Fluid Inclusion and H-O Isotope Geochemistry of the Phapon Gold Deposit, NW Laos: Implications for Fluid Source and Ore Genesis

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ABSTRACT: The Phapon gold deposit, located in northern Laos, is a unique large-scale gold deposit in Luang Prabang-Loïi metallogenic belt. It is hosted in the Lower Permian limestone and controlled by a NE-trending ductile-brittle fault system. There are three types of primary ore including auriferous calcite vein type, disseminated type, and breccia type, and the first two are important in the Phapon gold deposit. Based on fluid inclusion petrography and microthermometry, three types of primary fluid inclusions including type 1 liquid-rich aqueous, type 2 vapor-rich aqueous and type 3 daughter mineral-bearing aqueous were identified in hydrothermal calcite grains. The ore-forming fluids are normally homogeneous, as indicated by the widespread type 1 inclusions with identical composition. The coexistence of type 1 and type 2 inclusions, showing similar final homogenization temperature but different compositions, indicate that fluid immiscibility did locally take place in both two types of ores. The results of microthermometry and H-O isotopes geochemistry indicate that there are little differences on ore-fluid geochemistry between the auriferous calcite vein-type and disseminated type ores. The ore-forming fluids are characterized by medium-low temperatures (157–268 °C) and low salinity (1.6 wt.%–9.9 wt.% NaCl eq.). It is likely to have a metamorphic-dominant mixed source, which could be associated with dehydration and decarbonisation of Lower Permian limestone and Middle–Upper Triassic sandstones during the dynamic metamorphism. The fluid-rock interaction played a major role, and the locally occurred fluid-immiscible processes played a subordinate role in gold precipitation. Combined with the regional and ore deposit geology, and ore-fluid geochemistry, we suggest that the Phapon gold deposit is best considered to be a member of the epizonal orogenic deposit class.

KEY WORDS: fluid inclusion, H-O isotopes, fluid source, ore genesis, Phapon gold deposit, northern Laos.

0 INTRODUCTION

The Phapon gold deposit is a large-scale deposit initially discovered in the northern Laos in 1990s (Shao et al., 2011). It is located in the northern segments of the Luang Prabang-Loïi metallogenic belt (Fig. 1), which is characterized by multiple generations of successive arc-related magmatic events and its associated copper, gold and other polymetallic deposits (Goldfarb et al., 2014). In comparison with the regional porphyry-related skarn type copper-gold deposits and epithermal gold-silver deposits (Fig. 1; e.g., Qiu et al., 2016a, b), the Phapon gold deposit is unique for its individual ore characteristics. It is hosted in the Lower Permian limestone and controlled by a NE-trending ductile-brittle fault system. The lode-gold orebodies are surrounded by carbonatization zones with nearly no metal sulfides.

There are a number of previous studies of the Phapon gold deposit, including those focused on deposit geology (Xue and Shi, 2016; Shao et al., 2011), ore-controlling structures (Li et al., 2011), hydrothermal alteration (Shi et al., 2016), ore-forming fluids (Lu et al., 2015), and ore genesis (Niu et al., 2017, 2015; Yang et al., 2017; Dai and Niu, 2014). Some workers believe that a deep-seated magmatic water is the source of the ore-forming fluids and that these were gradually mixed with shallower meteoric water during mineralization, based upon interpretations of hydrogen and oxygen isotopic data (Niu et al., 2017, 2015; Lu et al., 2015). Li et al. (2011) and Yang et al. (2017) suggested that the ore-forming fluids were sourced from pressure dissolution result in shear dynamic metamorphism, based on microstructural studies. For ore genesis, Dai and Niu (2014) favored an epithermal model, based on a low-temperature carbonatization-argillization assemblage, and a low-trended ductile-brittle fault system.

orefluid-temperature down to around 200 °C. Based on deposit geology, ore-controlling structures, and ore deposit geochemistry, Niu et al. (2017) and Yang et al. (2017) concluded that the Phapon is a low-temperature hydrothermal deposit controlled by shear zone. Considering that there was no detailed fluid inclusion petrography and little comparison on regional geology in the previous publications, therefore, the fluid sources and ore genesis of Phapon still remain controversial.

Figure 1. (a) Simplified tectonic map showing structural units of Laos and adjacent regions (modified after Shi et al., 2015; Wang et al., 2015); (b) simplified geological map of the Luang Prabang-Loei metallogenic belt (modified from Lin et al., 2010).
In this study, we carried out detailed field work and petrography, fluid inclusion and H-O isotope geochemistry analysis, to define the nature and source of ore-forming fluids, and gold-deposition mechanism in the Phapon gold deposit, and try to discuss its ore genesis.

1 REGIONAL GEOLOGY

The Luang Prabang-Loei metallogenic belt, which lies along the western periphery of the Indochina terrane, is one of the important copper-gold-silver polymetallic metallogenic belts in Indo-China Peninsula (Fig. 1a). The belt extends from Phongsali in northern Laos through Luang Prabang and Pak Lay in western Laos to Loei Province and Phetchabun in central-northern Thailand (Fig. 1b). The metallogenic belt is bounded to the west by the Nan-Uttaradit suture and to the east by the Dien Bien Phu-Loei fold belt, with a length of ~800 km from north to south and a width of ~200 km from east to west, which can be divided into the western Simao-Phitsanulok Basin and Loei volcanic arc in the east (Fig. 1a).

The Simao-Phitsanulok Basin is located to the east of the Nan-Uttaradit suture (Fig. 1a). It is an intracratonic basin formed during the basin-to-mountain transition from Late Permian to Early Triassic, after the Nan-Uttaradit back-arc ocean basin closed, and showed foreland basin in nature in Middle–Late Triassic. The basin is mainly composed of Upper Triassic coal-bearing sandstone, shale, marl, conglomerate, and tuff sandstone, belonging to continental molasse deposits of the foreland basin, and Jurassic–Cretaceous continental clastic rock series consist of siltstone, sandstone, shale, and marl (Fig. 1b, Wang et al., 2015).

The Loei volcanic arc is distributed in parallel with the Dien Bien Phu-Loei fold belt on the east side (Fig. 1a). It developed a set of Late Carboniferous–Middle Triassic island arc calc-alkaline series, with volcanic rocks ranging from basic to intermediate and to acidic (Phajuy et al., 2005). The Carboniferous volcanic rocks are widespread from north to south in Laos (Qian et al., 2016a, 2015). The Late Permian to Early Triassic volcanic rocks are exposure around Luang Prabang in Laos and to the west of Phetchabun in Thailand (Rossignol et al., 2016; Salam et al., 2008). The Middle–Late Triassic volcanic rocks are confined to the southwest or around Luang Prabang (Qian et al., 2016b; Blanchard et al., 2013). The intrusive rocks, dominated by porphyry-related skarn type copper-gold deposits (e.g., Phu Lon and Phu Thap Fah in Thailand, and Pangkuan in Laos), and epithermal gold-silver deposits (e.g., Chatree and Wang Yai in Thailand; Fig. 1b). The Phu Lon and Phu Thap Fah deposits are hosted in Devonian–Permian limestone, shale, muddy sandstone, carbonaceous siltstone, and volcanioclastics. These host sediments have been intruded by Early–Middle Triassic subalkalic to calc-alkaline quartz monzonite and diorite–monzodiorite (granodiorite) porphyry. Zircon U-Pb analyses yielded 248–241 Ma crystallization ages for these intrusions (Zaw et al., 2011; Kamvong and Zaw, 2009), which are responsible for the local skarns and ore formation. The low-sulfidation Ag-Au epithermal Chatree and Wang Yai deposits are associated with Early Permian to Late Triassic anodesitic to rhyolitic volcanic/volcanioclastic units (Zaw et al., 2014; Tangwattanakul et al., 2009), and formed at ca. 251 Ma (40Ar/39Ar adula-

2 LOCAL GEOLOGY

2.1 Ore Deposit Geology

The Phapon gold deposit locates about 30 km northeast to the Luang Prabang (Fig. 1b). The exposed strata around the mining area are mainly Carboniferous, Lower–Middle Permian, Middle–Upper Triassic and Quaternary (Fig. 2). Carboniferous is a set of marine carbonaceous and silicon-bearing fine-grained clastic-carbonate sedimentary formation. It consists of mottled sandstone, siltstone, mudstone, gray-black claystone and limestone with banded chert. Strong brittle shear occurring during the Variscan orogeny, showing obvious plastic flow in the carboniferous rock. The main lithology of the Lower Permian is thick layer microcrystalline limestone and bioclastic limestone with marlstone and siltstone at the bottom. The limestone masses occur as lens which strikes 35º–50º, and dips 15º–45º towards the NE. It shows strong ductile-brittle shear deformation in the ore-bearing section. The Upper Permian is composed of gray-green andesite, andesitic tuff and basalt, and shows unconformable or fault contact relationship with the underlying strata. The Middle–Upper Triassic distributes northeast in the mining area, and mainly consist of purplish red conglomerate, sandstone, siltstone and feldspar sandstone, representing dry and oxidizing deposition in the foreland basin and intermountain basin. The Quaternary is mainly composed of residual red clay, with discontinuous distribution. The area is lenticular in shape with locally distributed epigenetic lateritic gold deposits.

The structures in the mining area are mainly characterized by NE-trending ductile-brittle shear zones and brittle faults in different directions. The NE-trending Luang Prabang ductile-brittle shear zone runs through the whole area and has a width of several hundred meters with multi-stage activities. The ductile-brittle shear zone developed in Carboniferous in the early stage and was dominated by ductile deformation. It developed strong plastic deformation including strong mylonitization, plasticity rheology, sheath fold, book slant tectonics and pyrite stress shadow during the Variscan orogeny. In the late stage, the reactivation of Luang Prabang ductile-brittle shear zone in the Upper Permian limestone led to secondary faults with different orientations and controlled the NE-zonal distributed gold mineralization (Fig. 2, Yang et al., 2017).
The main brittle faults in the mining area can be divided into NE-trending and NNW-trending groups, and the latter group is the main ore-controlling structure of the Phapon gold deposit. The NE-trending faults are well developed with multi-period activities, including F₁, F₂, F₃, F₄, and F₅ fault (Fig. 2). The F₁ and F₂ are compressive-torsional reverse faults and along the contact zones of the Lower Permian limestone and the Middle–Upper Triassic sandstone on the southeast and northwest sides, respectively. The F₁ fault is about 3 km in length and 2–8 m in width, and strikes 40°–60° and dips 55°–70° towards the SE. The F₂ fault is about 3 km long and 1–5 m in width, and strikes 40°–50° and dips 45°–55° towards the SE. Both of them are marked by strong extrusion and foliated rocks. The F₃ extensional-torsional fault strikes 222° and dips 70°–80° towards the NW, and is ~1 km long and 10–15 m wide. The F₄ fault is about 600 m in length and 20–30 m in width, with NE-trend and SE-dip. It is marked by crushing limestone with carbonatization and calcite veins, showing a post-mineralization feature. The NNW-trending faults are a series of ore-bearing faults, and vary from 300 to 800 m in width and 1 to 10 m in width. They strike 330°–350° and dip 45°–65° towards the SWW, and are surrounded by hydrothermal alteration zones.

There is no large intrusive rock mass in the mining area, except for effusive-facies volcanic rocks exposed in the northwestern part. Its lithology mainly contains andesite and andesitic tuff, with locally diabase and dioritic porphyrite. The andesite is cryptocrystalline with few phenocrysts, and is gray-green in color showing weak propylitization (Shao et al., 2011).

There are five orebodies found in the Phapon gold deposit, which are controlled from east to west by the NNW-trending faults, and respectively named No. V-1, II-4, II-2, IV, and VI. All of the orebodies occur in Lower Permian limestone and are controlled by the regional NNW-trending brittle faults. These vein-shaped orebodies are subparallel with a spacing of about ~300 m, and generally strike ~355° and dip ~35° towards the west (Fig. 2). The No. V-1 orebody, which comprise more than 90% of the proven reserves in the Phapon deposit, shows normally vein-shaped and locally cystic or lenticular-shaped orebodies (Fig. 3). It is about 650 m long, generally strikes 330°–355°, and dips 40°–50°SW with large variations locally. It ranges in thickness from 0.3 to 10 m, averaging about 3.4 m, and extends down-dip about 350 m. The thickness of the orebody and the ore type change with its occurrence, and the average gold grade is 6.28 g/t.

### 2.2 Alteration and Mineralization

The hydrothermal alteration at Phapon developed in the Lower Permian limestone and is controlled by the NNW-trending fault zones. It is characterized by medium-low temperature alteration including carbonation, siderite alteration, hematite alteration, and silicification, and show macroscopic red-color alteration and light gray-color carbonation (Fig. 4).

The red-color alteration is mainly caused by siderite alteration and hematite alteration that infiltrate the surrounding limestone, showing a light red or red color. It distributes several centimeters to several meters wide along the ore-bearing faults (Fig. 4b). It has close relationship with gold mineralization and is a special alteration in the area. Siderite and hematite are distributed as disseminations or in place fill micro fractures in limestone (Fig. 4b), and siderite is locally overprinted by magnetite (Fig. 4i). Carbonation occur mainly as planar alteration, which is characterized by the in situ dissolution and
Figure 3. Geological cross-sections along line AA′ (modified from Hu et al., 2013).

Figure 4. Typical alteration and mineralization type in Phapon gold deposit. (a) Auriferous calcite vein; (b) siderite and hematite alteration zone; (c) carbonatization clumps locally existed in the siderite and hematite alteration zone; (d) calcite veins branched and intercalated into the siderite and hematite alteration zone; (e) auriferous calcite veins filled with dark-colored carbon layers and siderite and hematite alteration veinlets; (f) breccia type ore; (g) calcite vein in limestone; (h) siderite is distributed as disseminations in limestone; (i) native gold appears as fine disseminations in calcite. Au. Gold; Cal. calcite; Mag. magnetite; Sd. siderite.
recrystallization of limestone and the formation of fine calcite grains, showing pale in color of surrounding limestone (Fig. 4a). Carbonation spread outside of the siderite and hematite alteration and is one of the main alterations of the deposit. The silification is normally weak and intergrown with carbonation, and the anhedral quartz is distributed as disseminations in the wallrock.

The alteration strength is weakened from the center of the fault zone to the two sides. It mainly consists of a narrow proximal zone of red alteration, and a wide outer zone of carbonation (Fig. 4c). In some cases, carbonation clumps locally existed in the siderite and hematite alteration zone (Fig. 4c), and the calcite veins branched and intercalated into the siderite and hematite alteration zone (Fig. 4d).

There are three types of primary ore in the Phapon gold deposit: auriferous calcite vein type (Fig. 4a), the disseminated type (Fig. 4b), and breccia type (Fig. 4f). The auriferous calcite veins filled the NNW-trending tensile fractures and are dominated by grey-white calcite and in place dark-colored carbon layers and siderite and hematite alteration veinlets (Fig. 4e). The disseminated type ores occurred in siderite and hematite alteration zone, with NNW-trending secondary fractures (Figs. 4c, 4d). The breccia type ore normally developed on one side of the calcite veins, and the breccia includes red altered limestone and auriferous calcite veins, whereas the cements are carbonate minerals such as calcite and siderite (Fig. 4f). The breccia type gold ore has higher gold grade, with gold minerals in both breccia and cements. The ores from siderite and hematite alteration zone generally have high gold grade, and their gold grade has positive correlation with the strength of alteration. The auriferous calcite vein ore type has large variable ranges but generally lower gold grade. The coarser the grains of calcite are, the lower gold grade they appear. Given the locally developed breccia type ore, the auriferous calcite vein-type and disseminated type ores are the two main ore types in Phapon.

The metallic minerals are mainly siderite, magnetite, and hematite, with minor native gold. The non-metallic minerals are mainly calcite with minor realgar, orpiment and quartz (Figs. 4g, 4h). The realgar and orpiment are found only in auriferous calcite veins at present. Calcite is the main gold-bearing mineral. Native gold appears as fine disseminations or in microfractures in calcite (Fig. 4i). Mineral paragenesis and mineralization stages are difficult to define and still remain controversial. It is generally believed the auriferous calcite vein-type and disseminated type ores formed in the same metallogenic event and through similar gold-deposition processes. The calcite veins normally show crosscutting, variation of calcite sizes, or filled with dark-colored carbon layers and siderite and hematite alteration veinlets (Fig. 4e), indicating a characteristic of multi-stage of mineralization. Based on ore texture and mineral assemblage, the three alteration-mineralization geological bodies including carbonation, siderite and hematite alteration, and auriferous calcite vein formed in sequence but are not distinguished sharply (Fig. 5).

3 SAMPLING AND ANALYTICAL METHODS

3.1 Fluid-Inclusion Analyses

Samples for fluid inclusion analyses were selected from both auriferous calcite vein type and disseminated type ores. Thirteen doubly-polished sections (about 0.1 mm thick) were chosen and examined petrographically: of these, seven samples were selected for microthermometry on calcite grains. Fluid inclusion microthermometry was made on the Linkam THMSG 600 heating-cooling stage (-198 to 600 ºC) on a Leitz microscope at the Fluid Inclusion Laboratories, Chengdu Center of China Geological Survey. The reproducibility of measurements was ±1 ºC at temperatures >30 ºC, and ±0.1 ºC at temperatures <30 ºC. The measurements of melting temperatures of ice ($T_m$) were made at the heating rate of 0.2 ºC/min, and for final homogenization temperature ($T_{h\text{TOT}}$), the heating rate was 1.0 ºC/min.

3.2 H-O Isotope Analyses

Hydrothermal calcite formed with mineralization was collected from respectively auriferous calcite vein and siderite and hematite alteration zone. Eight typical samples were crushed to 60 meshes and the pure calcite separates were prepared for the carbon, hydrogen, and oxygen isotope analysis at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology.

The isotopic compositions were measured following the detailed procedures outlined by Liu et al. (2013). For hydrogen isotope analyses, the calcite was heated to ~600 ºC in an induction furnace for releasing water, and the water was passed a zinc powder that was overheated to 400 ºC and was converted to hydrogen. A MAT-253 mass spectrometer was used for hydrogen analyzed. For oxygen isotope analyses, the calcite samples were ground to 200 meshes in an agate mortar, and then baked in an oven at temperature of 105 ºC for 2 h to remove the adsorbed water. After drying, about 0.1 mg of the sample was put into a sample tube and flowed by high purity helium. An excess of 100% phosphoric acid was added to the sample tube, and CO2 gas was produced by reaction between phosphoric acid and calcite samples. The generated CO2 gas was then introduced into the MAT253 mass spectrometer using high purity helium gas to test the O isotopic composition. The H-O analysis

![Figure 5. Paragenetic sequence of mineralization and alteration in Phapon, deduced from ore texture and mineral assemblage. Line thickness indicates relative abundance of minerals in the paragenetic sequence. The stages respectively named carbonation, siderite and hematite alteration, and calcite vein are not distinguished sharply, thus separated from each other with dashed lines.](image_url)
results adopted the Standard Mean Ocean Water (SMOW), denoted as $\delta D_{\text{SMOW}}$ and $\delta^{18}O_{\text{SMOW}}$, with a precision of $\pm 1\%$ for $\delta D$, and $\pm 0.2\%$ for $\delta^{18}O$.

4 FLUID INCLUSION STUDY

4.1 Fluid Inclusion Petrography

From petrography and microthermometry, we identified three types of primary fluid inclusions trapped in calcite grains that are related to the ore-forming event: type 1 liquid-rich aqueous, type 2 vapor-rich aqueous and type 3 daughter mineral-bearing aqueous. Both type 1 and 2 fluid inclusions comprise two phases (liquid H$_2$O+vapor H$_2$O) at room temperature (Figs. 6a, 6b). The vapor H$_2$O volumetric proportion is 5%–30% in type 1 liquid-rich fluid inclusions, and about 50%–80% in type 2 vapor-rich fluid inclusions. The type 1 fluid inclusions are 2–10 $\mu$m in diameter, have regular to negative crystal shape or irregular shape, and appear as clusters or along pseudosecondary trails (Fig. 6d), whereas the type 2 fluid inclusions are rare and generally larger (4–10 $\mu$m). They normally have regular shape and occur coeval with type 1 inclusions as clusters (Fig.

![Photomicrographs of typical fluid inclusions and FIA in the Phapon gold deposits.](image)
6g). The type 3 fluid inclusions, consisting of H₂O liquid, H₂O vapor, and a daughter mineral phase (one or two calcite crystals in H₂O liquid), are very rare and occur locally in red altered rock type ores. They normally have an irregular shape with 2–10 µm in diameter, and the vapor phase account for 5%–30% (mainly 10%–20%) of the inclusion volume (Fig. 6c).

A mass of type 1 inclusions, which are identical in composition, occur together within the same growth zone, and constitute a fluid inclusion assemblage (FIA 1; Goldstein and Reynolds, 1994). These FIAs occur wide spread in both auriferous calcite vein type and disseminated type ores (Fig. 6d; Table 1). The coexisting types 1 and 2 inclusions, which have different compositions and densities, but similar total homogenization temperaturates, constitute FIA 2. These FIAs occur locally in both two ore types (Figs. 6f, 6g; Table 1). Only two type 3 inclusions are identified and occur isolated. They show a same composition with the type 1 inclusions except for the daughter calcite grains.

4.2 Results of Microthermometry

4.2.1 Auriferous calcite vein type ore

Three samples from auriferous calcite vein are selected for microthermometry. Both types 1 and 2 primary fluid inclusions are found in calcite grains, and the melting temperatures of ice (T_mice) final homogenization temperature (T_hTOT) were measured. Type 2 inclusions are much less than type 1 inclusions, and the FIA 2 consisting of types 1 and 2 inclusions locally exist. The results of microthermometry for each sample are shown in Table 1 and Fig. 7.

For all the type 1 inclusions from the auriferous calcite vein type ores, melting temperatures of ice range between -6.5 and -2.2 ºC (mean -3.9±1.0 ºC; 1σ; n=30), and total homogenization into liquid occurs between 162 and 256 ºC (mean 212±25 ºC; 1σ; n=35). Type 2 inclusions show final ice melting temperatures between -4.4 and -2.1 ºC (mean -3.3±0.7 ºC; 1σ; n=7), and total homogenization into vapor occurs between 186 and 268 ºC (mean 224±25 ºC; 1σ; n=9). Besides, some type 2 inclusions show the vapor volume increases with the temperature, but decrepitates before homogenization.

4.2.2 Disseminated type ore

Four samples from siderite and hematite alteration zone are selected for microthermometry. Similarly, both types 1 and 2 primary fluid inclusions are found in calcite grains, and the FIA 2 consisting of types 1 and 2 inclusions exist locally. There are two type 3 daughter mineral-bearing aqueous inclusions identified with independent distribution. Given the daughter minerals are rhombus in shape and not melted when heating to 400 ºC, thus they are believed to be calcite. The H₂O liquid and H₂O vapor finally homogenized to liquid phase respectively at 194 and 205 ºC, with T_mice not measured. Except for the two type 3 inclusions, the results of microthermometry for the four samples are shown in Table 1 and Fig. 7.

For all the type 1 inclusions from the disseminated type ores, melting temperatures of ice range between -5.2 and -0.9 ºC (mean -3.2±0.9 ºC; 1σ; n=39), and total homogenization into liquid occurs between 157 and 236 ºC (mean 199±24 ºC; 1σ; n=42). Type 2 inclusions show final ice melting temperatures between -3.9 and -2.6 ºC (mean -3.2±0.4 ºC; 1σ; n=7), and total homogenization into vapor occurs between 184 and 239 ºC (mean 214±18 ºC; 1σ; n=10). Similarly, some type 2 inclusions decrepitate before final homogenization into vapor phase.

4.3 Composition and Density of Fluid Inclusions

Calculations of salinity (wt.% NaCl eq.) and bulk density were carried out according to the program of Bakker (2003) and the software MacFlincor (Brown and Hagemann, 1995). The results are presented in Table 1.

4.3.1 Salinity

For the auriferous calcite vein type ores, salinities in type 1 liquid-rich aqueous inclusions vary between 3.7 wt.% and 9.9 wt.% NaCl eq. with an mean value of 6.2 wt.% NaCl eq. Type 2 aqueous inclusions contain 3.5 wt.% to 7.0 wt.% NaCl.

Figure 7. Histograms of microthermometric data showing temperatures of T_mice and T_hTOT, and salinity.
**Table 1** Summary of the microthermometric data for fluid inclusions trapped in calcite from two types of ores.

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Sample No.</th>
<th>Fluid inclusion type</th>
<th>(T_{\text{m, ice}}) (ºC)</th>
<th>(T_{\text{h TOT}}) (ºC)</th>
<th>Salinity (wt.% NaCl eq.)</th>
<th>Bulk density (g/cm³)</th>
<th>(P_{\text{h}}) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auriferous calcite vein</td>
<td>PB-ZKB04</td>
<td>Type 1 liquid-rich aqueous</td>
<td>-6.5– -3.5 (-4.7±1.1, (n=9))</td>
<td>162–256 (202±32, (n=10))</td>
<td>5.70–9.86 (7.36±1.47, (n=9))</td>
<td>0.836–0.976 (0.916±0.049, (n=9))</td>
<td>0.61–4.25 (1.82±1.43, (n=9))</td>
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<tr>
<td></td>
<td></td>
<td>Type 2 vapor-rich aqueous</td>
<td>-3.5– -3.0 (-3.3±0.3, (n=3))</td>
<td>186–247 (214±24, (n=11))</td>
<td>4.94–5.70 (5.40±0.40, (n=3))</td>
<td>-</td>
<td>1.10–2.40 (1.66±1.06, (n=9))</td>
</tr>
<tr>
<td>Disseminated PB-ZKB05-1</td>
<td>Type 1 liquid-rich aqueous</td>
<td>-5.4– -2.4 (-3.6±0.9, (n=12))</td>
<td>178–246 (217±20, (n=14))</td>
<td>4.01–8.40 (5.75±1.31, (n=12))</td>
<td>0.846–0.931 (0.893±0.022, (n=12))</td>
<td>0.93–3.23 (2.04±1.06, (n=9))</td>
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</table>

For the disseminated type ores, salinities in type 1 and type 2 inclusions are 1.6 wt.%–8.1 wt.% and 4.3 wt.%–6.3 wt.% NaCl eq., respectively, with mean value of 5.2 wt.% and 5.3 wt.% NaCl eq., respectively. The type 1 inclusions have generally large variations but similar mean values of salinities to the type 2 inclusions (Fig. 8).
5 H-O ISOTOPE GEOCHEMISTRY

Eight typical samples were respectively selected from auriferous calcite vein type and disseminated type ore for $\delta^{18}O$, and $\delta D$ analyses (Fig. 9; Table 2).

The measured $\delta^{18}O$ values of hydrothermal calcite ($^{18}O_{calcite}$) range from 23.8‰ to 29.6‰, with an average value of 28.0‰ (Table 2). $\delta^{18}O$ values of calcite in auriferous calcite vein range from 23.8‰ to 29.6‰, with an average of 27.7‰. The calcite in disseminated type ore has a slightly higher and narrow $\delta^{18}O$ values of 27.5‰–28.8‰, with an average of 28.3‰.

The $\delta^{18}O$ values of hydrothermal fluids ($^{18}O_{SMOW}$ (%o, fluids), Fig. 9; Table 2) in equilibrium with hydrothermal calcite, were estimated using the trapping temperature of associated fluid inclusions. Fluid immiscibility occurred in both auriferous calcite vein type and disseminated type ores (see below), and the trapping temperature must be calculated from FIA 2 consisting of types 1 and 2 inclusions, which represent unmixed fluid pairs. Based on the homogenization temperatures from our fluid inclusion study, equilibrium temperatures for auriferous calcite vein type and disseminated type ores are estimated to be 214 and 202 °C, respectively (Table 2).

The $\delta^{18}O$ values of hydrothermal fluids were calculated using an extrapolation of the fractionation formula from O’Neil et al. (1969): $\delta^{18}O_{fluid}=\delta^{18}O_{calcite}-2.78\times10^6T^{-2}+2.89$. The calculated $\delta^{18}O_{fluid}$ values of auriferous calcite vein type ore are 15.0‰–20.8‰; and in red altered rock type ore, 18.1‰–19.4‰.

The $\delta D$ values of fluid inclusions in hydrothermal calcite range from -68‰ to -51‰, with an average value of -58‰ (Table 2, Fig. 9). $\delta D$ values of calcite in auriferous calcite vein range from -59‰ to -51‰, with an average of -54‰. $\delta D$ values of calcite in siderite and hematite alteration zone range from -68‰ to -55‰, with an average of -62‰.

6 DISCUSSION
6.1 Nature and Sources of Ore-Forming Fluids
6.1.1 Nature of ore-forming fluids

As stated above, the type 1 liquid-rich aqueous and type 2 vapor-rich aqueous primary fluid inclusions occur in both of the two ore types. There is also no obvious difference on fluid inclusion quantities, distributions, shapes, sizes, and densities for each type of inclusions from the two ore types (Fig. 6). Even though there are two type 3 daughter mineral-bearing aqueous inclusions found in the disseminated type ores, the solid daughter mineral can be excluded from the bulk composition of the inclusions, thus which can be regarded as type 1 inclusions.

The results of microthermometry indicate that there are little differences on final homogenization temperature and salinity between the two types of ore, and the ore-forming fluids belong to H2O-NaCl system, which is characterized by medium-low temperatures (157–268 °C) and low salinity (1.6 wt.%–9.9 wt.% NaCl eq.; Table 1).

6.1.2 Sources of ore-forming fluids

The $\delta^{18}O$ values of hydrothermal calcite range from 23.8‰ to 29.6‰, with similar average values for two ore types (27.7‰ for auriferous calcite vein type ore and 28.3‰ for disseminated type ore), indicating that the hydrothermal calcite in the two types of ore is probably the same. At the same time, the calculated $\delta^{18}O$ values of ore-forming fluids vary from 15.0‰ to 20.8‰, with nearly constant average values for two ore types (18.8‰ for auriferous calcite vein type ore and 18.9‰ for disseminated type ore). The $\delta D$ values of fluid inclusions in the calcite range from -68‰ to -51‰. And the auriferous calcite vein type ores have relatively higher $\delta D$ values (average -54‰) than the disseminated type ores (average -62‰).

The $\delta^{18}O$ and $\delta D$ compositions of ore-forming fluids in the Phapon gold deposit are shown in Fig. 9, with all the data falling in the fields of metamorphic water. Lu et al. (2015) concluded that the ore-forming fluids of the Phapon deposit came mainly from magmatic water, and mixed with meteoric water, based on the H-O isotopic composition (Fig. 9). Nevertheless, the $\delta^{18}O$ values of ore-forming fluids range from 10.1‰ to 13.4‰, which are higher than the range of magmatic fluids, and far away from the meteoric water line in Fig. 9. Similarly, none of the data in this study lie in the fields of primary magmatic water (e.g., Qiu et al., 2015, 2017), considering that the low salinity (<10 wt.% NaCl eq.) is different from the normally high salinity magmatic fluids (Rusk et al., 2008), and there is no large intrusive rock mass in the mining area, the ore-forming fluids of the Phapon gold deposit are probably not derived from magmatic fluids.

Table 2 Hydrogen and oxygen isotope compositions of two types of ores.

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Sample</th>
<th>$\delta D_{VSMOW}$ (%o)</th>
<th>$\delta^{18}O_{VSMOW}$ (%o, calcite)</th>
<th>$T$ (ºC)</th>
<th>$\delta^{18}O_{VSMOW}$ (%o, fluids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auriferous calcite vein</td>
<td>PB-PDB04-1</td>
<td>-52</td>
<td>29.6</td>
<td>214</td>
<td>20.8</td>
</tr>
<tr>
<td></td>
<td>PB-PDB04-2</td>
<td>-59</td>
<td>28.5</td>
<td>214</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>PB-PDB04-3</td>
<td>-54</td>
<td>28.7</td>
<td>214</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>PB-ZKB04</td>
<td>-51</td>
<td>23.8</td>
<td>214</td>
<td>15.0</td>
</tr>
<tr>
<td>Disseminated</td>
<td>PB-ZKB05-1</td>
<td>-56</td>
<td>27.5</td>
<td>202</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>PB-ZKB05-2</td>
<td>-68</td>
<td>28.2</td>
<td>202</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>PB-ZKB05-3</td>
<td>-55</td>
<td>28.7</td>
<td>202</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>PB-ZKB05-4</td>
<td>-68</td>
<td>28.8</td>
<td>202</td>
<td>19.4</td>
</tr>
</tbody>
</table>

Notes: $\delta^{18}O_{VSMOW}$ (%o, fluids) is calculated by $\delta^{18}O_{VSMOW}$ (%o, calcite) from the equation: $\delta^{18}O_{calcite}=\delta^{18}O_{VSMOW}-2.78\times10^6$ $T^{-2}+2.89$ (O’Neil et al., 1969); equilibrium temperatures of ore samples from auriferous calcite vein and red alteration zone are 214 and 202 °C, respectively.
Even though the H-O isotopic composition indicates a metamorphic-dominant source of the ore-forming fluids, and there is lack of old regional metamorphic rocks in the Phapon area. However, the Phapon deposit was located in a large ductile-brittle shear zone, which might have multi-periodic activities from Carboniferous to Cretaceous (Shao, 2011). A thrust nappe system, extending along the northwest margin of the ore-hosted Lower Permian limestone, was observed and now was in the form of F2 fault (Fig. 2; Yang et al., 2017; Li et al., 2011; Shao, 2011). It developed strong plastic deformation including strong mylonitization and plasticity rheology along the F2 in both Lower Permian limestone and Middle–Upper Triassic sandstones. Combined with overturned strata, it is believed the Lower Permian limestone in the Phapon area was a nappe on Middle–Upper Triassic sandstones, which indicates a strong dynamic metamorphism. The carbon isotopic composition of hydrothermal calcites from Phapon range from 0.7%o to 1.7%o (average 1.4%o), which are higher than organic material in sedimentary rocks and mantle reservoir values, and basically within the range of marine carbonate (Guo et al., 2018). The hydrothermal calcite, therefore, was probably formed by recrystallization of the local Lower Permian limestone. Thus, the metamorphic fluids that derived from regional dynamic metamorphism should be considered as a most likely source of ore-forming fluids. Although magmatic rocks are rare in Phapon, there are andesite, andesitic tuff, with local diabase and dioritic porphyrite exposure in the northwestern part, which might be produced by crystallization differentiation of mantle-derived basic magma (Niu et al., 2017).

In view of the H-O isotopic composition and regional geology, the ore-forming fluids may have a metamorphic-dominant mixed source. The potential fluid reservoirs could be associated with dehydration and decarbonisation of Lower Permian limestone and Middle–Upper Triassic sandstones during the dynamic metamorphism, although magmatic contribution or mantle source cannot be excluded.

6.2 Fluid Immiscibility and Gold-Deposition Mechanism

6.2.1 Fluid immiscibility

As described above, the ore-fluids normally have homogeneous composition in both auriferous calcite vein type and disseminated type ores, shown as FIA 1 which consists of type 1 fluid inclusions (Fig. 6d). However, for some calcite grains, the type 1 liquid-rich aqueous and type 2 vapor-rich aqueous inclusions locality occur together in a cluster (FIA 2), and shows similar final homogenization temperature (Figs. 6f, 6g; Table 1). Pichavant et al. (1982) suggested that three possible processes may lead to the coexisting fluid inclusions with different compositions: (1) fluid immiscibility from the homogeneous H2O-NaCl fluid; (2) fluid mixing of multi-source hydrothermal fluids (Anderson et al., 1992); and (3) deformation after entrapment (Bakker and Jansen, 1994).

Although ductile-brittle deformations were exhibited in the wall rocks, the undeformed calcite grains were carefully selected for fluid inclusion study. Combined with the regular shape and the generally constant composition of the inclusions in FIA 2, the post-entrapment deformation can be excluded. For fluid mixing of multi-source hydrothermal fluids, the inclusions would exhibit widely variable composition and vapor volumetric proportion (Xavier and Foster, 1999). In this study, however, the type 1 and 2 inclusions have uniform salinity, and show respectively constant vapor/liquid ratios, suggesting the mixing of two hydrothermal fluids cannot be a main process.

Nevertheless, evidences for fluid immiscibility using criteria outlined by Ramboz et al. (1982) are as follows: (1) the type 1 and 2 inclusions were trapped in the same fluid inclusion assemblages (FIA 2, Figs. 6g–6i), which can be considered to be formed contemporaneously; (2) these two types of inclusions contain similar salinities and have uniform variation of final homogenization temperature (Fig. 8); (3) type 1 inclusions homogenise to the liquid, and type 2 inclusions homogenise to the vapor; (4) type 1 inclusions show slightly higher salinities (average value of 5.6 wt.% NaCl eq.) than type 2 inclusions (average value of 5.3 wt.% NaCl eq.), which is consistent with phase separation, as salt is preferentially fractionated into the aqueous phase (Fig. 8; Lawrence et al., 2013). All these evidences indicate that fluid immiscibility did take place locally in both types of ores.

6.2.2 Gold-deposition mechanism

Based on the hydrothermal mineral assemblage in Phapon, with presence of calcite and absence of K-feldspar, the ore-forming fluid pH is thought to have been near-neutral to weakly alkaline. Considering that gold is primarily dissolved and transported as gold chloride complexes (AuCl3−) exist in near-neutral ore fluids at >400 °C (Gammons et al., 1994; Seward, 1990, 1973), the initial ore-forming fluids with medium-low temperatures (157–268 °C) in Phapon are considered to have gold bisulfide complexes (Au(HS)2−), which are in important near-neutral ore fluids with temperatures of <400 °C, as gold-transporting species (Pokrovski et al., 2009; Benning and Seward, 1996; Hayashi and Ohmoto, 1991). Thus gold-deposition may be the result of H2S loss from the ore-forming fluids and destabilization of (Au(HS)2−), which was caused by both fluid-wallrock interaction and fluid immiscibility (Mikucki, 1998; Cox et al., 1995; Naden and Shepherd, 1989).

Hydrothermal alteration, particularly the siderite and hematite alteration, is widely developed in the Phapon gold deposit (Fig. 4b). Interaction between Fe-bearing orefluids and carbonate minerals in wall-rocks, to form siderite would decrease the solubility of Au(HS)2− and lead to gold deposition (e.g., Guo et al., 2017; Guo, 2016; Phillips and Powell, 2010), in terms of the following equations (Williams-Jones et al., 2009).

\[
\begin{align*}
\text{Fe}^{2+} + (\text{HCO}_3^-) &= \text{FeCO}_3^- + \text{H}^+ \\
\text{H}_2\text{S}(g) &= \text{H}^+ + \text{HS}^- \\
4\text{Au}^0(s) + 2\text{H}_2\text{O} + 8\text{H}^+(&\text{aq}) &= 4\text{Au}^0(s) + 8\text{H}_2\text{S(aq)} + \text{O}_2 \\
\text{H}_2\text{S} \text{ loss from the ore fluids could be achieved by both siderite alteration and fluid immiscibility. As discussed above, homogeneous fluids, represented by FIA 1 consist of type 1 inclusions that are identical in composition, are widespread. It indicates that fluid immiscibility, characterized by existing of FIA 2, occurred locally in ores of both types. Considering that the ores from siderite and hematite alteration zone generally have high gold grade, which has positive correlation with the}
\end{align*}
\]
strength of alteration, fluid-wallrock interaction must have played a major role in gold deposition. Wilkinson and Johnston (1996) suggested fault movements, which lead to fluid-pressure cycling during the evolution of the vein system, are likely to induce a fluid immiscibility process. The ore deposit geology and fluid inclusion results suggest that, fluid-immiscible processes caused by multi-period seismic movement along the NE-trending fault zones and the secondary NWW-trending faults that host lode-gold orebodies and subsequent lowering of the gold-complex solubility, are interpreted to be another precipitation mechanism of gold deposition.

6.3 Implications for Ore Genesis

The fluid-inclusion studies at Phapon show that the ores were deposited from low salinity (<10 wt.% NaCl eq.) aqueous fluids with low to intermediate homogenization temperatures (~180–240 °C). This, together with C-H-O isotopes geochemistry, which demonstrates that the ore-forming fluids may have a metamorphic-dominant mixed source, has led to the classification of Phapon as orogenic deposits (Groves et al., 1998). A number of features are compatible with their classification as orogenic gold systems. These include the strong structural control on the deposits by NWW-trending brittle faults (Li et al., 2011; Shao, 2011), the lack of metal zonation, the lack of high, near-magmatic, the occurrence of free gold in calcite, and the extremely high Au/Ag ratio (≫10, with average silver grade of 0.05 g/t) of the ores (Xue and Shi, 2016). Even though there was no CO2-rich fluid inclusions found in this study, the CO2 loss from the ore fluids might be achieved by formation of siderite and hydrothermal calcite.

The final homogenization temperature and pressure of the fluid inclusions can be regarded as the P-T conditions of gold mineralization when fluid immiscibility occurred (e.g., Guo et al., 2017; Yang et al., 2016a). Given the fluid-immiscible processes locally occurred and is interpreted to be one of the precipitation mechanisms of gold deposition, the final homogenization pressure (P hom, Table 1) of the type 2 inclusions in FIA 2 can be used for calculation of mineralization depth. The homogenization pressure of type 2 inclusions in ores are 1.05–5.16 MPa (mean 2.22 MPa). Taking into consideration that the multiple seismic movements and pressure pulsations occurred during the fluid immiscibility (Weatherley and Henley, 2013), the metallogenic pressure can be estimated between hydrostatic pressure (10 Mpa/km) in the open system and lithostatic pressure (ca. 24 Mpa/km for limestone) in the closed system. Thus the mineralization depth in Phapon is about 0.11–0.22 km, generally coinciding with the previous studies (Lu et al., 2015; Dai and Niu, 2014).

The Nan-Sra Keao back arc basins may have begun to close from Late Permian to Early Triassic through east-vergent subduction beneath western Indochina, forming Nan-Uttaradit suture, which created the Loei continental arc magmatism and its associated porphyry-related skarn (e.g., Phu Lon) and epithermal (e.g., Chatree) deposits (Fig. 1). Continuous subduction along the Loei fold belts finally brought about the Indochina–Sibumasu collision during the Late Triassic, which represents the significant metallogenic epoch for many orogenic gold deposits along the Sukhothai- and East Malaya-terrane/fold belts (Fig. 1; Zaw et al., 2014). As discussed above, the potential fluid reservoirs could be associated with dehydration and decarbonisation of Lower Permian limestone and Middle–Upper Triassic sandstones, the mineralization events can’t be earlier than Early to Middle Triassic. As Zaw et al. (2014) pointed out, many of the Loei belt mineralization systems are linked to one of the subduction-related systems, i.e., the Late Permian–Middle Triassic continental arcs, as well as the Late Triassic–Jurassic post-collisional magmatism (Fig. 10a). Even there were no geochronological data reported in the Phapon deposit yet, the gold deposition in the Phapon deposit occurred, more likely, during the regional dynamic metamorphism, driven by Late Triassic–Jurassic post-collisional magmatism.

In the Paben area, the deep-seated magmatism and tectonic activities resulted in a thrust nappe system extending along the boundary of Lower Permian limestone and Middle–Upper Triassic sandstone in the shallow part (Fig. 10b). The strong collision drove limestone to thrust over the sandstone, and formed a series of NWW-trending secondary brittle fractures in limestone. The initial ore fluids could be dynamic metamorphic-dominated fluids derived from dehydration and decarbonisation of limestone, and the regional magmatism may provide a heat source for driving fluid circulation. The metamorphic fluids entered the limestone along the NWW-trending fractures and reacted with the surrounding rock, forming weak carbonation zone. As mineralization progresses, the Fe-bearing fluid reacted with the surrounding rock to form a red alteration zone which overlaid on carbonation alteration, accompanied by locally fluid immiscibility and gold precipitation. The meteoric water might inclue the ore-forming fluids during the late stage of mineralization. Considering the gold mineralization was associated with the subduction and collision, and the appearance of realgar and orpiment indicating a relatively low ore-forming temperature (Fig. 2; Yang et al., 2016b; Gebre-Mariam et al., 1993), the Phapon gold deposit is best considered to be a member of the epizonal orogenic deposit class.

7 CONCLUSIONS

(1) The ore-forming fluids for the auriferous calcite vein-type and disseminated type ores show little difference and were characterized by medium-low temperatures (157–268 °C) and low salinity (1.6 wt.%–9.9 wt.% NaCl eq.).

(2) The ore-forming fluids have a metamorphic-dominant mixed source, and could be associated with dehydration and decarbonisation of Lower Permian limestone and Middle–Upper Triassic sandstones during the dynamic metamorphism.

(3) The fluid-wallrock interaction, which leads to the distinct red-color alteration, is considered to play a major role in gold precipitation, and the locally existed fluid immiscibility was another gold deposition mechanism.

(4) The Phapon gold deposit is best considered to be a member of the epizonal orogenic deposit class, and the gold mineralization occurred probably during the regional dynamic metamorphism, driven by Late Triassic–Jurassic post-collisional magmatism.

ACKNOWLEDGMENTS

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Figure 10. (a) Regional geological setting during Late Triassic–Jurassic (Modified after Zaw et al., 2014); (b) a suggested genetic model of Phapon.

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Fluid Inclusion and H-O Isotope Geochemistry of the Phapon Gold Deposit, NW Laos