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Formation of secondary non-sulfide zinc ore in Cho Dien Pb - Zn deposits

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ABSTRACT

Non-sulfide zinc ore in the Cho Dien deposit has been exploited for a long time and remains the major exploited ore in Cho Dien. There are numerous studies of Cho Dien Pb-Zn ore, however, many of the studies have dedicated to description of mineralogical and chemical compositions. Built on the mineralogical studies and the content of Pb and Zn in groundwater determined by reflective microscope, SEM, EPMA and ICP-MS methods, the study explained the formation of secondary non-sulfide zinc ore in the Cho Dien deposit. The upper part of ore bodies was weathered and completely oxidized. Difference in geochemical behavior of lead (Pb) and zinc (Zn) in the oxidation process of Pb-Zn ore led to the formation of non-sulfide zinc ore in the Cho Dien deposit. Oxidation of primary Pb-Zn ore minerals such as sphalerite, pyrite and galena creates a low pH environment and transforms zinc from immobile (sphalerite - ZnS) to mobile (Zn^{2+}) and is retained in solution under low(acidic) pH conditions; whereas lead has the tendency to form soluble minerals (anglesite, cerussite). The acid neutralization of the surrounding rock causes zinc to precipitate to form secondary non-sulfide zinc minerals.

Keywords: Non-sulfide zinc ore; Cho Dien Pb-Zn ore; secondary zinc ore.

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1. Introduction

“Non-sulfide zinc” is a term used by previous researchers, referred to a group of ore deposits consisting of Zn-oxidized minerals, mainly represented by smithsonite, hydrozincite, hemimorphite, sauconite and willemite. The minerals are markedly different from sphalerite zinc ores, typically exploited for zinc (Nicola Mondillo, 2013).

In the world, from Roman times up to the 18th century, the non-sulfide Zn-ores, a mix-

ture of silicates and carbonates known as "Lapis Calaminarius", "Calamine", "Galmei", or "Galman". In the Latin, French, German, and Polish speaking world, non-sulfide Zn-ores were used as the source minerals for the production of brass, a zinc-copper ±tin alloy fairly widespread throughout Europe and the Mediterranean area over the centuries (Boni, 2003). However, until the beginning of the 20th century, the production of zinc metal was focused on non-sulfide ore thanks to the development of solvent-extraction (SX) and electro-winning (EW) processes, and with the

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modernization of the Wälz technology for the treatment of non-sulfide zinc ores. Non-sulfide zinc deposits are rapidly becoming an important source of metallic zinc. Since then, scientific studies on non-sulfide zinc ore have also been increased. A number of studies on supergene non-sulfide zinc deposits have been carried out and published: Silesia, Southern Poland (Coppola et al., 2007, 2009); Skorpion, Namibia (Borg et al., 2003); Mae Sod, Thailand (Reynold et al., 2003); Shaimerden, Kazakhstan (Boland et al., 2003).

Heyl and Bozion (1962), Large (2001) and Hitzman et al. (2003) have proposed the classification of non-sulfide zinc deposit. Following Hitzman (2003), non-sulfide zinc deposits are divided into two major geologic types, including supergene and hypogene non-sulfide zinc deposits, in which supergene deposits are the most common type of non-sulfide zinc deposit and are distributed worldwide. Supergene non-sulfide zinc deposits are subdivided into three subtypes: direct replacement, wall-rock replacement, and residual and karst-fill deposits. Hypogene non-sulfide zinc deposits appear to have formed owing to the mixing of a reduced, low-to moderate-temperature (80°-200°C), zinc-rich, sulfur-poor fluid with an oxidized, sulfur-poor fluid (Hitzman et al., 2003).

Mineral ore resources in North Vietnam are interested in the study by many workers (Chau et al., 2017, Hoang et al., 2017). Cho Dien Pb-Zn deposit has become an object of many studies (Tran, 2005; Tran, 2010; Hoa et al., 2010; Anh et al., 2011; Dao Thai Bac, 2012). But studies only describe mineralogical and chemical composition of Pb-Zn ore. There has been no publication on non-sulfide zinc ore in the Cho Dien deposit except the “*Wet tropical weathering in Viet Nam*” reference book of Nguyen (Nguyen, 2013). Mean-

while, Cho Dien deposit is a typical example of non-sulfide zinc ore in Vietnam, with ore bodies have complex shape, which were formed in karst cavities. This ore has been exploited for a long time. Up to now, the non-sulfide zinc ore is still the major ore being exploited in Cho Dien. Even in the published study of Hitzman et al. (2003), non-sulfide zinc deposit in Cho Dien is classified as “residual and karst-fill” (Hitzman et al., 2003).

This paper presents new study on the mineralogy and geochemistry of Pb-Zn ore, and the composition of ground water to clarify the behavior of zinc element in the oxidation of Pb-Zn ore, and to explain the formation of non-sulfide zinc ore in the Pb-Zn Cho Dien deposit.

2. Study area

Red-River shear zone is the main structure separating Northeast and northwest regions of Vietnam. This shear zone is bounded by Chay River fault to the North, by Red river fault to the south.

Pb-Zn Cho Diendeosit is located in the Cho Don District, Bac Kan province, about 36 km northwest of Bac Kan town (Figure1). The study area has a heterogeneous terrain, the lowest is 220-250 m, the highest is 1004.67 m (Lung Le peak). There are limestone mountain ranges from 750 to 960 m (including Phia Khao peak 933 m high).

The Pb-Zn deposit is mainly distributed in the Phia Phuong Devonian terrigenous-carbonate sediment formation, which consists of shale, bituminous black argillite, limestone and marble, cropping out in the Phia Khao anticlinal structure. Pb-Zn mines are discovered mainly in the wing of Phia Khao anticlinal along the northwestern-southeastern fault system; popular mines including Phia Khao, Lung

Hoai, Ban Thi, Bo Luong and Deo An (Figs. 2, 3). In the study area, the presence of northeast-southwest faults is favorable condition for Pb-Zn ore concentrates. Orebodies have complex shapes although ore veins, which fill in the

faults and broken zones, are dominant. The upper part of the orebodies had been completely oxidized and transformed to oxide ores. Sulfide Pb-Zn ore is only found in the lower part of the orebodies (Tran Tuan Anh, 2010).

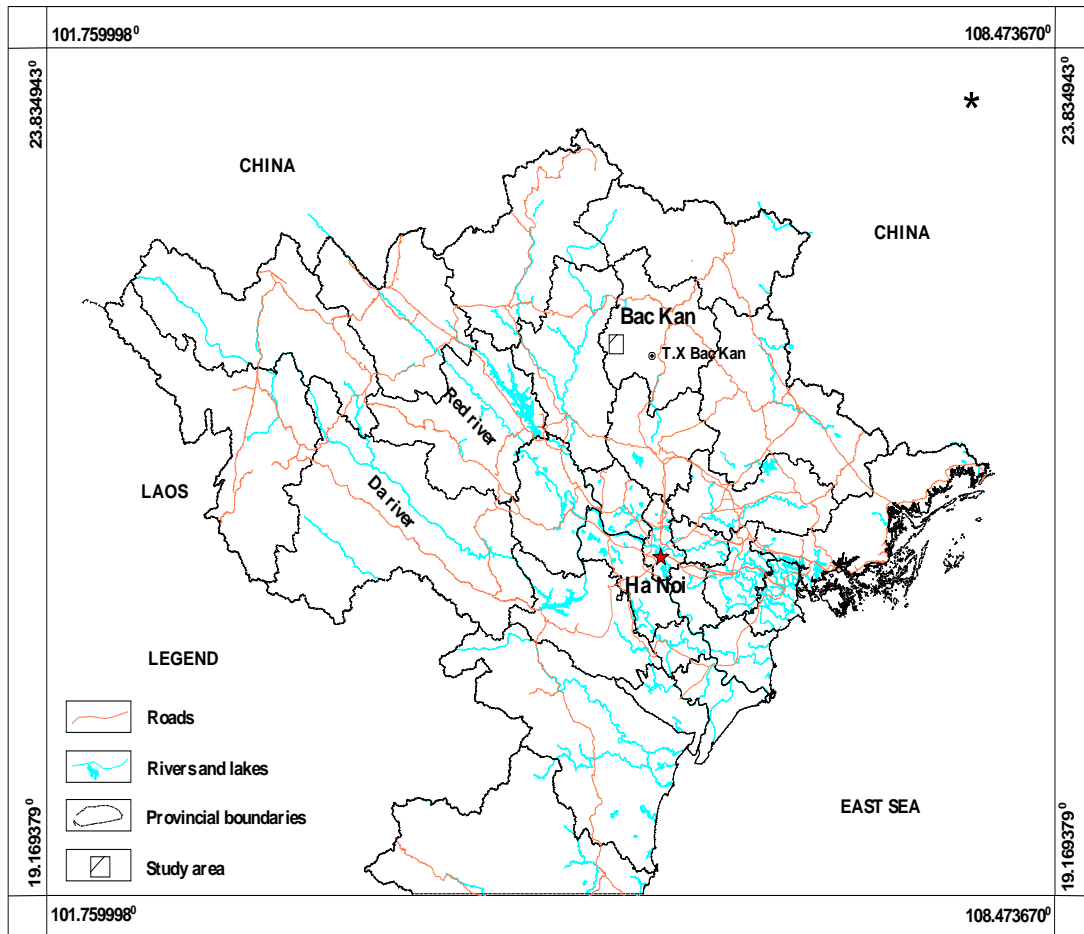


Figure 1. Location of study area

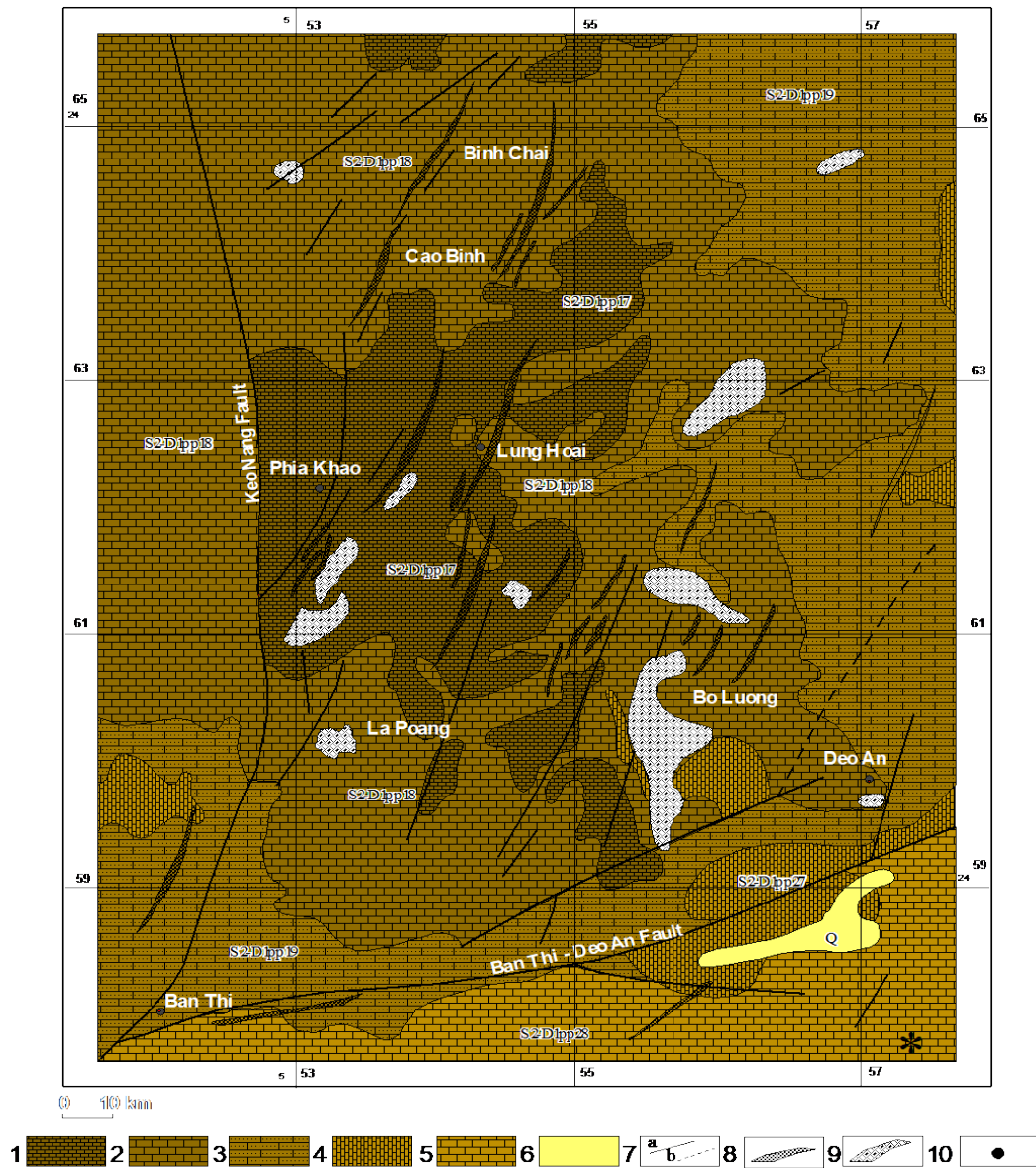


Figure 2. Geological map of Cho Dien Pb-Zn deposits

Legend: 1. Sericite schist, limestone and siliceous limestone; 2. Dark grey bituminous limestone intercalates with thin sericite schist layer; 3. Bituminous white marble intercalates with thin of sericite schist layer; 4. Sericite - quartz schist, siliceous schist contains manganese, iron ore; 5. Marble, rhyolite tuf, amphibole schist; 6. Pebbles, gravel, sand, clay; 7. Faults: a - confirmed, b - assumed; 8. Primary Pb-Zn ores; 9. oxidized Pb-Zn ores; 10. Pb-Zn mines



Figure 3. Photos of oxidized ore mining in the Cho Dien deposit: A-Bo Luong mine; B-Lung Hoai mine

3. Material and Methods

Samples for the research include primary Pb-Zn ore and oxidized Pb-Zn ore taken from Lung Hoai, Phia Khao, Ban Thi, Deo An mines.

Morphological properties of ore mineral were examined using a FEI Quanta 450 scanning electron microscope at the Institute of Geological Sciences, Vietnam Academy of Science and Technology (VAST). Chemical

compositions of the minerals were identified using a Cameca sx -five Electron Probe Microanalyzer (EPMA) equipped with an energy dispersive X-ray spectroscopy (EDS), also at the Institute of Geological Sciences.

Concentrations of heavy metals such as Pb, Zn, Cd, As in the ground water were analyzed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Institute of Geological Sciences. Data are shown in Table 1.

Table 1. Content of As and some heavy metals in groundwater in Ban Thi mine

| No | Samples | Location | pH | Content (mg/l) | | | |
|----|---------|--------------|------|----------------|-------|--------|--------|
| | | | | Pb | Zn | Cd | As |
| 1 | M1 | Ban Thi mine | 6,9 | 0,0036 | 0,04 | 0,0172 | 0,0048 |
| 2 | M2 | Ban Thi mine | 7,15 | 0,0048 | 0,023 | 0,0001 | 0,0055 |
| 3 | M3 | Ban Thi mine | 7,07 | 0,0051 | 0,551 | 0,001 | KPH |

Note: 1-3: groundwater. All samples were analyzed by ICP-MS method in IGS -VAST

4. Result

4.1. Mineralogical composition of primary ores

The primary ores consist mainly sphalerite, galenite and pyrite; and minor amount of arsenopyrite, pyrrhotite and chalcopyrite, and were observed in detail by reflective microscope (Figure 4).

4.2. Mineralogical composition of secondary ores

In the Cho Dien deposit, the upper parts of ore bodies are completely oxidized. Field study

observed secondary ore minerals filled in a network of karst. (Figure 5, 6). Secondary ore minerals include mostly hemimorphite (calamine), smithsonite, goethite, anglesite and cerussite, which were observed clearly by under a reflective microscope (Figure 7). Sphalerite is oxidized patchy and replaced by smithsonite, which forms a rim around sphalerite (Figure 7A) or is transformed into calamine as shown in Figure 7C, where a clear boundary is seen between sphalerite is oxidized and calamine (Figure 7C).

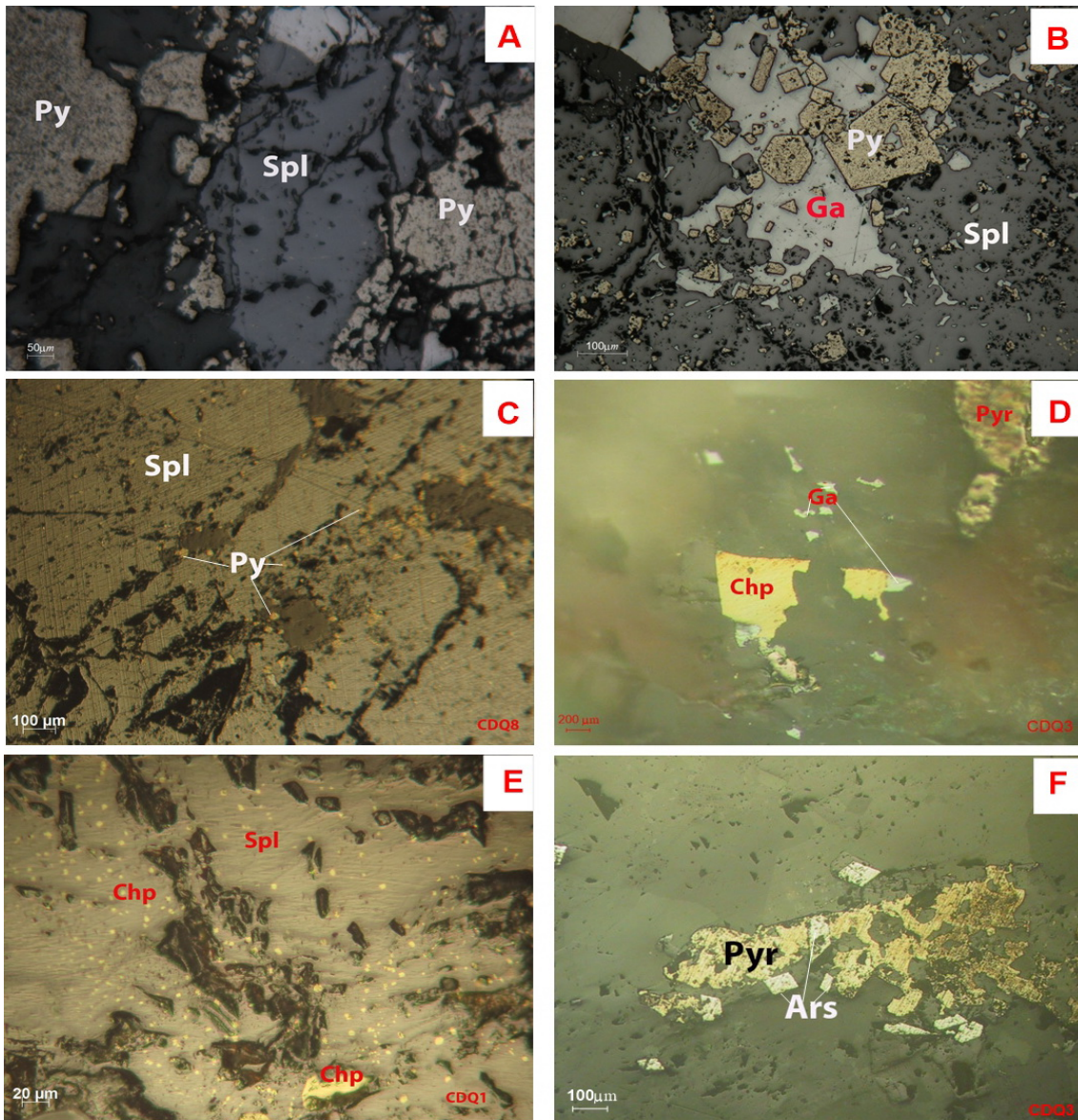


Figure 4. Primary ore minerals in Cho Dien Pb-Zn ore: A- Large sphalerite alternates between cracks of pyrite grains; B- small- to large-grained xenomorphic galena and pyrite particles, disseminated in sphalerite background; C- Small pyrite particles disseminated in sphalerite background; D- Galena particles formed after cutting through chalcopyrite, xenomorphic pyrrhotite is oxidized; E-Chalcopyrite formed in sphalerite background (emulsion texture); F- Arsenopyrite particles intercalate with pyrrhotite



Figure 5. Secondary minerals in crystal form filled in karst cavities



Figure 6. Secondary minerals in white - rough structure form in karst breccia zone

Result analyzed by the scanning electron microscopy (SEM) method shows that secondary ore minerals were formed and filled in a network of karst in form of crystals (Figure 8) or spherical structure in karst breccia zone (Figure 9).

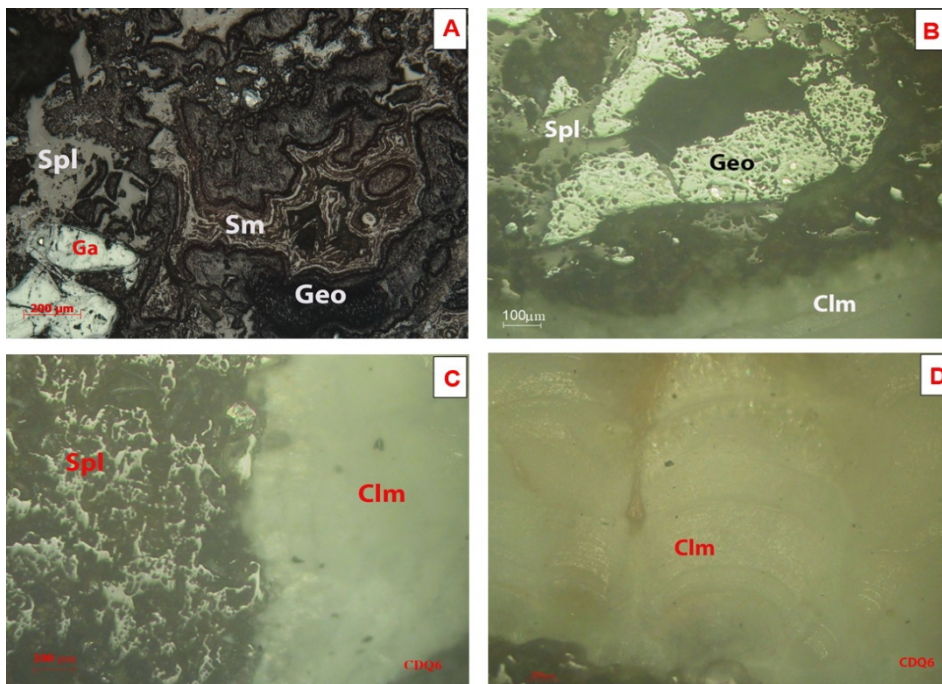


Figure 7. A-Oxidized sphalerite being replaced by smithsonite; oxidized galena edge changed to anglesite and goethite, secondary minerals of iron sulfides; B-Oxidized sphalerite being replaced by calamine and goethite; C-Boundary between oxidized sphalerite and calamine; D- Sphalerite completely changed into calamine with concentric texture

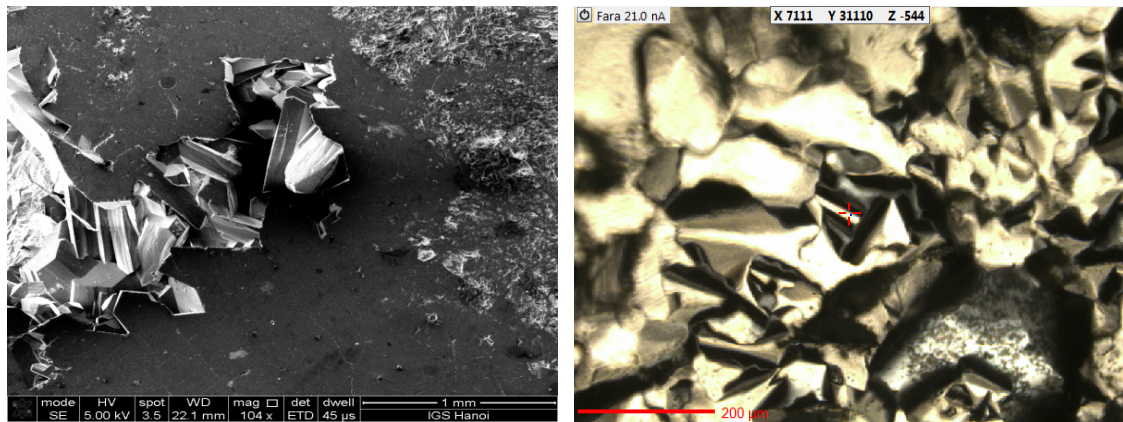


Figure 8. SEM (left) and EPMA (right) photomicrographs of crystals of a secondary ore mineral in karst cavities

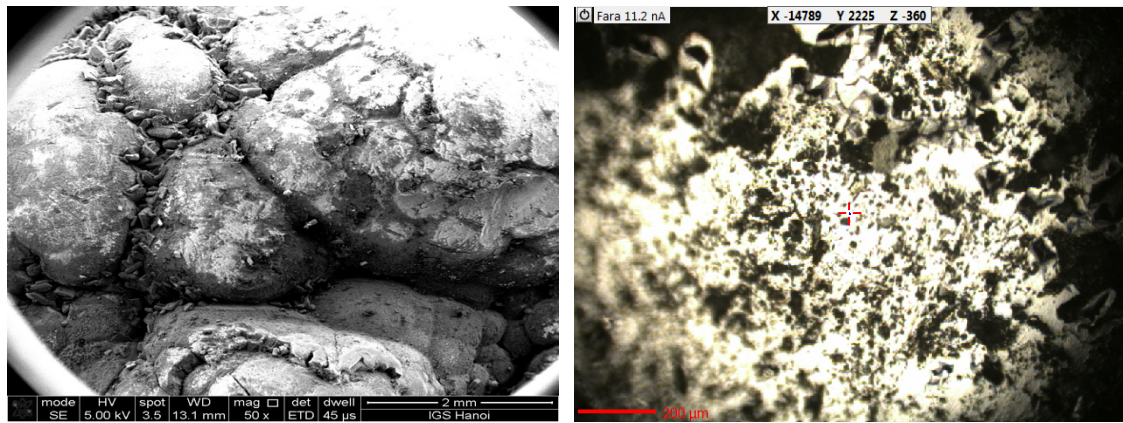


Figure 9. SEM (left) and EPMA (right) photomicrographs of a spherical secondary ore mineral in karst breccia zone

The EPMA-EDS results show the presence of silica (Si) in the chemical composition. This confirms that crystals grow in karst cavities (Figure 8) and that spherical structure (Figure 9) is of hemimorphite mineral ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$) (Figures 10,11). This

is consistent with result analyzed by mineralographic method, that the secondary ore mineral is mainly hemimorphite. The presence of sodium (Na) in the chemical composition may be due to clay minerals clinging to the surface.

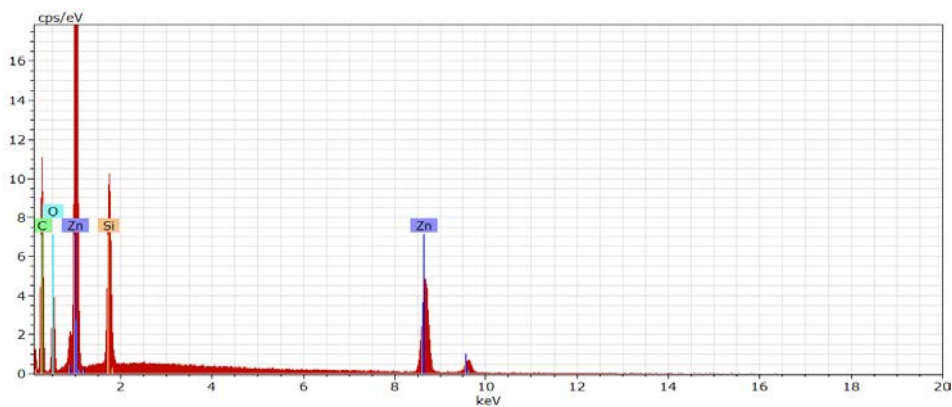


Figure 10. EDS spectrum of crystal in photomicrographs Figure 8

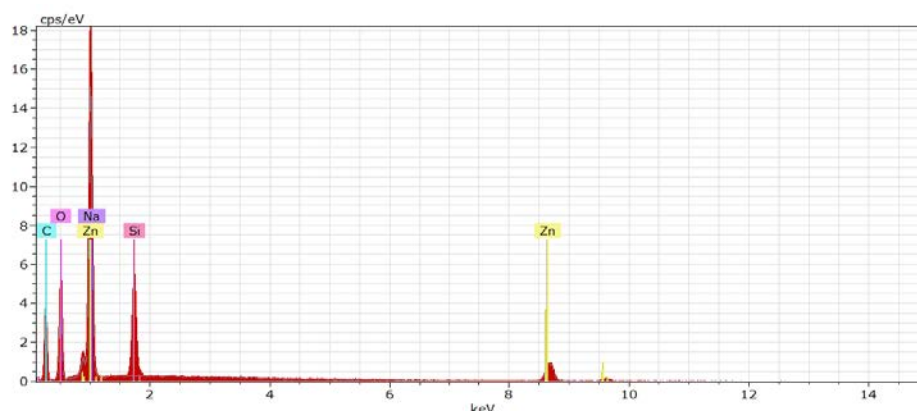


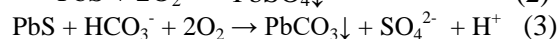
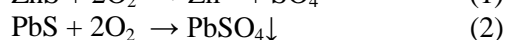
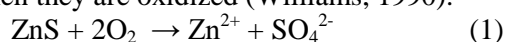
Figure 11. EDS spectrum of spherical structure in photomicrographs Figure 9

4.3. Heavy elements in groundwater

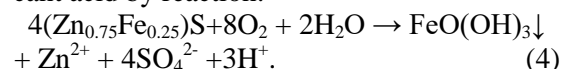
Ban Thi is one of the Pb-Zn mines in the Cho Dien deposit. ICP-MS result of the ground water samples collected at Ban Thi Pb- Zn mine (Table 1) shows that the content of Zn in groundwater of all samples is 5 to 10 times higher than Pb content. This proves that the solubility and flexibility of Zn in aqueous solution is stronger than Pb.

5. Discussions

Oxidation of sulfide minerals generates acid, which is capable of dissolving and transporting metal, especially pyrite (FeS_2) which is easily oxidized when exposed to air and water. Sangameshwar and Barnes (1983) show that, at temperatures between 25°C and 60°C and in an oxidizing environment, zinc remains in solution as Zn^{2+} under acid pH conditions; lead instead, tends to form minerals (sulfates or carbonates) at any pH-Eh range. Thus, acid is produced by oxidation of sulfide minerals, which play an important role in the retention of zinc in solution and drive to a complete leaching of this metal from the system. Sphalerite and galena produce relatively small quantities of acid sulfate-bearing solutions when they are oxidized (Williams, 1990).



However, iron (Fe) can replace zinc (Zn) in sphalerite. Thus, oxidation of iron-sphalerite has the potential to generate significant acid by reaction:



For this reason, the presence of iron sulfide minerals in the original Pb- Zn ore composition is essential. Pyrite oxidation and the relative acid production play an important role in the genesis of supergene non-sulfide ores (Hitzman et al., 2003; Reichert and Borg, 2008).

An important issue is the metal mobility in the fluids. Based on experiments on tailings, Jurjovec (2002) proves that metal mobility greatly depends on pH. For an orebody containing mixed sulfides, and continuously leached in a column experiment, metals can be divided in three groups based of their mobility: Zn, Ni, and Co are mobile at pH of 5.7, Cd, Cr, V, and Pb become mobile under pH=4.0, whereas Cu remain unaffected by changes in pH (Jurjovec et al., 2002). In fact, during oxidation, zinc is transformed from immobile (ZnS) to mobile (Zn^{2+}) and remained in solution under acidic pH condition whereas lead is converted to anglesite or cerussite which is less soluble in aqueous solution. Thus, lead is relatively immobile.

In the Zn-Pb deposit, as said before, oxidation of Pb-Zn ore, zinc is more mobile than

lead and tends to migrate toward the lower portions of the original sulfide body; lead instead is relatively immobile and remains in the original sulfide body as galena, replaced by anglesite and cerussite (Sangameshar and Barnes, 1983). In the Cho Dien Pb-Zn deposit, the primary Pb-Zn ore consist mainly sphalerite, galenite and pyrite; minor amount of arsenopyrite, pyrrhotite, and chalcopyrite. During oxidation, the presence of pyrite in the main ore composition is the source which provides acid and maintain low pH condition. Specifically, the process of oxidation of primary Pb-Zn ore provided low pH and transformed zinc from immobile (ZnS) to mobile (Zn^{2+}) in aqueous solutions. Zinc (Zn^{2+}) can be transported down deeper into the aquifer or farther horizontally into surface water. This is evidenced by the analysis results in Table 1, the content of Zn in groundwater of all samples is 5 to 10 times higher than Pb content. On the move, under different conditions, the acid neutralization actions of the host rock will allow zinc to precipitate from aqueous solution. Smithsonite, hemimorphite, and hydrozincite are the common products of oxidation of the sphalerite-rich deposits. The presence of smithsonite or hydrozincite depends on the pCO_2 and pH values, which is shown in figure 12 (Figure 12). Hemimorphite precipitation depends on the availability of silica (Si) in the system. It is stable at lower pH values than either smithsonite or hydrozincite and with the buffering action of carbonate host rocks it might not be expected to form under normal, nearly neutral weathering conditions. Characteristically, hemimorphite forms where sufficient acid is generated by sulfide weathering to achieve and maintain low pH conditions and low total carbonate activity (Takahashi, 1960). In the Cho Dien Pb-Zn deposit, the presence of sericite schist layers, siliceous limestone and siliceous schist in the lithological component of Phia Phuong formation (Figure 2) is the source which pro-

vides Si for the formation of hemimorphite in the study area.

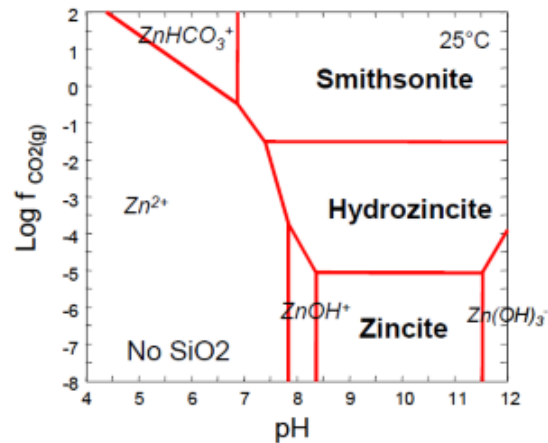


Figure 12. Zinc mineral stabilities in the chemical system Zn-O-H-C (25°C). The activity of Zn^{2+} is 10^{-5} . Atmospheric $CO_2(g)$ is $\log f_{CO_2(g)} = -3.5$ (McPhail et al., 2003)

At favorable locations “ore trap” zinc non-sulfide precipitations are accumulated to form different ore bodies. In the Cho Dien deposit, the presence of karst breccia zones play an important role, breccia fragments are characterized by a large surface area, their pore is big and good permeability. This allows the zinc - loaded ground water to penetrates easily and precipitate zinc non-sulfide minerals from aqueous solution which as cement fill the cavities of karst rock fragments. The result is the formation of non-sulfide zinc ore in the area. Follow classification of Hitzman et al (2003), non-sulfide zinc ore in the Cho Dien deposit may be classified as residual and karst-fill deposits from either mechanical or chemical accumulation of secondary zinc minerals in karstic depressions or in cave systems that formed as a land surface was reduced by weathering.

Residual and karst-fill non-sulfide zinc deposits are mainly found in uplifted areas in wet tropical climates or temperate climates with alternating wet and dry cycles (Hitzman et al., 2003; Nuspl, 2009). Because in these

areas, the weathering and erosion of terrain occurs strongly. This creates favourable conditions for the oxidation of primary ore and karst. Oxidation of sulfide bodies results in the formation of acidic, oxidized solutions that help promote deep weathering and karst development (Thornber and Taylor, 1992).

Another example of supergene non-sulfide zinc ore deposits in the formation of residual and karst-fill deposits is Padaeng, Thailand. The non-sulfide deposit is believed to have formed when a substantial body of sulfide ore was uplifted on the margin of the Mae Sod Tertiary intermontane basin. Acidic fluids, generated by oxidation of the precursor sulfide body, promoted deep weathering and karst formation, allowing mineralization to extend down dip in sandstone units for at least 150 m and vertically for a similar distance in steep structural zones. Non-sulfide zinc ore comprises dominant hemimorphite with minor smithsonite and hydrozincite (Reynolds et al., 2003).

6. Conclusions

In the Cho Dien deposit, strong weathering process makes the upper part of ore bodies completely oxidized. Primary ore minerals are mainly sphalerite, pyrite, galena which are replaced by secondary ore minerals such as hemimorphite (calamine), smithsonite, goethite, anglesite and cerussite.

Difference in geochemical behavior of lead (Pb) and zinc (Zn) in oxidation process of Pb - Zn ores is the cause to form supergene zinc non-sulfide in Cho Dien deposits. Oxidation creates a low pH environment and transforms of zinc from immobile (sphalerite - ZnS) to mobile (Zn^{2+}) and retained in solution under acid pH conditions whereas lead has the tendency to form soluble minerals (anglesite, cerussite). On the move, the acid neutralization actions of the surrounding rocks cause the zinc to precipitate. Under these conditions, smithsonite, hemimorphite and hydrozincite

are common products of oxidation of sphalerite-rich mines.

Cho Dien deposit is a typical example of non-sulfide zinc ore in Vietnam and may be classified as residual and karst-fill deposition from either mechanical or chemical accumulation of secondary zinc minerals in a network of karst cavities.

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