varying in each deposit (Figs. 3a, b). Primary ore minerals are various in size and shape, ranging from coarse- to fine-grained, euhedral to anhedral. Predominant phases comprise galena and sphalerite. The samples recovered from the Cho Don ore districts are generally higher in galena (up to 70 vol %) but much lower in sphalerite compositions than those collected from the Cho Dien ore district (up to 75vol % sphalerite). Pyrite appears with significant amounts in few samples recovered from both Cho Don and Cho Dien ore districts (up to 75 vol %). Small amounts (1-2%) of chalcopyrite, pyrrhotite, marcasite, and arsenopyrite present as accessory phases in some polished sections. Geochemical characteristics of essential ore minerals were semi-quantitatively determined by SEM-EDX and are depicted in Figure 4.

Sphalerite and galena commonly occur in samples as anhedral crystals with grain sizes varying from 0.2-2.6 mm, rarely up to >4 mm. They are closely associated with pyrite (Fig. 3d-i), replacing the earlier rock-forming minerals (Fig. 3c). The texture of sphalerite and galena filling in the microcrack systems, forming veinlets or branches, is commonly recorded.

Pyrite is often euhedral to subhedral in most of the studied samples, with grain size varying from 0.1-2.5 mm. The rim of pyrite is often corroded and replaced partly by sphalerite, suggesting that pyrite is the earliest crystallized phase of the ore. Chalcopyrite is a trace mineral in the studied samples, occurring widely as tiny rounded grains, blebs (10-20 µm) in larger grains of sphalerite, forming typical emulsion texture of the ores (Figs. 3g-i).

http://doi.org/10.29227/IM-2021-02-01 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

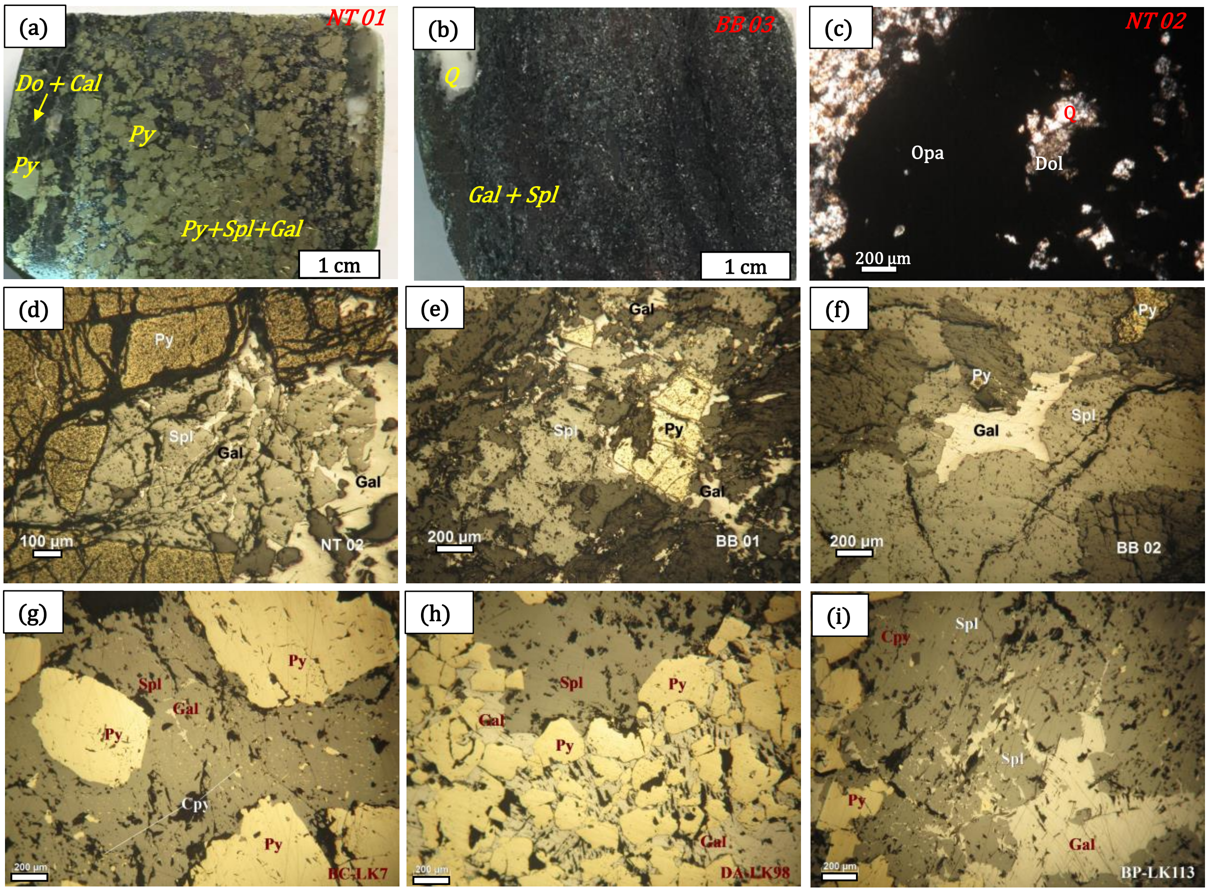


Fig. 3. Representative photos of Pb-Zn ores (a: massive pyrite-sphalerite-galena ore; b: banded galena-sphalerite-pyrite ore) and microphotographs showing (c: embayment and dissolution texture of rock-forming mineral in ore background), (d-i) mineral assemblages of the studied Pb-Zn ores. NT, BB, BC, DA, BP: Na Tum, Ba Bo, Binh Chai, Deo An, Bo Pen deposits, respectively. Py: Pyrite. Spl: Sphalerite. Gal: Galena. Dol: Dolomite. Cal: Calcite. Q: Quartz. Sul: Sulphides.

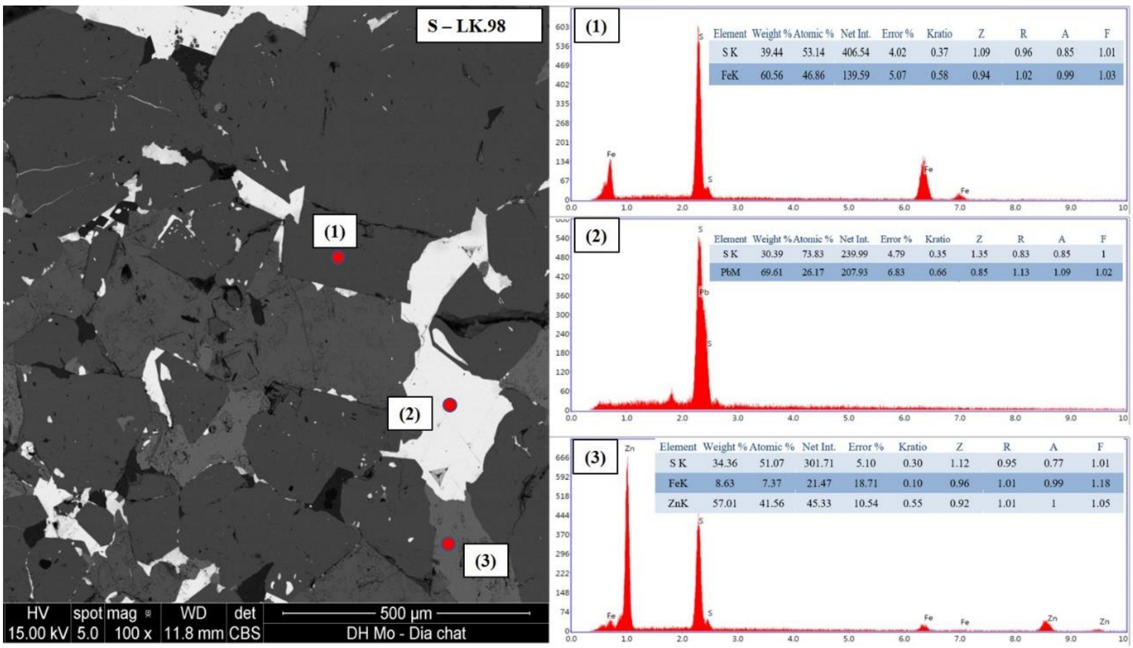


Fig. 4. Representative SEM results for minerals: (1) Pyrite; (2) Galena; (3): Sphalerite (Sample LK.98 in the Suoc deposit).

http://doi.org/10.29227/IM-2021-02-24 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

Tab. 1. Major and trace element compositions of ore samples from the Cho Don ore district.

Deposit	Na Tum				Ba Bo						
Samples	NT.01	NT.02	NT.04	NT.05	BB.01	BB.02	BB.03	BB.04	BB.07	BB.08	BB.09
Ore Type	Sul.	Sul.	Ox.	Ox.	Sul.	Sul.	Sul.	Sul.	Tail.	Pb-Con.	Zn-Con.
Na_2O	0.61	0.58	0.59	0.51	0.57	0.40	0.49	0.49	0.56	0.51	0.49
K_2O	0.30	0.24	0.43	0.19	2.07	0.45	1.23	1.68	1.94	0.33	0.27
MgO	1.18	1.07	0.99	1.37	1.38	9.94	1.74	2.40	3.18	1.53	1.26
Al_2O_3	0.44	0.50	3.38	0.79	6.48	1.34	3.49	4.70	7.41	0.77	0.70
Fe_2O_3	28.36	19.43	34.82	36.05	1.13	7.87	6.26	22.54	13.78	8.15	8.86
P_2O_5	0.02	0.02	0.04	0.05	0.02	0.01	0.02	0.03	0.03	0.03	0.03
MnO	1.37	0.44	15.54	7.83	0.09	2.21	2.38	9.68	2.44	1.08	1.06
Zn	10.08	5.12	0.56	5.64	20.94	8.62	1.51	0.18	1.89	3.69	44.56
Pb	14.59	8.74	2.25	4.32	5.49	0.32	41.46	6.11	0.33	55.46	0.54
As	3.761	0.69	0.03	2.79	0.53	0.01	0.01	0.003	0.85	0.95	0.03
Ba	642.85	631.51	1,405.98	691.72	521.70	1,430.68	1,042.37	882.87	1,100.73	909.00	1,349.74
Th	8.20	12.14	8.23	2.84	10.11	3.82	4.49	9.24	15.80	33.66	3.68
Ti	19.65	23.98	139.52	28.35	291.28	39.44	140.55	161.70	168.77	101.41	45.34
Ge	2.97	1.84	4.21	3.74	0.27	1.17	0.76	2.85	1.78	0.87	1.07
Cd	34.70	19.14	2.18	21.19	126.78	66.38	12.79	1.11	11.07	23.52	2,412.36
In	273.53	7.71	3.45	128.51	0.53	0.25	0.52	0.13	1.32	1.20	1.14
Y	3.41	8.27	41.73	26.05	1.41	11.95	4.50	11.91	20.86	9.50	4.14
Cr	7.33	10.12	14.38	12.32	8.26	6.70	9.98	13.80	15.94	11.23	8.30
Co	12.67	10.55	24.00	14.68	12.33	4.78	13.97	9.26	13.90	11.19	9.29
Ni	13.50	14.73	27.68	14.74	19.85	13.15	13.76	15.76	26.75	34.17	20.26
Cu	2,373.57	1,290.90	21.72	1,369.38	33.68	16.47	483.81	15.85	21.50	3,124.05	1,182.53
Ag	170.65	9.87	2.05	9.83	9.67	2.03	527.10	14.72	2.98	1,089.13	9.30
Sb	23.14	2.62	2.56	4.84	21.18	4.41	918.01	12.72	6.15	2,144.37	16.06
Sn	698.71	30.36	7.40	171.57	16.96	4.94	8.30	17.29	16.19	21.47	43.31
Ga	13.58	12.17	26.23	15.22	8.89	23.29	18.73	16.67	21.33	16.72	24.77
Mo	6.73	5.13	14.71	7.31	3.62	2.97	3.45	4.55	8.57	17.40	3.96
La	6.51	3.93	6.25	6.56	4.94	5.39	4.55	4.14	7.88	7.55	4.24
Ce	10.28	6.20	10.07	9.44	9.51	11.37	6.41	8.47	12.87	10.70	8.43
Pr	0.81	0.39	0.81	0.95	0.68	0.65	0.57	0.59	1.11	1.00	0.65
Nd	2.22	0.98	2.42	2.98	2.09	1.75	1.46	1.62	3.07	2.12	1.71
Sm	2.31	0.94	3.56	4.27	2.54	1.79	2.16	2.33	5.45	4.99	1.50
Eu	1.78	1.09	4.18	2.36	1.31	2.63	1.87	4.18	5.15	7.39	2.67
Gd	2.79	2.10	6.00	5.07	2.69	3.55	2.24	3.62	7.65	7.03	2.64
Tb	0.45	0.19	0.67	0.57	0.17	0.36	0.23	0.42	2.04	4.90	0.15
Dy	0.73	0.83	3.87	2.64	0.40	2.27	1.13	2.11	5.10	5.38	0.66
Ho	0.27	0.17	0.88	0.57	0.10	0.40	0.18	0.39	2.01	4.57	0.15
Er	0.43	0.59	2.59	1.93	0.22	1.01	0.52	1.61	2.75	5.09	0.44
Tm	0.18	0.10	0.34	0.26	0.02	0.19	0.07	1.61	1.67	4.45	0.02
Yb	0.28	0.30	2.38	1.35	0.15	1.11	0.37	0.24	2.46	4.16	0.26
Lu	0.19	0.09	0.29	0.17	0.01	0.18	0.08	0.01	1.61	4.26	0.04
∑ REE	29.24	17.88	44.31	39.13	24.84	32.65	21.85	31.34	60.81	73.59	23.57

Note: Na_2O – As in %, Ba – Mo in ppm. Sul. – Sulfide ore, Ox. – Oxidized ore.
Pb-Con. – Pb Concentrate. Zn-Con. - Zn-Concentrate. Tail.- Tailing.

Tab. 2. Major and trace element compositions of ore samples from the Cho Dien ore district.

Deposit	Lung Hoai		Binh Chai		Bo Pen		Deo An	Suoc	Ore concentrate		Tailing
Samples	LK44/2	LK63A/2	LK7	LK3	LK111	LK113	LK90	LK98	TQ.01	TQ.02	DT
Ore Type	Sul.	Sul.	Sul.	Sul.	Sul.	Sul.	Sul.	Sul.	Pb-Con.	Zn-Con.	Tailing
Na_2O	0.28	0.25	0.27	0.27	0.28	0.27	0.28	0.29	0.24	0.28	0.29
K_2O	0.09	0.08	0.26	0.17	0.42	0.31	0.66	0.09	0.06	0.08	0.28
CaO	12.47	3.40	1.24	0.47	0.43	0.47	2.13	0.92	0.78	1.17	15.56
MgO	1.97	0.23	0.36	0.24	0.27	0.25	1.13	0.20	0.27	0.38	3.59
Al_2O_3	2.37	0.27	0.73	0.77	1.26	0.87	1.83	0.15	0.11	0.22	0.94
Fe_2O_3	11.29	0.99	29.47	29.06	19.97	11.62	25.39	8.28	7.03	9.02	11.63
P_2O_5	0.05	0.02	0.03	0.03	0.04	0.03	0.05	0.06	0.03	0.03	0.05
MnO	1.41	0.13	0.06	0.04	0.02	0.04	0.25	0.12	0.04	0.14	1.38
Zn	17.85	55.36	6.74	13.78	18.43	38.79	2.28	51.60	7.70	53.89	0.69
Pb	0.42	0.66	0.42	7.02	8.46	13.06	2.78	0.16	54.36	0.95	0.32
Cu	0.08	0.11	0.03	0.03	0.09	0.20	0.03	0.08	0.37	0.27	0.02
As	0.02	0.00	0.39	0.27	0.33	0.09	0.94	0.01	0.34	0.23	1.19
Ba	24.20	14.53	25.97	22.79	32.31	23.13	60.44	19.13	17.89	11.36	32.49
Th	3.60	0.64	1.52	1.31	1.76	1.16	2.40	0.47	0.91	2.22	1.46
Ti	112.55	80.41	73.85	78.72	146.71	82.38	199.36	39.76	40.13	46.18	97.66
Ge	6.26	3.05	16.54	16.40	12.15	5.60	14.72	3.78	3.43	5.11	8.20
W	61.31	36.13	500.38	193.18	207.39	56.88	324.00	51.48	13.04	16.59	89.05
In	4.63	7.53	4.20	0.54	0.44	0.63	0.58	411.41	3.21	64.20	1.45
Y	7.88	0.83	0.30	0.31	0.69	0.30	1.25	0.58	0.29	1.29	3.95
Cr	258.47	88.95	187.58	191.77	225.67	212.80	212.84	135.38	251.64	257.75	159.67
Co	9.89	8.87	45.82	46.20	9.51	5.30	17.12	18.17	4.67	6.39	11.44
Ni	22.35	18.62	14.41	25.01	18.53	12.54	28.92	17.88	15.84	14.30	14.00
Ag	45.72	144.97	36.78	261.17	143.21	246.26	115.66	36.90	1,573.12	287.75	20.95
Sb	2.25	48.52	4.88	30.77	20.01	36.59	15.58	1.22	92.37	4.73	3.64
Sn	52.05	61.44	38.29	53.74	228.78	406.86	133.38	129.16	67.78	131.72	47.34
Ga	5.62	5.64	2.45	2.75	5.06	6.60	4.94	2.90	1.01	4.30	2.56
Mo	6.53	4.73	3.33	3.03	2.70	1.81	1.93	1.60	3.93	2.48	1.75
La	10.20	2.01	0.68	1.16	1.16	0.84	7.18	2.00	1.59	7.26	5.13
Ce	33.01	3.30	1.22	1.83	1.86	1.27	12.95	3.48	2.41	14.37	9.46
Pr	2.29	0.39	0.16	0.23	0.26	0.17	1.41	0.39	0.31	1.51	1.05
Nd	7.87	1.42	0.53	0.71	0.98	0.62	4.67	1.26	0.99	4.16	3.93
Sm	1.45	0.30	0.11	0.15	0.18	0.13	0.63	0.25	0.19	1.21	0.79
Eu	0.48	0.07	0.05	0.04	0.05	0.03	0.11	0.06	0.04	0.64	0.27
Gd	1.52	0.22	0.08	0.12	0.17	0.10	0.51	0.22	0.14	1.03	0.77
Tb	0.29	0.04	0.03	0.02	0.03	0.02	0.06	0.03	0.02	0.59	0.11
Dy	1.37	0.16	0.07	0.06	0.13	0.07	0.24	0.11	0.08	0.77	0.60
Ho	0.37	0.04	0.02	0.02	0.03	0.02	0.05	0.03	0.02	0.62	0.13
Er	0.98	0.08	0.05	0.04	0.08	0.04	0.15	0.06	0.04	0.67	0.38
Tm	0.22	0.03	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.61	0.05
Yb	0.99	0.08	0.04	0.04	0.06	0.04	0.14	0.05	0.04	0.59	0.33
Lu	0.23	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.60	0.04
∑ REE	61.27	8.18	3.07	4.45	5.02	3.39	28.15	7.95	5.88	34.64	23.04

Note: Na_2O–As in %, Ba–Mo in ppm. Sul. –Sulfide ore. Pb-Con. –Pb Concentrate. Zn-Con.- Zn-Concentrate.

3.2 Ore geochemistry

http://doi.org/10.29227/IM-2021-02-24 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

In order to examine the variation in the chemical composition of Pb-Zn ores in the Cho Don - Cho Dien area, 22 samples containing various ore types (rich/poor ores as well as sulfide/oxidized ores, Pb/Zn concentrates, and tailing) have been selected for detailed ICP-MS analyses. Results are presented in Figure 5 and Tables 1, 2.

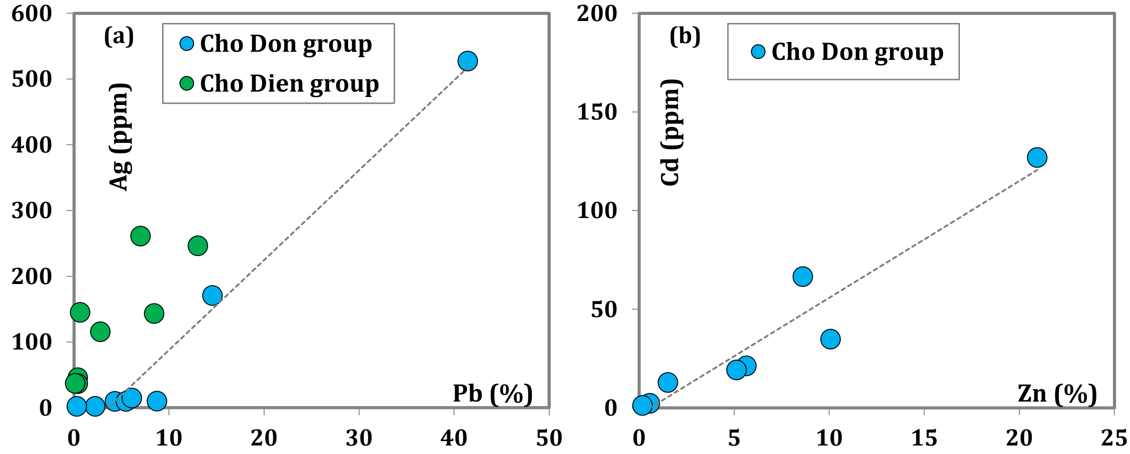


Fig. 5. Binary diagrams for (a) Pb-Ag, and (b) Zn-Cd of the studied Pb-Zn ores.

In general, the chemical compositions of lead-zinc ores have wide ranges of variation. The sulfide ores are commonly higher in Pb, Zn but lower in Fe contents than those in the oxidized samples. The total Pb-Zn content in ores from Cho don and Cho Dien ranges from 2.81-42.97% and 5.07-56.03%, respectively. The values commonly exceed 8% in rich ores, reaching the maximum of 41.46% Pb; 20.94% Zn (Cho Don), and 13.06% Pb; 55.36% Zn (Cho Dien). After flotation, the ore concentrates in the Cho Don area are up to 55.46% and 44.56% of Pb and Zn components. The total Pb and Zn content is 1.01-2.22% in the tailing.

Overall, there are excellent correlations only between Pb-Ag in the entire data and between Zn-Cd in only samples from the Cho Don area (Fig. 5). Most of the trace elements have low concentrations in the studied ore samples. The concentration of many components (i.e., Ge, Cr, Co, Ni, etc.), and the radioactive elements (Th, U), rare earth elements, and yttrium do not exceed the Clarke values. However, several components are enriched during the flotation process. These characteristics will be discussed more in detail in section 4.2.

4. Discussion

4.1 Genetic type of the Cho Don-Cho Dien ore district

Based on microscopic observations and paragenetic relationships of various hydrothermal minerals, the mineralization process in the Cho Don-Cho Dien ore districts can be classified into three stages (Tab. 3): (1) sedimentary diagenesis through (2) hydrothermal mineralization, ending by (3) supergene oxidization.

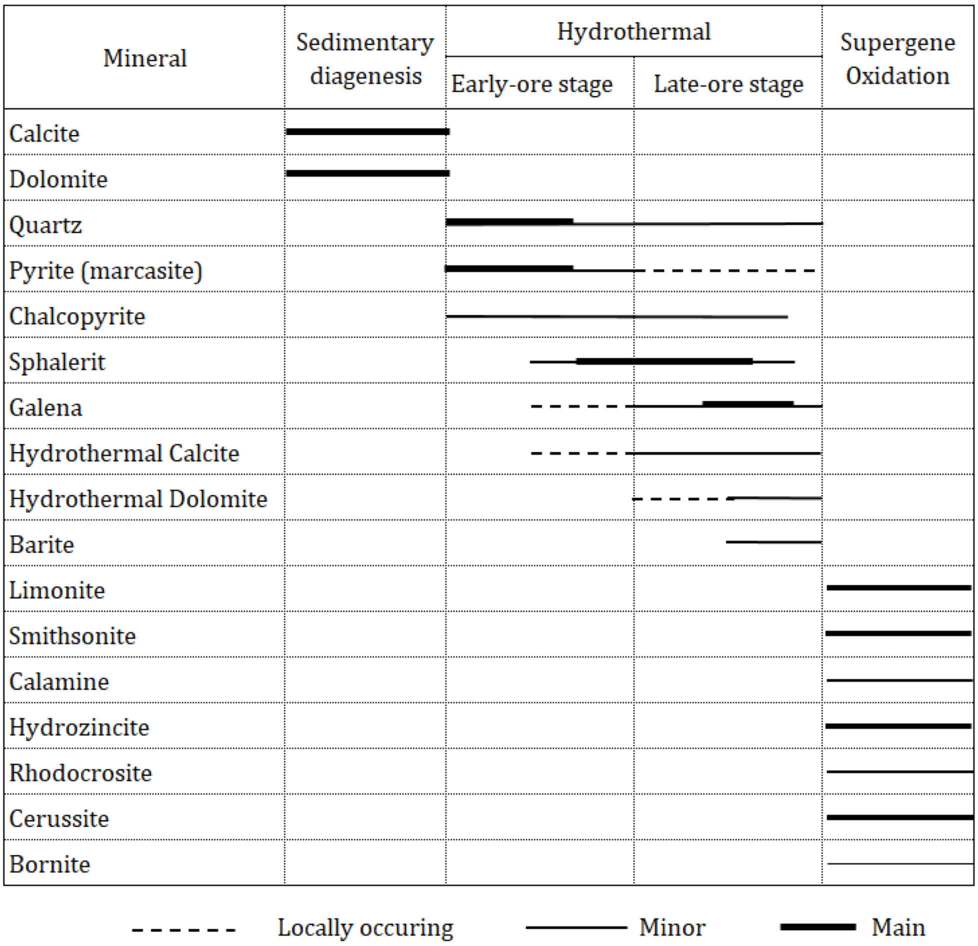
The hydrothermal process forming Pb-Zn ore in the Cho Don-Cho Dien areas can be divided into early-stage and late-stage based on distinct mineral assemblages. The early stage of mineralization mainly produces massive ores, containing euhedral to subhedral coarse- to medium-grained sulfide minerals (pyrite, sphalerite, and galena). The process continues to form lesser amounts of veins or disseminated ores comprising fine subhedral to anhedral grains (dominated by galena). The late-stage mineralization ends with the formation of hydrothermal dolomite, calcite, and barite. Therefore, the mineralization in the Cho Don–Cho Dien ore districts can be divided into pyrite-sphalerite-galena and/or galena-sphalerite mineralization types in terrigenous carbonate rocks. These observations are well consistent with the descriptions presented in previous studies, such as [1, 5, 7, 8, 19].

Regarding the geneses of sulfide ore deposits, sulfur isotopic ratios ($\delta^{34}S$) of PbS and/or ZnS are commonly applied. Because most of the Pb-Zn ore deposits in the Cho Don district appear in Paleozoic sedimentary (carbonatic rocks, shale, and sandstone), it is generally believed that the ore geneses are of stratiform (Mississippi Valley-MVT or even SEDEX) type. To conclude the origin of Mississippi Valley-type ores, the sulfur isotopic values should be similar to those of Pb-Zn ores in the Mississippi Valley area,

http://doi.org/10.29227/IM-2021-02-01 Received 15 Jun 2021, Accepted 15 Sep 2021, Published: 10 Nov 2021

ranging from +0.5 to +15.3 ‰ with an average of +11.0 ‰. However, such a wide range of variation and high $\delta^{34}S$ values and low Fe content as those in Pb-Zn ore deposit of the MVT ores are absent from the data of Pb-Zn ores in the Cho Don-Cho Dien areas (Fig. 6).

Tab. 3. Mineral paragenesis in the Cho Don-Cho Dien areas.



The $\delta^{34}S$ values of zinc concentrate from the Cho Don district do not vary much, ranging from +6.9 (one sample from Na Bop - Pu Sap deposit) to +7.5 ‰ (both two values from Na Tum mine) [4]. In addition, the $\delta^{34}S$ values of lead-zinc ore and concentrates from Cho Dien district are even much lower, varying from -3.4‰ to +1.1‰ [4, 5]. These clearly suggest that the ore-forming fluids that formed Pb-Zn deposits in the Cho Don-Cho Dien ore districts are probably related to the felsic-granitic rocks occurring widely in the area rather than the stratiform ore deposit type.

Although the essential ore minerals in the Cho Don area are similar to those in the Cho Dien district, the ores from Cho Don are generally richer in galena but less abundant in sphalerite compositions than those from the Cho Dien district. Based on these observations and the $\delta^{34}S$ values from various deposits (Fig. 6), we propose that the nature of the Pb-Zn mineralization process in the Cho Don district might differ from that in the Cho Dien ore district, leading to further variation in accompanying economic elements and need more detailed studies in the future.

4.2 Accompanying elements and potential by-products

As presented in the previous section, the crude ores and Pb/Zn concentrates from the Cho Don-Cho Dien ore districts include some minor and trace elements with noticeable concentrations. Of which As, Cu, Ag, Sb, and Cd could be of commercial interest (Tabs. 1, 2). Geochemical characteristics and sources of those elements are as follows:

Arsenic presents mainly as arsenopyrite in sulfide ores; therefore, it also appears in oxidized samples, ranging from 0.003-3.761% in studied samples. In the Pb concentrates, it is 0.95%. Since arsenic is toxic, it is necessary to recover in flotation and smelting processes. Unfortunately, most of the factories do not pay much attention to this yet.

Copper is often present as chalcopyrite and bornite in sulfide and oxidized ores, respectively. The Cu contents vary widely in the crude ores, generally higher abundances in samples from the Cho Dien than in representatives from the Cho Don ore district. It is enriched up to 0.37% and 0.27% in Pb and Zn concentrates. It could be economically extracted as one of the by-products during smelting processes.

Silver and antimony concentrations also have wide ranges of variation in studied samples, occasionally up to 527.1 (ppm) and 918.01 (ppm) in samples from the Cho Don area. They are enriched in the Pb concentrates, showing a strong positive correlation to the lead content in the bulk ores (Fig. 5, Tab. 4). Although some trace minerals containing high contents of Ag, Sb (i.e., tetrahedrite) were observed in the Cho Don-Cho Dien area and were reported [16, 20], they could not play an essential role as a source for those trace elements in the bulk ore analyses. The Ag, Sb contents increase sharply in the commercial Pb-concentrates (1089.13 and 2,144.37 ppm) in samples from the Cho Don ores, suggesting an intimate relationship between these elements and the galena mineral. A strong positive correlation between Pb-Ag is also observed in ore from the Cho Dien district.

Tab. 4. Correlation coefficients for major and selected trace elements in Pb-Zn ores. Data applied in the calculation are compiled from references [1, 9], and this study.

Element	*Zn*	*Pb*	*As*	*Cd*	*In*	*Cu*	*Ag*	*Sb*	*Sn*	*Ga*
					Cho Don ore district					
Zn	1									
Pb	0	1								
As	0.12	0.13	1							
Cd	**0.53**	-0.22	-0.11	1						
In	-0.06	-0.07	**0.56**	-0.06	1					
Cu	0.04	0.41	0.34	0.21	0.51	1				
Ag	-0.13	**0.89**	0.03	-0.15	-0	0.52	1			
Sb	-0.09	**0.9**	-0.08	-0.14	-0.14	0.47	**0.96**	1		
Sn	-0.09	-0.11	**0.52**	-0.03	**0.54**	0.43	0.06	-0.02	1	
Ga	-0.3	-0.3	-0.14	0.3	0.38	0.49	-0.05	-0.1	0.38	1
					Cho Dien ore district					
Element	*Zn*	*Pb*	*As*	*W*	*In*	*Cu*	*Ag*	*Sb*	*Sn*	*Ga*
Zn	1									
Pb	-0.26	1								
As	-0.29	-0.11	1							
W	-0.33	-0.06	-0.13	1						
In	0.42	-0.12	-0.14	-0.14	1					
Cu	-0.23	0.30	-0.08	-0.08	0.07	1				
Ag	-0.17	**0.97**	-0.12	-0.09	-0.11	0.19	1			
Sb	-0.28	0.04	**0.97**	-0.20	-0.17	-0.04	0.03	1		
Sn	-0.14	0.31	-0.16	0.05	0.06	**0.88**	0.18	-0.12	1	
Ga	0.01	0.10	-0.20	-0.01	0.04	0.88	-0.01	-0.18	0.90	1

Note: Significant values of correlation coefficients are highlighted in bold-typed.

Geochemical behavior of cadmium shares a lot of similarities to that of Ag and Sb. There is no independent mineral of Cd found and reported in the studied area, and its concentrations strongly correlate to the occurrence of sphalerite. Despite the poor Cd composition in both sulfide and oxidized ores, the Cd content in Zn-concentrate from the Cho Don reaches 2,412.36 ppm. It could be considered as one of the by-products during the smelting of the Zn concentrates processes. The sphalerite is relatively abundant in samples from the Cho Dien ore district; however, Cd might not be a by-product of ore from the Cho Dien area (Cd contents in the bulk ores do not exceed the Clarke value: data are not presented here).

Last but not least, indium is often paid much attention in the Pb-Zn deposits due to their utilities in high-technological industries. It is also pointed out that the Cho Don - Cho Dien ore districts have a high potential of In and that sphalerite is the host for the element [4]. However, the indium concentrations are often very low not only in the crude ores but also in both the Pb/Zn concentrates and the tailing, suggesting that the sphalerites from different deposits have various amounts of the element. The indium contents are markedly high in 2 samples from the Na Tum (Cho Don) deposit (273ppm and 128 ppm in the samples NT.01 and NT.05, respectively), where are also high in Sn, Cu, As contents (Tabs. 1, 2). These observations, coupled with the strong correlations between In and (Sn, Cu, As) but weak correlation between In and Zn (Tab. 4), suggesting that indium might be presented mostly in (Sn, Cu/As)-rich phases rather than in the sphalerite as recorded earlier in the Cho Don ore district.

5. Conclusion

The main results of this work can be summarized as follows:

- The Pb-Zn mineralization in Paleozoic terrigenous carbonate rocks from the Cho Don-Cho Dien ore districts can be divided into sphalerite-galena-pyrite and/or galena-sphalerite mineralization types. Based on $\delta^{34}S$ values from previous studies, ore-forming fluids might be driven from the felsic-granitic magmas in the area rather than a genesis of stratiform ore deposits (MVT or SEDEX types).

- The chemical compositions of the ores have wide ranges of variation, even in each deposit from Cho Don-Cho Dien ore districts. Apart from the essential ore components (Pb and Zn), several minor and trace elements concentrate with significant amounts in the ores; some are enriched during flotation. Of which As, Cu, Ag, Sb, and Cd could be potential by-products and can be extracted during smelting Pb/Zn concentrates processes, but this is required more detailed studies in the future.

6. Acknowledgments

We would like to thank Dr. Khuong The Hung from Hanoi University of Mining and Geology for the initial discussion on the genesis of lead-zinc ore deposits. This is really helpful in improving the quality of the presenting manuscript.

The paper was presented during the 6th VIET - POL International Conference on Scientific-Research Cooperation between Vietnam and Poland, 10-14.11.2021, HUMG, Hanoi, Vietnam.

7. References

1. Ishihara, Shunso, Tuan Anh Tran, Yasushi Watanabe, and Trong-Hoa Tran, 2010. Chemical Characteristics of Lead-Zinc Ores from North Vietnam, with a Special Attention to the in Contents. Bulletin of the Geological Survey of Japan, 61(9-10): 307-23, https://doi.org/10.9795/bullgsj.61.307.
2. Tran Van Tri and Vu Khuc (Editor), 2011. Geology and Earth Resources of Vietnam. Hanoi: Publishing house for Science and Technology, 2011. ISBN: 9786049130472.
3. Tran Tuan Anh, Gas'kov, I.V., Tran Trong Hoa, Nevol'ko, P.A., Pham Thi Dung, Pham Ngoc Can, 2012. Complex Deposits in the Lo Gam Structure, Northeastern Vietnam: Mineralogy, Geochemistry, and Formation Conditions. Russian Geology and Geophysics, 53(7): 623-35, https://doi.org/10.1016/j.rgg.2012.05.001.
4. Ishihara, S., Tuan Anh Tran, Kezhang, Q, 2010. Reconnaissance Study on Sulfur Isotopic Ratios of Lead-Zinc Ores from North Vietnam. Bulletin of the Geological Survey of Japan, 61(11-12): 485-88, https://doi.org/10.9795/bullgsj.61.485.
5. Dao Thai Bac. Study on Characteristics and Distribution Rules of Lead - Zinc Mineralisation in Viet Bac Region, Ph.D Thesis, University of Mining and Geology, Ha Noi, 2011 (In Vietnamese with abstract in English).

6. Tran Trong Hoa, 2004. Investigation and Assessment the Prospect of Accompanying Minerals in Some Lead-Zinc and Copper Deposits in the North of Viet Nam. Institute of Geological Sciences, Vietnamese Academy of Science and Technology, Hanoi, Vietnam. (In Vietnamese with abstract in English).
7. Do Quoc Binh. Investigation and Assessment the Prospect of Lead-Zinc, Gold and Accompanying Minerals at Phia Da - Na Cang Area, Cao Bang and Bac Kan Province. General Department of Geology and Minerals of Vietnam, Hanoi, 2005 (In Vietnamese with abstract in English).
8. Do Quoc Binh. Assessment the Prospect of Copper, Lead-Zinc and Accompanying Minerals at Quan Ba - Pac Nam Ore Band in Ha Giang, Cao Bang and Bac Kan Province. General Department of Geology and Minerals of Vietnam, Hanoi, 2009 (In Vietnamese with abstract in English).
9. Tran Tuan Anh. Study on Accompanying Components in Promising Deposits of Basic Metal and Rare Metal in the North of Vietnam to Improve the Efficiency of Mineral Exploitation and Processing, and Environmental Protection. Institute of Geological Sciences, Vietnamese Academy of Science and Technology, Hanoi, Vietnam, 2010, 376 (In Vietnamese with abstract in English).
10. Phuong Nguyen, Hang Thu Thi Nguyen, Nam Dinh Tang, Houmphavanh Phatthana, 2017. Application of some geological properties for surveillance prospects and Pb-Zn prospects forlands capeonly. Journal of Mining and Earth Sciences, 58 (5): p. 363-378. (In Vietnamese with abstract in English).
11. Phuong Nguyen, Dong Phuong Nguyen, Huong Thi Nguyen, Huong Thi Le, Dinh Van Do, 2020. Features of lead-zinc mineralization in the Phia Dam -Khuoi Man region. Journal of Mining and Earth Sciences, 61 (5): p. 120-134, http://doi.org/10.46326/JMES.2020.61(5).14. (In Vietnamese with abstract in English).
12. Sangameshwar, S.R., Barnes, H.L., 1983. Supergene Processes in Zinc-Lead-Silver Sulfide Ores in Carbonates. Economic Geology, 78(7): 1379-97, https://doi.org/10.2113/gsecongeo.78. 7.1379.
13. Tran Tuan Anh, Gaskov, I.V., Tran Trong Hoa, Nevolko, P.A., Pham Thi Dung, Bui An Nien, Pham Ngoc Can, 2011. Mineralogical and Geochemical Characteristics and Forming Conditions of Lead-Zinc Deposits in Lo Gam Structure, Northern Vietnam. Vietnam Journal of Earth Sciences, 33(3): 393-408, https://doi.org/10.15625/0866-7187/33/3/348. (In Vietnamese with abstract in English).
14. Jiaxi, ZHOU, HUANG Zhilong, ZHOU Guofu, LI Xiaobiao, DING Wei, and BAO Guangping, 2011. Trace Elements and Rare Earth Elements of Sulfide Minerals in the Tianqiao Pb-Zn Ore Deposit, Guizhou Province, China. Acta Geologica Sinica - English Edition 85(1): 189-99, https://doi.org/10.1111/j.1755-6724.2011.00389.x.
15. Bui An Nien, Tran Trong Hoa, Tran Tuan Anh, Pham Thi Dung, Pham Ngoc Can, Tran Van Hieu, Tran Quoc Hung, Ngo Thi Phuong, 2011. New Research Results on Distribution and Compositional Characteristics of the Na Son Lead-Zinc Ore. Vietnam Journal of Earth Sciences, 33(1): 63-77, https://doi.org/10.15625/0866-7187/33/1/278.
16. Pham Thi Dung, Tran Tuan Anh, Tran Trong Hoa, Ngo Thi Phuong, Nguyen Viet Y, Shunsho Ishihara, Pham Ngoc Can, Tran Van Hieu, 2012. Indium-Potential by-Product in Lead-Zinc Ore of the Cho Don Deposits. Vietnam Journal of Earth Sciences, 32(4): 9, https://doi.org/10. 15625/0866-7187/32/4/1032.
17. Frenzel, M., Tamino, H., Jens, G., 2016. Gallium, Germanium, Indium, and Other Trace and Minor Elements in Sphalerite as a Function of Deposit Type - a Meta-Analysis. Ore Geology Reviews, 76: 52-78, https://doi.org/10.1016/j.oregeorev.2015.12.017.
18. Li, Z., Lin, Y., Yusi, H., Chen, W., Zhilong, H., Yulong, Y., Leonid, D., 2020. Trace Elements in Sulfides from the Maozu Pb-Zn Deposit, Yunnan Province, China: Implications for Trace-Element Incorporation Mechanisms and Ore Genesis. American Mineralogist, 105(11): 1734-51, https://doi.org/10.2138/am-2020-6950.
19. Nguyen Tuan Anh. Ore Chemical Characteristics and Orientation of Prospecting and Exploration

of Lead-Zinc Ore in Northeast Vietnam. Ph.D Thesis, Hanoi University of Mining and Geology, Hanoi, 2014. (In Vietnamese with abstract in English).

20. Tran Trong Hoa, Tran Tuan Anh, Pham Thi Dung, Tran Quoc Hung, Bui An Nien, Tran Van Hieu, Pham Ngoc Can, 2012. By-Products in Lead-Zinc and Copper Ores of Northeast Vietnam. Vietnam Journal of Earth Sciences, 32(4): 10, https://doi.org/10.15625/0866-7187/32/4/1031.