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Hydrothermal evolution and ore genesis of the Zhaiping Ag-Pb-Zn deposit in Fujian Province of Southeast China: Evidence from stable isotopes (H, O, C, S) and fluid inclusions



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ABSTRACT

The Zhaiping Ag-Pb-Zn deposit (204 t Ag, average grade: 221.8 g/t) is located in the coastal area of the Cathaysia Block, Southeast China. Vein-type Ag-Pb-Zn orebodies are mainly hosted in the early Cretaceous volcanic and subvolcanic rocks, and structurally controlled by a group of NW-trending extensional faults. Ore-related hydrothermal alteration is well developed on both sides of the veins, dominated by silicic, phyllic, propylitic, and carbonate alteration. Mineralization can be divided into three stages: (1) the pre-ore quartz-pyrite stage, (2) synore quartz-Ag-base metal stage, and (3) post-ore quartz-calcite stage. Microthermometric measurements of fluid inclusion assemblages in quartz, fluorite, sphalerite, and calcite from various hydrothermal stages reveal that from the pre-ore, syn-ore to post-ore stages, the homogenization temperatures range from 365 to 319 °C, from 317 to 222 °C, and from 233 to 172 °C, respectively. Fluid salinities range from 1.7 to 10.8 wt% NaCl equivalent. The microthermometric data indicate that the fluid cooling and fluid-rock interaction are two important mechanisms for ore precipitation. The $\delta^{34}S_{V-CDT}$ values of sulfide minerals (pyrite, sphalerite, galena, pyrrhotite and tetrahedrite) range from -1.9 to 6.2‰, and mostly between 1.0 and 4.5‰, consistent with a deep-seated magmatic sulfur source. Hydrogen and oxygen isotopic compositions of quartz indicate a primarily magmatic origin for the ore-forming fluids, and the proportion of meteoric water increased during the ore-forming processes. Post-ore stage calcite has $\delta^{13}C_{V\text{-PDB}}$ values of -2.8 to -0.8% and $\delta^{18}O_{V\text{-SMOW}}$ values of 4.2–6.4‰, corresponding to calculated values of fluids of -3.2 to -1.1%, and -4.9 to -2.8%, respectively. The carbon isotopes indicate a magmatic source for carbon but the oxygen isotopes indicate a significant contribution of meteoric water during calcite precipitation. We therefore proposed that the Zhaiping deposit is a typical mesothermal deposit that formed in an extensional environment related to the early Cretaceous subduction of the paleo-Pacific plate.

1. Introduction

Vein-type Ag-Pb-Zn deposits constitute an important source of silver and base metals, and their close temporal, spatial, and genetic relationships with porphyry and/or skarn systems has been well documented in many cases (e.g., Guilbert and Park, 1986; Sillitoe, 2010; Bonsall et al., 2011; Box et al., 2012; Catchpole et al., 2015a,b). Previous geochronological, fluid inclusion, and stable isotope data suggest that these deposits are most likely the distal products of magmatichydrothermal systems (Lawley et al., 2010; Williams-Jones et al., 2010; Deng et al., 2016; Li et al., 2017). However, some base metal sulfide veins do not appear to be spatially and genetically linked to porphyry or skarn systems, and their genesis remains controversial. The classification of vein-type Ag-Pb-Zn mineralization is also a matter of considerable debate. In a recent review paper, Kissin and Mango (2014) proposed that vein-type Ag-Pb-Zn deposits should be classified as Cordilleran-type vein deposits and Ag-Pb-Zn veins hosted in clastic metasedimentary rocks. Examples for the former type include the Magma Mine (Arizona), Tintic Mine (Utah), and Casapalca (Peru) (Rye and Sawkins, 1974; Hull, 1980). The source of the Cordilleran-type vein deposits in most instances has been attributed to a magmatic-hydrothermal solution, although an appropriate genetically related to igneous intrusion is not apparent in some cases. The second type Ag-Pb-Zn veins are generally linked to greenschist to amphibolite facies metamorphism

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Main characteristics of typical Au-Ag-Pb-Zn deposits related to late Mesozoic magmatism in the costal area of the South China.

No	Deposit	County/ Province	Metal assemblage	Reserves (t, Mt) @ grade (g/t, %)	Intrusions and age	Host rocks and age	Occureance of orebody	Major alteration and stage	Data source
-	Yinshan	Dexing/ Jiangxi	Ag-Pb-Zn- Cu-Au	Ag: 2600 t @196 g/t; Pb: 0.38 Mt @ 1.75%; Zn: 0.42 Mt @ 1.91%; Cu: 0.86 Mt @0.53%; Au: 1144 @ 0.65 of t	Late Jurassic dacite and quartz porphyry	Mesoproterozoic Shuangqiaoshan Gp. Phyllite, Late Jurassic Ehuling Fm. meroclastic roote shuolita	Veins in fault zones	phy + Cu + Au \rightarrow Pb + Zn + qz + carb + chl + ser	Mao et al. (2011); Wang et al.
2	Shatan	Qianshan/ Jianoxi	Au-Ag	Au. 1141 (0.02 g/t) Au: $\sim 5 \text{ t}$ ($0 2.0-10.4 \text{ g/t}$; Ag: < 200 t ($0 151-236 g/t$)	Subvolcanic rocks	pyroclasuc rocks, myonte Late Jurassic Ehuling Fm. Tuff	Veins, lens, stratiform in faults	$phy \rightarrow qz + adl + Au + Ag \rightarrow kao + ill$	Ye (1993)
ŝ	Huxingshan	Dongxiang/ Jiangxi	Au-Pb-Zn	Au: < 5 t @ 1.5-100 g/t; Pb: < 0.1 Mt @1.6-8.8%; Zn: < 0.1 Mt @1.4-18.6%	Subvolcanic rocks	Neoproterozoic Zhoutan Gp. Quartz-mica schist, phyllite	Veins, lens, bed- shaped in interlaver fracture	chl + ser \rightarrow qz + carb + Au + Pb + Zn \rightarrow kao + hem	Liu (2012)
4	Haoshi	Shengxian/ Zhejiang	Ag	Ag: > 2001 @?	Late Jurassic dacite	Late Jurassic Xitoushan and Jiulipiang Fm. pyroclastic	Veins in fault zones	chl + ser \rightarrow qz + fl + Ag \rightarrow carb + kao	Xu et al. (1994)
ß	Bamao	Xinchang/ Zhejiang	Ag	Ag: $> 200t @$ n $\times 10-n \times 100 $ g/t	Subvolcanic rocks	Early Cretaceous Chaochuan Fm. breccias, tuff and andesite	Veins in fault zones	$phy \rightarrow qz + di + Ag \rightarrow qtz + btt + Ag \rightarrow qtz + carb + fl$	Liu et al. (1990); Zhu et al. (2009)
9	Zhilingtou	Suichang/ Zhejing	Au-Ag-Pb-Zn	Au: > 20 t @ 8.4-46.2 g/t; Ag: > 1000 t @165-685 g/t; Pb: > 0.1 Mt @0.9-6%; Zn: > 0.1 Mt @ 0.9-6%	Late Jurassic subvolcanic rocks	Paleoproterozoic Badu Gp. metamorphic rocks; Late Jurassic Dashuang Fm.	Veins, lens tabular in ductile shear zones and fracture	phy + chl \rightarrow qz + adl + carb + Au + Ag \rightarrow carb + qz	Zhou and Qian (1996); Zhu et al. (2009)
~	Dalingkou	Tiantai/ Zhejiang	Au-Pb-Zn	Ag: > 2000t @16-1186 g/t; Pb: ? @0.7-2.0%; Zn: ?@ 1.5-3.5%	Early Cretaceous subvolcanic rocks	Late Jurassic Xitoushan Fm. pyroclastic rocks, Early Cretaceous Chaochuan Fm.	Veins, lens, stratiform in caldera-related faults	$qtz + arg \rightarrow qz + Ag + Pb + Zn \rightarrow brt \rightarrow qz + fl$	Li and Zhang (2008)
ø	Wubu	Huangyan/ Zhejing	Pb-Zn	Pb: > 0.5 Mt @1.2-1.5%; Zn: > 0.5 Mt @ 1.9-2.2%	Quartz felsophyre	Late Jurassic Xishantou, Dashuang , and Early Cretaceous Guantou Fm.	Veins, lens in fault zones	$phy + chl \rightarrow qtz + Pb + Zn \rightarrow carb$	Huang et al. 1983; Zheng and Xie
6	Zhaiping	Shouning/ Fujian	Ag-Pb-Zn	Ag: > 204t @221.8 g/t	Early Cretaceous subvolcanic rocks	For the second s	Veins in fault zones	$qz \rightarrow phy + Ag + Pb + Zn \rightarrow qz + carb + fl + chl$	This study
10	Tianchi	Shouning/ Fujian	Ag-Pb-Zn-Au	Ag: ? @40-867 g/t; Pb: ? @ 0.15-1.35%; Zn: ? @0.2-2.26%; ^ ? @0.1 7 5.2.4	Early Cretaceous biotite granite,	granne porpuyry Early Cretaceous Nanyuan Fm. tuff and rhyolite	Veins in fault zones	$phy \rightarrow qz + carb + Ag + Pb + Zn + Ag \rightarrow chl + kao$	Chen (2017)
11	Yingshan	Tuorong/ Fujian	Ag	Ag: > 200t @295-410 g/t	gramme porpuyry Early Cretaceous subvolcanic rocks	Early Cretaceous Nanyuan Fm. tuff and rhyolite, Early Ctetaceous Xiaoxi Fm. volcanic- sedimentary mocks	Veins in fault zones	$qz \rightarrow phy + Ag \rightarrow qz + carb + chl$	Ye (2013)
12	Ancun	Dehua/Fujian	Au	Au: 3.5 t @7.56 g/t	Early Cretaceous monzonitic	Early Paleozoic quartz diorite	Veins, lens in fault zones	$phy \rightarrow phy + chl + carb + Au \rightarrow qz + carb + ill$	Liang et al. (2011); Li
13	Dongyang	Dehua/Fujian	Au	Au: 22 t @ 2.83 g/t	grante porpnyry Early Cretaceous subvolcanic rocks	Early Cretaceous Nayuan Fm. rhyolite porphyry and volcanic rocks	Veins in fault zones	phy + chl \rightarrow Au + qz \rightarrow carb + qtz	et al. (2018a) Huang et al. (2013); Li et al. (2018b)
14	Dongji	Zhenghe/ Fuiian	Au	Au: $< 5 t @4.35 g/t$	Early Cretaceous	Early Ctetaceous Xiaoxi Fm. volcanic. sedimentary rocks	Veins, lens in fault	phy + chl \rightarrow qz + Au \rightarrow qz + carb	Liu (2016)
15	Maluntou	Zhenghe/	Чu	Au: < 5 t @4.8 g/t	Early Cretaceous	Early Cretaceous Shimaoshan	Veins, lens in fault	$phy + chl \rightarrow qz + Au \rightarrow hem$	Fang (2006)
16	Shangshangang	Fujian Zhenghe∕ Fujian	Au	Au: < 5 t @4.59 g/t	subvoicanic rocks Early Cretaceous subvolcanic rocks	чр. voteante rocks Early Cretaceous Shimaoshan Gp. volcanic rocks	zones Veins, lens in fault zones	$phy + chl \rightarrow qz + Au \rightarrow qz + carb$	Liu (2016)
Notes.	: Reserves: Mt-m	villion ton; t-to	n.						

Alteration and mineralization: Ag-silver mineralization; arg-argilic alteration; Au-gold mineralization; adl-adulatization; brt-baratization; carb-carbonatization; di-dickitization; fl-fluoritization; hem-hematitization; ill-illitization; kao-kaolinitization; pb-lead mineralization; phy-phyllic alteration; gz-selicification; sc-sericitization; Zn-zinc mineralization.

(Beaudoin and Sangster, 1992; Li et al., 2013; Kissin and Mango, 2014). Examples for this type of Ag-Pb-Zn veins include Keno Hill (Yukon), Coeur d'Alene (Idaho), and Cierco (Spain) (Beaudoin and Sangster, 1992; Johnson et al., 1996). These veins commonly are connected with crustal-scale faults, lacking direct genetic relationship to igneous intrusions (Beaudoin and Sangster, 1992; Johnson et al., 1996).

The South China Block hosts a great number of porphyry Cu-Mo, epithermal Au-Ag, hydrothermal vein-type Ag-Pb-Zn, skarn Cu-Pb-Zn, and granite-related U deposits (Mao et al., 2013; Li and Jiang, 2017; Zhong et al., 2017). Previous studies suggest that the formation of these deposits is related to late Mesozoic large-scale tectono-magmatic and hydrothermal events (Mao et al., 2008, 2013; Wang et al., 2011, 2016a,b). A series of Au-Ag-Pb-Zn deposits related to the late Mesozoic magmatism has been discovered in the costal area of the South China Block in recent decades (Table 1). The Shouning-Nanyang region, located in the eastern part of the South China Block, is one of the most important metallogenic belts for Ag-Pb-Zn mineralization in Fujian Province. Exploration in this area started in the early 1970s, and early targets were identified by geochemical exploration. Numerous Ag-Pb-Zn sulfide veins were discovered through private mining and prospecting efforts in the early 2000s. The area currently hosts tens of Ag-Pb-Zn deposits of varying sizes, including the Zhaiping, Tanshan, Daan, Tianchi, Yingshan, Tieguping, Wailou, and Shanjikeng deposits (Table 1, Shi, 2008; Zhong, 2017). However, previous studies of these deposits in the region merely provided a rough description of individual deposits (Table 1, Shi, 2008; Zhong, 2017), the origin, nature and evolution of the ore-forming fluids, and the genetic type of the deposits are still poorly understood, which limits our understanding of the Ag-Pb-Zn mineralization in the region.

In this paper, we carried out a detailed study of the geology, alteration and mineralization of the Zhaiping deposit based on field observations and petrographic studies. Wu further carried out studies on fluid inclusions and stable isotopes (sulfur isotopes of sulfides, hydrogen-oxygen isotopes of quartz, and carbon-oxygen isotopes of calcite) to clarify the origin, nature, and evolution of the ore-forming fluids and the ore precipitation mechanisms of the Zhaiping deposit. Lastly, based on the regional tectono-magmatic events, ore geology, and fluid inclusions and stable isotopes obtained in this study, the ore genesis is discussed.

2. Regional geological setting

The South China Block is composed of the Yangtze Block in the northwest and the Cathaysia Block in the southeast, which amalgamated in the Neoproterozoic (900–830 Ma) along the Jiangshan-Shaoxing and Pingxiang-Yushan suture zones (Fig. 1A, B; Chen and Jahn, 1998; Wang et al., 2013a,b). The South China Block was subsequently overprinted by at least three tectonothermal events in the early Paleozoic (~420–460 Ma), Triassic (Indosinian) and Jurassic-Cretaceous (Yanshanian) (e.g., Zhou et al., 2006; Shu, 2012; Pirajno, 2013).

The basement of the Cathaysia Block is mainly composed of the Paleo- to Mesoproterozoic metamorphic rocks, which include the metasedimentary rocks (mainly schist and granulitite) and meta-igneous rocks (such as amphibolite) (Jiang et al., 2009; Zhou et al., 2012). During the early Neoproterozoic, the Cathaysia Block was consolidated with the Yangtze Block by the Jinning orogenic event at ca. 970-890 Ma (Wang and Li, 2003; Li et al., 2009). The basement was overlain by voluminous Neoproterozoic-Paleozoic continental to neritic marine sedimentary rocks and tholeiitic mafic rocks (Jiang et al., 2009; Shu, 2012). The Early Paleozoic Wuyi-Yunkai Orogeny was characterized by strong thrusting/transpression, magmatism and metamorphism (Charvet et al., 2010; Li et al., 2010). In response to the Indosinian Orogeny caused by collision between the South China Block and Indochina, the pre-Mesozoic sequences were unconformably overlain by the lower Mesozoic terrestrial clastic rocks (Wang et al., 2007). Early Mesozoic granites are widespread in the South China Block and are thought to represent a magmatic response to the Indosinian Orogeny (Wang et al., 2007, 2016a,b). Late Mesozoic magmatism is the most intensive and widespread in the Cathaysia Block, which formed the SE China volcanic-intrusive complex belt (Fig. 1B; Zhou et al., 2006). The associated Jurassic and Cretaceous granitoids appear to be oceanward younging trend and a northwestern younging trend to the Middle-Lower Yangtze River Valley metallogenic belt in SE China (Fig. 1B; Zhou et al., 2006; Li et al., 2014). The volcanic rocks were mainly formed during Cretaceous and crop out along the coastal area (Fig. 1B). Previous studies suggest that the extensive magmatism during the late Mesozoic was induced by the subduction of the paleo-Pacific plate (Zhou et al., 2006; Li and Li, 2007; Jiang et al., 2015).

Mesozoic large-scale magmatism and associated mineralization in the South China Block is peaked at late Triassic (230–210 Ma), mid-late Jurassic (170–150 Ma), and early-mid Cretaceous (120–80 Ma) (Mao et al., 2008, 2013; Wang et al., 2011). The 230–210 Ma age range is characterized by greisens, skarn, and vein type W-Sn-Nb-Ta mineralization and ore-related peraluminous granites (Mao et al., 2008, 2013). Mineralization of the mid-late Jurassic (170–150 Ma) period is mostly of porphyry and skarn type Cu-Au, and granite-related W-Sn deposits. The 120–80 Ma event consists of epithermal Au-Ag-Cu, hydrothermal vein-type Ag-Pb-Zn, and granite-related polymetallic W-Sn mineralization (Wang et al., 2011; Mao et al., 2013; Zhong et al., 2017).

The Zhaiping Ag-Pb-Zn deposit is located in the northeastern region of the Fujian Province in the Cathaysia Block (Fig. 1B). The regional basement includes the Neoproterozoic Longbeixi Formation metamorphic rocks, which are covered by the Cretaceous volcanic rocks (Fig. 1C). The Longbeixi Formation mainly consists of feldspar-quartz schist, quartz-mica schist, diopside marble, gneiss, and amphibolites (Zhang et al., 2013). Over 80% area of the Shouning-Nanyang region is covered by the Cretaceous clastic sediments and volcanic rocks, from the bottom to the top namely the Nanyuan Formation (K₁n), the Xiaoxi Formation (K_1x) sandstone and tuff, the Huangkeng Formation (K_2h) and the Zhaixia Formation (K₂z) siltstone and rhyolite, the Taishun formation (K2ts) siltstone and tuff. Among them, the Nanyuan Formation is the most widely distributed strata in the region, and mainly consists of rhyolitic- or dacitic-tuff lava, rhyolite, welded tuff, tuffaceous sandstone, and sandy mudstone units with trace amounts of siliceous rocks, andesites, and dacites (Huang et al., 1998; Li et al., 2018a). In addition, most of the Ag-Pb-Zn deposits (e.g., Tanshan, Zhaiping, Daan, Tianchi, Yingshan) in the region are hosted in the Nanyuan Formation volcanic rocks (Fig. 1C).

The Neoproterozoic basement and Cretaceous strata have been intruded by several phases of granitic rocks including porphyritic granite, granite porphyry, monzogranite, quartz diorite and rhyolite porphyry, and some intermediate-mafic dikes. Structurally, the regional tectonic framework is dominated by NE, NW, and nearly NS trending faults. Intensive magmatism and hydrothermal mineralization in the region were controlled by the NE and NW trending faults.

3. Deposit geology

The Zhaiping Ag-Pb-Zn deposit (27°32′00″ to 27°32′45″N, 119°34′30″ to 119°36′00″E), about 20 km northeast of the Shouning County, Fujian Province, was first discovered in the early 2000s. To the end of the 2017, the deposit had proven reserves of 204 t Ag at an average grade of 221.8 g/t. The strata exposed in the ore district mainly belong to the early Cretaceous Nanyuan Formation, comprised by dacitic- to rhyolitic- crystal tuff with minor amount of silicic volcaniclastic rocks. The early Cretaceous volcanic strata have been intruded by several phases of granitic rocks including granite porphyry (Fig. 3A) and quartz porphyry (Fig. 2A). Granite porphyry is the main igneous rock, accounting for over 25% of the surface outcrop across the mining area. The fresh granite porphyry displays a typical porphyritic texture and contains 30–50% phenocrysts that are mainly quartz (20–25%), K-feldspar (10–15%), plagioclase (5–10%) and biotite (3–5%). Its



Fig. 1. (A) Tectonic scheme of the eastern China. (B) Schematic map of SE China showing the distribution of the Mesozoic granitic and volcanic rocks (modified after Zhou et al., 2006). (C) Geological map of the Shouning-Nanyang region showing the location of the Ag-Pb-Zn deposits (modified after Zhong, 2017). I-Jiang-shan–Shaoxing fault; II-Pingxiang–Yushan fault; III-Zhenghe–Dapu fault; IV-Changle–Nan'ao fault; V-Yunxiao–Shanghang fault.

groundmass consists mainly of quartz, K-feldspar, and plagioclase. The accessory minerals of the granite porphyry are dominated by apatite, zircon, and magnetite. The zircon U-Pb age is 127.7 ± 0.9 Ma (Our unpublished data). Quartz porphyry occurs both at the surface and various underground levels. These rocks consist of quartz (45–50%), K-feldspar (35–40%), plagioclase (10–15%), and minor biotite with a

zircon U-Pb age of 129.2 \pm 0.9 Ma (Our unpublished data).

In the mining area, the Ag-Pb-Zn orebodies are largely restricted to the alteration zones developed along the NE (F1, F2) and NW trending faults (F4, F5, F6), and less importantly the W-E trending F7 fault (Fig. 2A). The F1 fault is located in the boundary between the Nanyuan Formation and granite porphyry (Fig. 2A). The F1 fault is over 1500 m



Fig. 2. Geologic map (A) and representative cross section (B) of the Zhaiping deposit, showing distribution and morphology of the Ag-Pb-Zn veins (modified after Zhong, 2017).

long and 2–11 m wide, striking from 280 to 310° and dipping 50–75° to NE. The F5 fault strikes 40–75°, dips 53–72° towards the NE, and continues approximately 1600 m. These extensional normal faults are argued to be the subsidiary faults to the regional Shouning-Lianjiang fault system, and they have been active since the late Jurassic (Zhong, 2017). Commonly, open faults and fractures are the most favorable structures for the deposition of Ag-Pb-Zn ores.

The deposit consists of seven orebodies, and the mineralization features can be best represented by the No. I-1, No. II-2, and No. III-1 orebodies which comprise over 80% of the proven reserves at the Zhaiping deposit. The No. I-1 orebody strikes 290–310° and dips $60-65^{\circ}$ to NE, and it is over 200 m long, 0.89-1.18 m thick. This orebody is

structurally controlled by the F1 fault, and it contains 46.3–129.8 g/t Ag. The No. II-2 orebody is controlled by the NW-trending F4 fault and its subsidiary faults. It is more than 200 m long, with thickness of 1.47–2.62 m. The Ag grade varies from 97.91 to 332.5 g/t. The No. III-1 orebody is controlled by the fracture zone of the F5 fault. It is > 90 m long, with strike 45° and dips 66–75° towards NE, and ranges in thickness from 0.91 to 6.05 m. This orebody contains 40.8–392.5 g/t Ag (locally > 600 g/t).

The Ag-Pb-Zn mineralization at Zhaiping, including quartz veins, veinlets, and disseminations, is hosted in the early Cretaceous Nanyuan Formation of altered volcanic rocks, as well as the early Cretaceous granitic subvolcanic rocks (i.e. granite porphyry and quartz porphyry)



Fig. 3. Representative photographs of hydrothermal alteration and mineralization features in the Zhiping Ag-Pb-Zn deposit. (A) Contact relationship between granite porphyry and rhyolitic crystal tuff of Nanyuan fromation; (B) Mineralized quartz-Ag-base metal veins hosted by silicified rhyolitic crystal tuff; (C) Massive Ag-base metal ores. (D) Pre-ore stage ore barren quartz vein associated with quartz-sericite alteration assemblage. (E) and (F) Quartz-pyrite assemblage in the pre-ore stage. (G) Syn-ore stage quartz-Ag-base metal veins associated with pyrite-sericite-quartz assemblage in altered granite porphyry. (H) Syn-ore quartz-base metal vein crosscut the quartz-pyrite vein accompanied by pyrite-sericite-quartz alteration. (I) Silver-bearing breccia composed of fragments of pre-ore stage quartz that are cemented by syn-ore stage quartz and base metal sulfides. (J) Syn-ore quartz-Ag-base metal veins crosscut by post-ore quartz-calcite veinlets within the pyrite-sericite-quartz alteration, with post-ore quartz-calcite-fluorite veins in the quartz porphyry. (L) Post-ore stage quartz-calcite-fluorite assemblage. *Abbreviations*: Qz-quartz; Ser-sericite; Py-pyrite; Cal-calcite; Fl-fluorite; Chl-Chlorite, Ep-epidote.

(Fig. 3). Some shallow mineralized veins are oxidized at outcrop, providing a valuable guide for underground exploration (Fig. 3B). Sulfide minerals in the mineralized Ag-Pb-Zn veins are dominated by pyrite, sphalerite, and galena, with minor amounts of chalcopyrite, tetrahedrite, arsenopyrite, and pyrrhotite (Figs. 3F–J; 4A–F). Galena is the main silver-bearing mineral, but minor argentite is also present (Fig. 4F). Gangue minerals are quartz, sericite, chlorite, epidote, fluorite, and calcite.

Hydrothermal alteration is widespread in the Zhaiping deposit, with the most intensive alteration occurring in and around the mineralized Ag-Pb-Zn veins. The key components of alteration assemblages are quartz, sericite, chlorite, and calcite, with minor fluorite and epidote. Distinct episodes of hydrothermal alteration are recognized: an early episode of silicification, two intermediate episodes (phyllic and propylitic), and a late carbonatization. Silicification is the most widespread alteration type in the deposit, as fine quartz aggregates within silicified wall rocks (Fig. 3B). Silicification predates the main Ag-base metal sulfide mineralization, and coexists with minor early-precipitated pyrite (Fig. 3E–F). Early alteration was overprinted by phyllic alteration, which consists of quartz, sericite and subordinate pyrite (Figs. 3D–G, 4G). This type of alteration appears closely related to silver and base metal sulfides deposition (Fig. 3G–H, J). Phyllic alteration was followed by propylitic alteration, characterized by an assemblage of chlorite, epidote, and minor quartz. Chlorite occurs either in quartzcalcite veins (Fig. 4H), or as replacement of biotite in granite porphyry and quartz porphyry. The final stage of hydrothermal alteration is carbonatization, which overprinted all previous alteration types and usually coexists with fluorite along fractures (Fig. 3J–L). Carbonatization postdates formation of the silver minerals and base metal sulfides. In addition, there is no apparent spatial zonation of various hydrothermal alteration types, in most cases, alteration assemblages are superimposed upon one another.

Three hydrothermal stages can be recognized in the Zhaiping deposit based on field and petrographic relations (Fig. 5). Pre-ore stage (quartz-pyrite) is represented by milky and massive quartz accompanied with minor amounts of coarse-grained, euhedral to subhedral



Fig. 4. Reflected- (A-F) and transmitted-light (G, H) photomicrographs showing the typical morphology and textures of ore and gangue minerals in the Zhaiping deposit. (A) Pre-ore stage quartz-pyrite vein crosscut the altered dacitic crystal tuff of the Nanyuan Formation; (B) Coarse-grained pyrite grain with pyritohedral-like crystal distributed in the pre-ore stage pyrite-quartz-sericite alteration rock; (C) Syn-ore stage quartz-pyrite-sphalerite vein; (D) Syn-ore stage pyrite replaced by sphalerite (with some inclusions of chalcopyrite and tetrahedrite), and the pyrite grain showing distinct zoning structure, which has a core full of silicate inclusions, and a rim free of mineral inclusions; (E) Pyrite replaced by galena and sphalerite; (F) Early precipitated pyrite crystals were replaced by argentite; (G) Sericite aggregates intergrowth with pyrite; (H) Chlorite alteration. *Abbreviations*: Qz-quartz; Py-pyrite; Ser-sericite; Sp-sphalerite; Ttr-tetrahedrite; Cpy-chalcopyrite; Arg-argentite; Chl-chlorite.

pyrite (Figs. 3D–F; 4A, B). Syn-ore stage is marked by a quartz-Ag-base metal sulfides assemblage consisting of pyrite, galena, sphalerite and argentite (Figs. 3G–J; 4C–E). Calcite, chlorite and lesser amounts of fluorite characterize the post-ore stage (Fig. 3K–L). Syn-ore stage is the most important in terms of silver and base-metal sulfides deposition.

4. Sampling and analytical methods

4.1. Fluid inclusion measurements

Petrographic study (at 25 °C) of doubly polished thin sections (about 200 μm thick) was done on samples from different mineralization stages

Stage Mineral	Pre-ore stage	Syn-ore stage	Post-ore stage
Pyrite			
Sphalerite			
Galena			
Chalcopyrite			
Tetrahedrite			
Arsenopyrite		•••••	
Pyrrhotite		•••••	
Argentite			
Silver			
Quartz			
Sericite			
Fluorite			
Chlorite			
Epidote		•••••	
Calcite			

abundant — common minor

Fig. 5. Paragenetic assemblages of gangue and ore minerals in the Zhaiping Ag-Pb-Zn deposit. Line thickness represents relative amount of the minerals.

using the fluid inclusion assemblage (FIA) approach (Goldstein and Reynolds, 1994). A single FIA represent groups of temporally coeval inclusions present in clusters, in trails, or along the growth zone. We then selected FIAs showing the least evidence of necking-down or shape modifications for further microthermometric measurements and laser Raman spectroscopic analysis. Infrared (IR) microscopy was used to identify fluid inclusions in pyrite, but since Zhaiping pyrite contains Co, Ni, and As, only minor of the pyrite grains remained transmit under IR.

Microthermometric measurements were carried out using a Linkham THMS-600 heating-freezing stage (from -196 to 600 °C) which is attached to a Leica DM2700P microscope connected to a television camera and screen housed at the China University of Geosciences (Wuhan). The stages were calibrated using synthetic fluid inclusions at -56.6, 0.0, and 374.1 °C. The heating/freezing rate is generally 0.2-5.0 °C/min, but was reduced to < 0.2 °C/min near the phase transformation. The uncertainties for the measurements are \pm 0.5, \pm 0.2, and \pm 2.0 °C for runs in the range from -120 to -70 °C, from -70 to 100 °C, and from 100 to 600 °C, respectively. Ice melting temperatures were observed at a heating rate of less than 0.1 °C/min, and homogenization temperatures at a rate of ≤ 1 °C/min.

The measurements consisted of (1) final ice melting temperature ($T_{m,ice}$), (2) melting temperature of the carbonic phase ($T_{m,CO2}$), (3) melting temperature of the clathrate ($T_{m,clath}$), (4) homogenization temperature of the carbonic phase to the liquid ($T_{h,CO2}$), and (5) total homogenization temperatures of fluid phases ($T_{h,tot}$). Salinities were calculated using the equations of Bodnar (1993) for aqueous (NaCl-H₂O) inclusions, and of Collins (1979) for CO₂-bearing inclusions.

Compositions of fluid inclusions were identified using a Renishaw RM1000 laser Raman spectroscopic instrument housed at the State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences (Wuhan). The laser source was an argon laser with wave length of 514.5 nm and a source power of 5 mW. The area of the charge-coupled device (CCD) detector is $20 \,\mu m^2$. The spectra were recorded with counting time of 30 s, and ranged from 1200 to $3800 \,\mathrm{cm^{-1}}$. Spectrograph aperture was chosen as $25 \,\mu m$. Instrumental settings were kept constant during all analyses.

4.2. Stable isotope analyses

4.2.1. In-situ sulfur isotope analysis

Seven representative samples were chosen from three mineralization stages at Zhaiping Ag-Pb-Zn deposit for in-situ sulfur isotope analysis. The analysis was carried out in situ on sulfide grains from standard polished sections using Nu Plasma II MC-ICP-MS, which was equipped with the Resonetics-S155 excimer ArF laser ablation system housed at the State Key Laboratory of Geological Processes and Mineral Resources of China University of Geosciences (Wuhan). During the experiment, the diameter of laser beam was set to 33 µm with a laser repetition rate of 8 Hz, and the ablation process was set to last for 40 s. The national pyrite standard WS-1 and the international sphalerite standard NBS-123 were used in this study. Standard-sample bracketing (SSB) was used to determine the δ^{34} S values of samples throughout the MC-ICP-MS analytical sessions. The true sulfur isotope ratio was calculated by correction for instrumental mass bias by linear interpolation between the biases calculated from two neighboring standard analyses. The analytical precision (1 σ) was about \pm 0.1 per mil. Detailed analytical conditions and procedures can be seen in Zhu et al. (2016, 2017).

4.2.2. Hydrogen and oxygen isotope analysis

Hydrogen isotopic analyses were conducted on fluid inclusions hosted in quartz and oxygen isotopic analyses were conducted on grains of quartz. The analyses were conducted using a Finnigan MAT253 mass spectrometer at the Stable Isotope Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences in Beijing. Oxygen was liberated from quartz by reaction with BrF₅ (Clayton and Mayeda, 1963) and converted to CO₂ on a platinum-coated carbon rod. Water extracted from the fluid inclusions in quartz was reacted with zinc at 410 °C and the released H₂ for mass spectrometer measurement (Friedman, 1953). The analytical precision is better than 2‰ for δ D and 0.2‰ for δ ¹⁸O. The isotope data are reported in standard δ notion (‰) relative to the Vienna Standard Mean Water (V-SMOW) for oxygen and hydrogen.

4.2.3. Carbon and oxygen isotope analysis

Calcites collected from post-ore stage quartz-calcite-fluorite veins/ veinlets were crushed to ~ 200 mesh powders for carbon and oxygen isotope analysis. The CO₂ was extracted from calcite with pure phosphoric acid (H₃PO₄) at 50 °C. Evolved CO₂ was then purified and its C and O isotope compositions were measured by Finnigan MAT 251 isotope ratio mass spectrometer housed at the State Key Laboratory of Geological Processes and Mineral Resources of China University of Geosciences (Wuhan). Precision is better than 0.1‰ for δ^{13} C and δ^{18} O. Isotopic compositions are reported to the Vienna Pee Dee Belemnite standard (V-PDB), as express δ^{18} O_{V-SMOW} = 1.03086 × δ^{18} O_{V-PDB} + 30.86 (Friedman and O'Neil, 1977).

5. Results

5.1. Fluid inclusion data

5.1.1. Petrography and types of fluid inclusions

Based on texture, paragenesis, and phase proportions at room temperature, four distinct fluid inclusion types were recognized in the studied quartz, sphalerite, fluorite, and pyrite samples from Zhaiping, as follows:

- (1) Liquid-rich (L_0 -type) inclusions are the most abundant type in different paragenetic stages. Their sizes ranges from 5 to 25 µm with a negative-crystal, rounded, rectangular and irregular shape (Fig. 6A–D). They contain a vapor phase occupying 10–30 vol% of the inclusion volume, and have no daughter minerals. L_0 -type inclusions account for approximately 80% of the total population, and their hosts are quartz (Fig. 6A), sphalerite (Fig. 6B), pyrite (Fig. 6C), fluorite (Fig. 6D), and calcite. Commonly, L_0 -type inclusions are distributed along growth zone (Fig. 6I), randomly distributed as clusters within single mineral crystals (Fig. 6J–L), and within the healed fractures but not cross-cut grain boundaries (Fig. 6M).
- (2) Vapor-rich (V-type) fluid inclusions are identified in the syn-ore



Fig. 6. Sketch and photomicrographs showing types and distribution of fluid inclusions in various minerals at Zhaiping. (A) Liquid-rich (L₀-type) fluid inclusion with negative-crystal in the syn-ore stage quartz. L₀-type inclusions in the syn-ore stage sphalerite (B), pyrite (C, under infrared microscopy), and fluorite (D). (E) Coexisting vapor- and liquid-rich fluid inclusions in the syn-ore stage quartz. (F) Liquidrich, solid-bearing fluid inclusion with transparent daughter mineral in syn-ore stage sphalerite. (G) CO2-bearing fluid inclusion in the syn-ore stage quartz. (H) CO₂-bearing inclusion coexists with liquid-rich fluid inclusion in the syn-ore stage quartz. (I) Abundant liquid-rich (L₀-type) inclusions in growth zone of syn-ore stage quartz. (J) Vapor- and liquidrich fluid inclusions coexist as clusters in the core of the syn-ore stage quartz. (K) Primary V- and Lo-type fluid inclusions hosted in a quartz crystal as clusters. (L) Liquid-rich fluid inclusions distributed as clusters in the postore stage fluorite. (M) Pseudosecondary liquidrich fluid inclusion assemblage distributed within the healed fractures of the quartz crystal. (N) Liquid-rich, solid-bearing fluid inclusions with transparent and/or opaque daughter minerals from syn-ore stage sphalerite. Abbreviations: Qz-quartz; Sp- sphalerite; Py-pyrite; Cal-calcite; Fl-fluorite.

stage quartz crystals, and have 50–80 vol% vapor bubbles. They are generally negative-crystal or oval and 5–20 μm in diameter. In many cases, fluid inclusion assemblages consists of liquid-rich, two-

phase (L_0 -type) fluid inclusions coexist with vapor-rich (V-type) fluid inclusions (Fig. 6E, J, K).

(3) Liquid-rich, solid-bearing (Ls-type) inclusions consists of vapor,

able 2
ummary of microthermometric data of the fluid inclusions assemblages (FIAs) in the Zhaiping Ag-Pb-Zn deposit.

 Group	Assemblage	Stage	Mineral	FIs type	n	$T_{m,CO2}$ (°C)	$T_{m,ice}$ (°C)	$T_{m,clath}$ (°C)	$T_{h,CO2}$ (°C)	$T_{h,tot}$ (°C)	S.D.	Salinity (wt.% NaCl equivlant)	S.D.
 G01	I-LA1	Pre-ore	Quartz	L ₀	4		-6.2			365	8	9.5	2.1
G02	I-LA2	Pre-ore	Quartz	L ₀	5		-5.8			351	6	8.9	1.5
G03	I-LA3	Pre-ore	Quartz	L ₀	7		-6.0			347	12	9.2	3.0
G04	I-LA4	Pre-ore	Quartz	L ₀	3		-6.7			346	8	10.1	0.9
G05	I-LA5	Pre-ore	Quartz	L ₀	5		-6.4			343	9	9.7	3.0
G06	I-LA6	Pre-ore	Quartz	L ₀	4		-6.4			343	7	9.7	0.5
G07	I-LA7	Pre-ore	Quartz	L ₀	3		-5.1			341	8	8.0	0.9
G08	I-LA8	Pre-ore	Quartz	L ₀	5		-6.1			336	9	9.3	0.8
G09	I-LA9	Pre-ore	Quartz	L ₀	4		-6.2			334	10	9.5	0.9
G10	I-LA10	Pre-ore	Quartz	Lo	5		-6.5			327	8	9.8	2.7
G11	I-LA11	Pre-ore	Quartz	Lo	4		-5.6			327	7	8.7	1.8
G12	I-LA12	Pre-ore	Quartz	Lo	4		-4.6			321	7	7.3	1.2
G13	I-LA13	Pre-ore	Quartz	Lo	4		-5.3			319	7	8.3	1.2
G14	II-LA1	Syn-ore	Quartz	Lo	5		-5.8			317	4	8.9	1.8
G15	II-LA2	Syn-ore	Quartz	Lo	5		-5.5			315	6	8.5	3.4
G16	II-LA3	Syn-ore	Quartz	Lo	3		-7.3			306	7	10.8	0.7
G17	II-LA4	Syn-ore	Quartz	L	3		-6.5			303	6	9.9	1.2
G18	II-LA5	Svn-ore	Ouartz	Lo	2		-4.4			300	3	7.0	0.2
G19	II-LA6	Svn-ore	Ouartz	Lo	2		-4.8			288	4	7.6	0.7
G20	II-LA7	Syn-ore	Quartz	L	3		-4.3			285	6	6.9	0.2
G21	II-LA8	Svn-ore	Ouartz	Lo	4		-5.2			282	7	8.1	0.7
G22	II-LA9	Svn-ore	Ouartz	Lo	3		-3.9			278	5	6.3	1.6
G23	II-LA10	Syn-ore	Quartz	Lo	4		-6.0			277	5	9.2	1.1
G24	II-LA11	Syn-ore	Quartz	Lo	6		-62			271	5	95	1.6
G25	II-LA12	Syn-ore	Quartz	Lo	4		-59			269	3	9.1	1.0
G26	II-I A13	Syn-ore	Quartz	L ₀	4		-4.0			262	5	65	1.4
G27		Syn-ore	Quartz	ц.	3		-61			265	5	0.0	3.4
G28	II-LA15	Syn-ore	Quartz	L ₀	4		-5.0			261	6	7.9	13
G20	II-LA16	Syn-ore	Quartz	т0 т	5		-47			260	4	7.5	1.5
G29 G20	II-LAIT	Syn-ore	Quartz	ц 1	2		- 4.7			200		10.0	1.4
C21	II-LA17	Syn-ore	Quartz	ц т	4		-0.0			259	3	7.0	2.0
C22	II-LAIO	Syn-ore	Quartz	L ₀ т	4		- 3.0			256	2	10.1	2.0
632	II-LAI9	Syn-ore	Quartz	L0 т	5		-0.7			230	3	10.1	2.1
C24	II-LA20	Syn-ore	Quartz	L0 т	3		-4.1			255	27	0.0	2.7
G34 C25	II-LA21	Syn-ore	Quartz	L ₀ т	4		- 3.0			233	-	8.7	2.7
635	II-LA22	Syn-ore	Quartz	L ₀	4		-6.1			251	3	9.4	1./
G36	II-LA23	Syn-ore	Quartz	L ₀	4		-5.3			247	4	8.3	1.2
G37	II-LA24	Syn-ore	Quartz	L ₀	3		-6.1			244	1	9.4	2.2
G38	II-LA25	Syn-ore	Quartz	L ₀	3		-5.9			242	1	9.1	0.0
G39	II-LA26	Syn-ore	Quartz	L ₀	4		-6.0			240	4	9.2	0.7
G40	II-LA27	Syn-ore	Quartz	L ₀	6		-5.8			240	4	8.9	0.5
G41	II-LA28	Syn-ore	Quartz	L ₀	4		-5.5			236	4	8.5	3.4
G42	II-LA29	Syn-ore	Quartz	L ₀	3		-4.5			230	4	7.2	0.0
G43	II-LA30	Syn-ore	Fluorite	L ₀	4		-4.4			268	5	7.0	0.8
G44	II-LA31	Syn-ore	Fluorite	L ₀	5		-5.0			255	6	7.9	0.7
G45	II-LA32	Syn-ore	Sphalerite	L ₀	4		-5.8			267	6	8.9	0.9
G46	II-LA33	Syn-ore	Sphalerite	L ₀	4		-5.2			234	2	8.1	1.1
G47	II-LV1	Syn-ore	Quartz	L ₀ , V	4		-3.6			248	6	5.9	0.4
G48	II-LV2	Syn-ore	Quartz	L ₀ , V	5		-2.9			244	8	4.8	0.5
G49	II-LV3	Syn-ore	Quartz	L ₀ , V	5		-3.1			240	6	5.1	2.5
G50	II-LV4	Syn-ore	Quartz	L _{0,} V	6		-3.8			239	6	6.1	3.7
G51	II-LV5	Syn-ore	Quartz	L _{0,} V	4		-2.6			235	9	4.3	0.7
G52	II-LV6	Syn-ore	Quartz	L _{0,} V	3		-2.3			233	8	3.9	1.1
G53	II-LV7	Syn-ore	Quartz	L _{0,} V	3		-2.6			229	8	4.3	0.5
G54	II-LV8	Syn-ore	Quartz	L _{0,} V	4		-2.8			225	4	4.7	0.9
G55	II-LV9	Syn-ore	Quartz	L _{0,} V	7		-3.5			223	5	5.7	2.9
G56	II-LS1	Syn-ore	Sphalerite	L _{0,} L _S	3		-4.9			247	5	7.7	0.4
G57	II-LS2	Syn-ore	Sphalerite	L _{0,} L _S	4		-4.7			239	4	7.4	1.2
G58	II-LS3	Syn-ore	Sphalerite	L _{0,} L _S	5		-4.3			224	5	6.9	1.2
G59	II-LS4	Syn-ore	Sphalerite	L ₀ , L _S	3		-5.4			222	6	8.4	1.0
G60	II-C1	Syn-ore	Quartz	C	2	-56.8		6.7	30.1	248	6	6.2	0.4
G61	II-C2	Syn-ore	Quartz	С	2	-57.1		7.0	29.8	244	3	5.7	0.5
G62	II-C3	Syn-ore	Quartz	С	3	-56.9		7.3	28.6	242	6	5.1	0.4
G63	II-C4	Syn-ore	Quartz	С	3	-56.8		7.4	29.3	236	9	5.0	0.8
G64	III-LA1	Post-ore	Calcite	Lo	3		-4.5			233	4	7.1	0.2
G65	III-LA2	Post-ore	Calcite	Lo	3		-3.2			215	3	5.3	0.5
G66	III-LA3	Post-ore	Calcite	L	4		-2.9			206	2	4.9	0.8
G67	III-LA4	Post-ore	Calcite	L	3		-2.4			197	5	4.0	0.3
G68	III-LA5	Post-ore	Calcite	L	5		-2.2			192	3	3.7	0.7
G69	III-LA6	Post-ore	Calcite	L	3		-1.9			190	2	3.2	0.4
G70	III-LA7	Post-ore	Calcite	L	3		-1.2			181	2	2.0	0.4
G71	III-LA8	Post-ore	Calcite	Lo	3		-1.0			172	4	1.7	0.3
G72	III-LA9	Post-ore	Fluorite	Lo	3		-3.2			219	3	5.3	0.5
G73	III-LA10	Post-ore	Fluorite	Lo	2		-2.4			214	7	4.0	0.3
G74	III-LA11	Post-ore	Fluorite	L	3		-3.8			212	8	6.2	0.7
				-									

(continued on next page)

Table 2 (continued)

Group	Assemblage	Stage	Mineral	FIs type	n	T _{m,CO2} (°C)	T _{m,ice} (°C)	T _{m,clath} (°C)	T _{h,CO2} (°C)	$T_{h,tot}$ (°C)	S.D.	Salinity (wt.% NaCl equivlant)	S.D.
G75 G76	III-LA12 III-LA13	Post-ore Post-ore	Fluorite Fluorite	L ₀ L ₀	5 5		-2.6 -2.4			190 189	5 7	4.3 4.1	0.5 1.0

Notes: Data are reported as averages of fluid inclusions assemblages; n = the number of available analyses inclusions of each FIA; S.D. = 1 standard deviation. Fluid inclusion type: $L_0 =$ liquid-rich inclusions; V = vapor-rich inclusions; $L_s =$ liquid-rich, solid-bearing inclusions; $C = CO_2$ -bearing inclusions.

 $T_{m,CO2}$ = melting temperature of the carbonic phase; $T_{m,ice}$ = temperature of final ice melting; $T_{m,clath}$ = melting temperature of the clathrate; $T_{h,CO2}$ = homogenization temperature of the carbonic phase to the liquid; $T_{h,tot}$ = temperature of total homogenization.

liquid, and solid phase, are generally distributed in the syn-ore stage sphalerite (Fig. 6F). Vapor bubbles typically occupy 15–30 vol % of the inclusions' volume, and inclusions vary from 5 to 15 μ m in size. Daughter minerals in L_s-type inclusions are mainly transparent (calcite), and less commonly opaque (Fig. 6N).

(4) CO_2 -bearing (C-type) inclusions are three phase ($V_{CO2} + L_{CO2} + L_{H2O}$), and occurring only in the syn-ore stage quartz (Fig. 6G, H). Carbonic phase accounts for 15–40 vol% of the total volume. They are oval and irregular in shape with size ranging from 5 to 12 μ m. This type of fluid inclusions is very rare, and accounts only for 3% of the total population.

5.1.2. Results of microthermometry

The microthermometric data are reported as averages of assemblages with 1 σ and are summarized in Table 2 and graphically illustrated in Fig. 7. During the heating stage, all L₀-type inclusions homogenize to the liquid phase, and most of the V-type inclusions homogenize to vapor phase. The daughter minerals (transparent and opaque) of the L_s-type inclusions do not disappear during heating, and, therefore, the homogenization temperatures of this type inclusions refer only to liquid and vapor phases. And the L_s-type inclusions homogenize to liquid phase as revealed by the disappearance of vapor bubbles.

- (1) Pre-ore stage quartz: A total of 13 L_0 -type FIAs were measured in four quartz samples from the pre-ore stage quartz-pyrite veins. All the L_0 -type fluid inclusions assemblages have homogenization temperatures ranging from 365 to 319 °C (average 339 °C, n = 57), final ice melting temperatures ranging from -6.7 to -4.6 °C, and calculated salinities from 7.3 to 10.1 wt% NaCl equivalent.
- (2) Syn-ore stage quartz, fluorite, and sphalerite: Fifty FIAs from synore stage quartz-base metal sulfide veins were measured. Quartz, fluorite, and sphalerite of syn-ore stage are all dominated by L₀-type FIAs that have final ice melting temperatures from -7.3 to $-3.9\,^\circ\text{C},$ from -5.0 to $-4.4\,^\circ\text{C},$ and from -5.8 to $-5.2\,^\circ\text{C},$ respectively. Total homogenization temperatures of L₀-type FIAs in these three minerals are from 317 to 230 °C (quartz, average 266 °C, n = 111), from 268 to 255 °C (fluorite, average 261 °C, n = 9), and from 267 to 234 °C (sphalerite, average 251 °C, n = 8). The calculated salinities range from 6.3 to 10.8, from 7.0 to 7.9, and from 8.1 to 8.9 wt% NaCl equivalent, respectively. The V-type fluid inclusion assemblages in quartz homogenize to vapor at temperatures of 248–223 °C (average 235 °C, n = 41). The final melting temperatures of ice are between -3.8 and -2.3, corresponding to salinities of 3.9-6.1 wt% NaCl equivalent. In the same FIAs, the coexisting Lo-, and V-type inclusions commonly yielded similar homogenization temperatures, and the Lo-type inclusions have the salinities slightly higher than the V-type inclusions, indicative of fluid boiling in syn-ore stage quartz. The Ls-type fluid inclusion assemblages yielded homogenization temperatures of 247-222 °C (average 232 °C, n = 15), and final ice-melting temperatures of -4.3 to -5.4 °C, and corresponding to calculated salinities of 6.9-8.4 wt% NaCl equivalent. The C-type fluid inclusion assemblages yield melting temperatures of carbonic phase ranging from -57.1 to -56.8 °C, suggesting that the carbonic phase in these inclusions is nearly pure CO₂. Clathrate melting temperatures show a range from

6.7 to 7.4 °C, corresponding to salinities of 5.0-6.2 wt% NaCl equivalent. The total homogenization temperatures of these inclusions are between 248 and 236 °C.

(3) Post-ore stage calcite and fluorite: Calcite and fluorite from post-ore stage contain abundant L₀-type FIAs. Final ice melting temperatures of L₀-type FIAs in quartz and fluorite are from -4.5 to -1.0 °C, and from -3.8 to -2.4 °C; the homogenization temperatures are from 233 to 172 °C (average 198 °C, n = 27), and from 219 to 189 °C (average 201 °C, n = 18), respectively. Calculated salinities range from 1.7 to 7.1 wt% NaCl equivalent for L₀-type inclusions in calcite and from 4.1 to 6.2 wt% NaCl equivalent for those in fluorite.

5.1.3. Results of Raman spectroscopy

Representative fluid inclusions from the Zhaiping deposit were studied using laser Raman spectroscopy to determine their gas compositions. The results suggest that the vapor phases of the L_0 -type inclusions in quartz, either coexisting with vapor-rich V-type inclusions or as individual assemblages, are dominated by H₂O, with trace amount of CO₂ (Fig. 8A). The vapor phases of C-type inclusions in the syn-ore stage quartz contain abundant CO₂ (Fig. 8B). Trace amount of CO₂ and N₂ are also found in the vapor phases of the L_s-type inclusions in the syn-ore stage sphalerite (Fig. 8C), and the transparent daughter mineral is calcite as revealed by Raman spectroscopy (Fig. 8D). In summary, the fluid inclusions can be described as the H₂O-NaCl \pm CO₂ \pm N₂ system.

5.2. Sulfur isotope data

A total of sixty-six in-situ LA-MC-ICP-MS sulfur isotopic compositions were determined from seven represent samples from different hydrothermal stages, and the results are shown in Table 3 and Fig. 9. Sulfide analysis includes pyrite, galena, sphalerite, pyrrhotite and tetrahedrite, and the majority of sulfides are selected from the syn-ore stage quartz-Ag-base metal sulfide veins, in which sulfides are most abundant.

Sulfide minerals from the Zhaiping deposit have a relatively uniform sulfur isotope compositions, which range from -1.9 to 6.2‰, with an average value of 2.7 \pm 1.2‰ (n = 66). In detail, sulfide minerals with different ore textures from different paragenetic sequences show essentially similar $\delta^{34}S_{V-CDT}$ values. The $\delta^{34}S_{V-CDT}$ values of pyrite from pre-ore to post-ore stage range from 0.5 to 4.5‰ (average 2.4‰, n = 12), from 1.1 to 6.2‰ (average 3.7‰, n = 19, excluding 2 relatively low values of -1.9 and -1.6‰), and from 1.5 to 3.0‰ (average 1.9‰, n = 5), respectively. Sphalerite (2.7–4.2‰, average 3.2‰, n = 13) in the syn-ore quartz-Ag-base metal sulfide veins has slightly higher $\delta^{34}S_{V-CDT}$ values compared to the galena (1.6–3.1‰, average 2.2‰, n = 10). Three analyses of pyrrhotite yield $\delta^{34}S_{V-CDT}$ values of 2.–3.0‰ (average 2.7‰). Two analyses of tetrahedrite yield $\delta^{34}S_{V-CDT}$ values of 1.0–1.2‰ (average 1.1‰).

5.3. Hydrogen and oxygen isotope data

Hydrogen and oxygen isotope data are listed in Table 4 and shown in Fig. 11. The measured δ^{18} O values of nine representative quartz samples from different mineralization stages range from 8.3 to 14.4‰.



Fig. 7. Histograms of homogenization temperatures and salinities of fluid inclusions from the different stages of the Zhaiping deposit.

The calculated $\delta^{18}O_{fluid}$ values from pre-ore to post-ore stages are from 5.7 to 8.8‰, from 0.7 to 3.7‰, and from -3.5 to -3.4‰, respectively. The δD values of fluid inclusions in hydrothermal quartz range from -90 to -69‰, with an average of -79‰.

calcite-H₂O fractionation equation of O'Neil et al. (1969).

5.4. Carbon and oxygen isotope data

Carbon and oxygen isotope data of calcite (n = 7) from the post-ore stage are listed in Table 5. Calcite has $\delta^{13}C_{V\text{-PDB}}$ values of -2.8 to -0.8%, $\delta^{18}O_{V\text{-PDB}}$ values of -25.9 to -23.8%, and calculated $\delta^{18}O_{V\text{-SMOW}}$ values of 4.2–6.4‰, and both vary in a limited range. Using a temperature of 198 °C (average temperature estimated from fluid inclusions assemblages in post-ore stage calcite), the calculated $\delta^{13}C_{\text{fluid}}$ values of post-ore stage range from -3.2 to -1.1%, when using the CO₂-calcite fractionation equation reported by Bottinga (1968). While the calculated $\delta^{18}O_{\text{fluid}}$ values range from -4.9 to -2.8%, using the

6. Discussion

6.1. Sources of the ore-forming fluids

The sulfur isotope compositions of sulfide minerals can provide valuable insights into source of sulfur in the ore-forming fluids and help to decipher the conditions of metal precipitation in hydrothermal ore deposits (Ohmoto and Rye, 1979; Rollinson, 1993). The δ^{34} S values of sulfide minerals from Ag-Pb-Zn veins at Zhaiping range from -1.9 to 6.2‰, but mostly between 1.0 and 4.5‰. The narrow range of sulfur isotope compositions is consistent with a magmatic origin of the ore-forming fluids (Seal, 2006), and suggesting relatively constant physicochemical conditions of the ore-forming fluids during ore precipitation. In-situ sulfur isotope analysis shows that most of the pyrite and



Fig. 8. Representative laser Raman spectra for fluid inclusions from the Zhaiping Ag-Pb-Zn deposit. (A) H_2O and CO_2 spectra of the vapor phase in L_0 -type inclusion. (B) CO_2 spectra of the vapor phase in C-type inclusion. (C) CO_2 and N_2 spectra of the vapor phase in L_s -type inclusion. (D) Calcite spectra of the solid phase in L_s -type inclusion.

sphalerite grains are enriched in ³⁴S compared to galena in the syn-ore stage Ag-Pb-Zn veins (Table 3; Fig. 9), indicating that sulfides were in equilibrium with ore-forming fluids. A few samples have more negative or positive values, most likely resulting from local variations of temperature, redox conditions (f_{O2}), and pH (Ohmoto, 1972). Collectively, sulfides from the Aucun, Dongyang, Dongji, Maluntou, Shangshangang,

Haoshi, Yinshan, Dalingkou and Wubu deposits hosted in the late Mesozoic volcanic rocks in the coastal area of South China have δ^{34} S values mostly in the range of -3 to 5‰ (Fig. 10). These values are consistent with the sulfides of the Ag-Pb-Zn veins in the Zhaiping deposit which yielded δ^{34} S values mostly between 1.0 and 4.5‰, and indicating a magmatic sulfur source (Ohmoto, 1972; Seal, 2006).

Table 3

Sulfur isotopic compositions (‰) of sulfides from the Zhaiping Ag-Pb-Zn deposit.

Stage	Analysis_ID	Minerals	$\delta^{34}S_{V\text{-}CDT}$	Stage	Analysis_ID	Minerals	$\delta^{34}S_{V\text{-}CDT}$
Pre-ore	16NFJ259-py1	Pyrite	1.0		16NFJ267-sp1	Sphalerite	2.8
	16NFJ259-py2	Pyrite	0.5		16NFJ267-sp2	Sphalerite	3.2
	16NFJ259-py3	Pyrite	1.4		16NFJ268-sp1	Sphalerite	3.6
	16NFJ259-py4	Pyrite	0.5		16NFJ268-sp2	Sphalerite	4.2
	16NFJ259-py5	Pyrite	1.1		16NFJ268-sp3	Sphalerite	3.6
	16NFJ296-py1	Pyrite	3.2		16NFJ268-sp4	Sphalerite	3.4
	16NFJ296-py2	Pyrite	3.4		16NFJ268-sp5	Sphalerite	3.8
	16NFJ296-py3	Pyrite	2.9		16NFJ283-sp1	Sphalerite	3.2
	16NFJ296-py4	Pyrite	3.1		16NFJ283-sp2	Sphalerite	2.9
	16NFJ296-py5	Pyrite	3.1		16NFJ283-sp3	Sphalerite	2.7
	16NFJ296-py6	Pyrite	4.4		16NFJ297-sp1	Sphalerite	2.9
	16NFJ296-py7	Pyrite	4.5		16NFJ297-sp2	Sphalerite	3.0
Syn-ore	16NFJ267-py1	Pyrite	3.3		16NFJ297-sp3	Sphalerite	2.7
	16NFJ267-py2	Pyrite	3.4		16NFJ267-gn1	Galena	1.6
	16NFJ267-py3	Pyrite	1.1		16NFJ267-gn2	Galena	2.6
	16NFJ267-py4	Pyrite	-1.9		16NFJ268-gn1	Galena	1.6
	16NFJ267-py5	Pyrite	-1.6		16NFJ268-gn2	Galena	2.0
	16NFJ268-py1	Pyrite	4.7		16NFJ268-gn3	Galena	2.4
	16NFJ268-py2	Pyrite	2.7		16NFJ268-gn4	Galena	1.9
	16NFJ268-py3	Pyrite	4.6		16NFJ268-gn5	Galena	2.1
	16NFJ268-py4	Pyrite	4.4		16NFJ297-gn1	Galena	2.1
	16NFJ268-py5	Pyrite	3.3		16NFJ297-gn2	Galena	3.1
	16NFJ283-py1	Pyrite	5.1		16NFJ283-gn1	Galena	2.2
	16NFJ283-py2	Pyrite	6.2		16NFJ297-po1	Pyrrhotite	2.9
	16NFJ283-py3	Pyrite	4.4		16NFJ297-po2	Pyrrhotite	2.3
	16NFJ283-py4	Pyrite	4.1		16NFJ297-po3	Pyrrhotite	3.0
	16NFJ283-py5	Pyrite	4.3		16NFJ267-tr1	Tetrahedrite	1.2
	16NFJ283-py6	Pyrite	3.4		16NFJ267-tr2	Tetrahedrite	1.0
	16NFJ297-py1	Pyrite	3.0	Post-ore	16NFJ292-py1	Pyrite	1.7
	16NFJ297-py2	Pyrite	3.9		16NFJ292-py2	Pyrite	1.5
	16NFJ297-py3	Pyrite	4.2		16NFJ292-py3	Pyrite	1.7
	16NFJ297-py4	Pyrite	4.1		16NFJ292-py4	Pyrite	1.7
	16NFJ297-py5	Pyrite	4.0		16NFJ292-py5	Pyrite	3.0



Fig. 9. Histogram of sulfur isotope compositions of sulfides from the Zhaiping Ag-Pb-Zn deposit.

Oxygen and hydrogen isotope compositions of hydrothermal quartz can constrain possible origin of the ore-forming fluids. The pre-ore quartz-pyrite veins from Zhaiping show relative high $\delta^{18}O_{\text{fluid}}$ (5.7-8.8%) values, consistent with those reported in other magmatichydrothermal deposits (e.g., Cooke et al., 2011), and illustrating a magmatic signature (Sheppard and Gustafson, 1976; Taylor and Sheppard, 1986). The samples from the quartz-Ag-base metal veins in the syn-ore stage show relative lower $\delta^{18}O_{\text{fluid}}$ (5.7–8.8‰) values (Fig. 11) than those from pre-ore stage quartz-pyrite veins, and plotted in the area between the primary magmatic water box and the meteoric water line but still dominated by magmatic water. The $\delta^{18}O_{fluid}$ (-3.5to -3.4%) compositions of fluids which formed the post-ore stage quartz-calcite veins are extremely depleted, and strongly indicating the involvement of meteoric water in the post-ore stage. This is also consistent with the measured low homogenization temperatures (181-232 °C) and salinities (1.7-7.1 wt% NaCl equivalent) of fluid inclusions assemblages in this stage. In the $\delta D - \delta^{18}O_{\text{fluid}}$ diagram (Fig. 11), all isotope data of quartz gradually decrease from early to late, implying that the ore-forming fluids in the Zhaiping deposit have a dominately magmatic origin and were diluted by meteoric waters during the post-ore quartz-calcite stage.

The Zhaiping Ag-Pb-Zn deposit contains a large amount of hydrothermal calcite in the post-ore hydrothermal stage, and no graphite has been observed in the deposit. In addition, laser Raman analysis identified calcite daughter minerals in primary fluid inclusions in syn-ore stage sphalerite, suggesting that the ore-forming fluids carried carbonate species. Few CO_2 and no CH_4 were found in fluid inclusions from all hydrothermal stages as revealed by laser Raman analysis. Therefore, the temperature-corrected calcite carbon isotopic compositions were very likely to reflect the bulk carbon isotopes of the ore-forming fluids, and may provide useful constraints to trace the source of carbon in the ore-forming fluids (Ohmoto and Rye, 1979; Branam and Ripley, 1990). The δ^{13} C values of post-ore stage calcite at Zhaiping range from -3.2 to -1.1%, which are higher than those of organic matter (-30 to -10%, Faure, 1986), but are consistent with or slightly higher than the carbon isotopes of magmatic systems (-9 to -3%, Taylor et al., 1967). It is suggesting that the studied calcites are genetically related to a magmatic-hydrothermal fluid. During fluid evolution and cooling, the variations of carbon and oxygen isotopic compositions are mostly probably affected by the involvement of meteoric water and water-rock reaction between fluids and wallrocks. This interpretation coincides with the H-O isotopes.

6.2. Fluid evolution and pressure estimation

Petrographic and microthermometric data of fluid inclusion assemblages illustrate that different types of fluids were present during different paragenetic stages of ore formation in the Zhaiping Ag-Pb-Zn deposit. The evolution of hydrothermal fluids in terms of salinity, temperature, as well as pressure is reconstructed on the basis of fluid inclusion study. These data are used to establish a model of fluid evolution in the Zhaiping deposit.

6.2.1. Fluid evolution

Fluid inclusions identified in the pre-ore stage quartz-pyrite veins in the Zhaiping deposit have intermediate salinities (7.3–10.1 wt% NaCl equivalent), intermediate-density, low CO_2 contents, and homogenization temperatures of 365–319 °C. The characteristics of ore-forming fluids in the pre-ore stage are similar to the intermediate-density fluids in some magmatic-hydrothermal systems (Redmond et al., 2004; Seo et al., 2012). And the intermediate-density fluids in these magmatichydrothermal systems (e.g., porphyry, skarn) are generally interpreted to be exsolved from the magma chamber at shallow levels in the crust (Meinert et al., 2003, 2005; Catchpole et al., 2015a,b).

All the primary fluid inclusions types recognized in the quartz-Agbase metal sulfide veins of the syn-ore stage including intermediate- to low-salinity, liquid-rich, solid-bearing, and vapor-rich fluid inclusions and rare CO₂-bearing inclusions. They have homogenization temperatures of 317-222 °C, with salinities ranging from 3.9 to 10.8 wt% NaCl equivalent. From the pre-ore to syn-ore stages, the homogenization temperatures of fluid inclusion assemblages show a decreasing trend, whereas the salinities are very similar, indicating a simple cooling process during the evolution of the ore-forming fluids (Fig. 12, Shepherd et al., 1985). Commonly, liquid-rich and vapor-rich fluid inclusion assemblages coexist in the same growth zone or healed fractures could be used as an indicator for fluid boiling during entrapment in hydrothermal ore deposits (e.g., Bodnar et al., 1985; Heinrich, 2007; Wang et al., 2013a,b; Xiong et al., 2014; Rajabpour et al., 2018). In the Zhaiping deposit, the identification of boiling assemblages in some quartz crystals from the syn-ore stage quartz-Ag-base metal sulfide

Table 4

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Sample no.	Mineral	Stage	Temperature (°C)	$\delta^{18}O_{V-SMOW}(\%)$	$\delta D_{\rm fluid}(\%)$	$\delta^{18}O_{fluid}$ (‰)
16NFJ-261	Quartz	Pre-ore	339	14.4	-69	8.8
16NFJ-264	Quartz	Pre-ore	339	11.3	-87	5.7
16NFJ-286	Quartz	Pre-ore	339	13.5	-83	7.9
16NFJ-260	Quartz	Syn-ore	256	9.1	-77	0.7
16NFJ-262	Quartz	Syn-ore	256	9.8	-80	1.4
16NFJ-263	Quartz	Syn-ore	256	12.1	-72	3.7
16NFJ-290	Quartz	Syn-ore	256	9.2	-72	0.8
16NFJ-292	Quartz	Post-ore	198	8.3	-80	-3.5
16NFJ-300	Quartz	Post-ore	198	8.4	-90	-3.4

Notes: $\delta^{18}O_{\text{fluid}}$ values are calculated based on the quartz-water equilibrium temperature formula provided by Clayton et al. (1972); Temperatures are based on microthermometric results of fluid inclusion assemblages hosted in quartz.

Table 5	
Carbon and oxygen isotopic compositions of calcite in the Zhaiping A	Ag-Pb-Zn deposit

Sample no.	Mineral	Stage	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)	$\delta^{13}C_{\rm fluid}$ (‰)	$\delta^{18}O_{fluid}$ (‰)
16NFJ-302	Calcite	Post-ore	-2.7	-23.8	6.4	-3.1	-2.8
16NFJ-303	Calcite	Post-ore	-2.8	-24.1	6.0	-3.1	-3.1
16NFJ-305	Calcite	Post-ore	-0.8	-23.8	6.4	-1.1	-2.8
16NFJ-311	Calcite	Post-ore	-0.9	-24.1	6.0	-1.2	-3.1
16NFJ-314	Calcite	Post-ore	-2.5	-25.8	4.3	-2.8	-4.9
16NFJ-316	Calcite	Post-ore	-1.8	-25.4	4.6	-2.2	-4.5
16NFJ-317	Calcite	Post-ore	-1.9	- 25.9	4.2	-2.2	-4.9

Notes: $\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{V.PDB} + 30.86$ (Friedman and O'Neil, 1977); $\delta^{13}C$ values of fluids in equilibrium with calcite were calculated using equations of Bottinga (1968), and $\delta^{18}O_{fluid}$ values were calculated using the fractionation factors between calcite and water (O'Neil et al., 1969).



Fig. 10. Sulfur isotope composition of sulfides from Zhaiping and other typical Au-Ag-Pb-Zn deposits related to late Mesozoic magmatism in the coast area of the South China. Data sources: [1] Li et al. (2018a); [2] Li et al. (2018b); [3] Liu (2016); [4] Xu et al. (1994); [5] Wang et al. (2013a,b); [6] Geng (2005).



Fig. 11. Plot of δD vs. $\delta^{18}O$, showing the calculated compositions for the oreforming fluids in the Zhaiping Ag-Pb-Zn deposit. Metamorphic water field, magmatic water field, and meteoric water line are from Taylor (1974). The field of the H-O isotope compositions for ore fluids for other typical Au-Ag-Pb-Zn deposits related to late Mesozoic magmatism in the coast area of the South China is from Zhong et al. (2017) and Li et al. (2018a). SMOW = standard mean ocean water.

veins are based on the evidence as follows: (1) liquid-rich (L_0 -type) and vapor-rich (V-type) fluid inclusions coexist in the same petrographic assemblages (Fig. 6E, J, K); (2) liquid-rich and vapor-rich inclusions in the same FIA show two completely different modes of total homogenization, i.e., L_0 -type inclusions homogenized to the liquid phase and V-type inclusions show homogenization to vapor phase; (3) both liquid-rich and vapor-rich inclusions in the same FIA share similar homogenization temperatures but contrast salinities (Table 2). The possibility of fluid boiling is also consistent with presence of hydrothermal breccias in the syn-ore stage (Fig. 3I). Thus, fluid boiling may take place in the syn-ore stage quartz.

In the post-ore stage, the liquid-rich inclusions in calcite and fluorite exhibit lower homogenization temperatures (232 to 181 °C) and salinities (1.7–7.1 wt% NaCl equivalent), and they show a positive linear correlation between salinity and homogenization temperatures (Fig. 12). In addition, the post-ore stage quartz and calcite yield low δ^{18} O fluid values of –4.9 to –2.8‰, also illustrating the cooler and dilute meteoric water mixed with the magmatic fluid in the final stage of the hydrothermal process.

In summary, the ore-forming fluids responsible for Ag-Pb-Zn mineralization in the Zhaiping deposit is characterized by medium to low temperature (365 to 189 °C), medium to low salinity (1.7–10.8 wt% NaCl equivalent), and contains minor vapor component of CO_2 and N_2 . Fluid inclusion data from the Zhaiping deposit suggest a simple cooling process from the pre-ore to syn-ore stages, and a mixing process from the syn-ore to post-ore stage (Fig. 12), and small scale fluid boiling did take place in some syn-ore stage quartz. The microthermometric data points (homogenization temperature vs. salinity) in Fig. 13 plot essentially in the fields of hydrothermal vein-type deposits.

6.2.2. Pressure estimation

Commonly, homogenization temperatures derived from microthermometric measurements of fluid inclusion assemblages provide only a minimum estimate of temperature at the time of fluid entrapment. Trapping pressure can be estimated only when the actual trapping temperature is known or if fluid boiling or immiscibility were occurring in the fluid system at the time of fluid trapping. To constrain the pressure conditions of quartz veins in different mineralization stages, the "HOKIE_FLINCS_H2O-NACL" spreadsheet was used to calculate fluid pressure (Steele-MacInnis et al., 2012). This program could be used to calculate properties of inclusions for the NaCl-H₂O system and is generally valid from 21.2 to 700 °C, the LV curve to 6000 bar and 0 to 70 wt% NaCl equivalent. These calculations indicate that the preore stage quartz-pyrite veins formed at pressures of 190 to 110 bars (average value of 139 bars), which correspond to depths of 1.1-1.9 km, assuming hydrostatic conditions. Considering the evidence of fluid boiling in the syn-ore stage, homogenization temperatures of inclusions in this stage are interpreted to closely approximately trapping temperatures (Roedder and Bodnar, 1980). Thus, trapping pressures are estimated to range from 100 to 30 bars, with an average value of 46 bars, which would correspond to depths of 0.3-1.0 km in the hydrostatic regime for the syn-ore stage. Finally, further cooling of the ore-



Fig. 12. Homogenization temperature vs. salinity diagram showing the evolution of the ore-forming fluids for different groups of FIAs in the Zhaiping Ag-Pb-Zn deposit. Error bars are at 1σ level. Inset illustration for different fluid evolution paths is based on Shepherd et al. (1985).

forming fluids to temperatures between 232 and 181 °C for the formation of the post-ore quartz-calcite veins was accompanied by hydrostatic pressures normally below 30 bars. Overall, the data present above indicate that vein formation at the Zhaiping deposit occurred at progressively lower pressures and lower temperatures.

6.3. Ore precipitation mechanism

Commonly, silver occurs dominantly as Ag^+ in hydrothermal fluids (Williams-Jones and Migdisov, 2014), and it is predominantly transported as silver chloride ($AgCl_2^-$) and silver bisulfide complexes ($AgHS^0$) in hydrothermal solutions (Stefansson and Seward, 2003; Migdisov and Williams-Jones, 2013). Previous studies have shown that, at lower temperatures (~200 °C), the AgHS⁰ complexes are dominantly at near-neutral conditions (Seward, 1976; Gammons and Barnes, 1989). In contrast, at relatively high temperatures (~400 °C), silver chloride species play a very important role in most hydrothermal fluids, whereas silver bisulfide complexes are only stable in basic conditions (Gammons and Williams-Jones, 1995; Stefansson and Seward, 2003). The widespread sericite alteration suggests that the ore-forming fluids of the Zhaiping deposit are near-neutral to weakly acidic (Zhai et al., 2018). Taking into consideration that the fluids of the pre-ore and syn-ore stages are characterized by medium to low temperature (365 to 222 °C), it is likely that the silver was transported mainly by silver chloride complexes in the ore-forming fluids. Similar to silver, experimental studies demonstrate that chlorite complexes of Pb²⁺ and Zn²⁺ play important roles in the transport of lead and zinc in hydrothermal solutions (Ruaya and Seward, 1986).

Generally, ore precipitation in magmatic-hydrothermal deposits might by triggered by one or more of the following mechanisms: (1) boiling; (2) fluid mixing; (3) cooling; and (4) fluid-rock interaction (Roedder and Bodnar, 1997; Hezarkhani et al., 1999; Ulrich et al., 2002; Simmons et al., 2005; Williams-Jones et al., 2010). In the Zhaiping deposit, small scale fluid boiling did take place in some quartz



Fig. 13. Homogenization temperature vs. salinity diagram illustrating typical ranges for inclusions from different types of deposits (after Roedder, 1984). Most microthermometric data of FIAs in the Zhaiping deposit plot in the vein-type deposit field.

from the syn-ore stage, however, no boiling fluid inclusion assemblage has been observed in the sphalerite of the syn-ore stage quartz-Ag-base metal sulfide veins. This observation suggests that fluid boiling was not a key factor controlling the ore precipitation at Zhaiping. From the preore stage to syn-ore stage, the salinities do not change very significantly (Fig. 12). In contrast, there is a clear decreasing trend of temperatures during the ore formation (Fig. 12). Previous experimental and theoretical studies have shown that decreasing temperature can significantly influence the dissociation of metal chloride complexes, thus, the cooling (temperature decreasing) might be an important factors for mineralization at Zhaiping. As discussed earlier, the fluid mixing process mainly took place at the post-ore stage, and during which only trace amount of pyrite was precipitated. Thus, fluid mixing might not play an important role for the ore deposition. The Ag-Pb-Zn veins at Zhaiping are related to widespread sericite and pyrite-phyllic alterations (Fig. 3G-H, J). During the process of fluid-rock reaction, feldspars in the wall rocks were altered to sericite and quartz, and increasing pH causes a marked decrease in H⁺ concentration in the fluids, which has a significant effect on the deposition of ore minerals (Liu and McPhail, 2005; Yang et al., 2016). Therefore, water-rock interaction also played a role in the formation of the Zhaiping deposit.

6.4. Genetic model

As described earlier, the classification of the Ag-Pb-Zn vein-type mineralization is controversial and a matter of considerable debate. Many geological and geochemical features of the Zhaiping Ag-Pb-Zn deposit are consistent with the Cordilleran-type vein deposits (Kissin and Mango, 2014). These features include the following: (1) primary occurrence as open-space filling in extensional faults; (2) sulfide-rich character in main ore stage veins (Fig. 3C, massive ore); (3) vein formation mostly under epithermal conditions at shallow levels (0.3-1 km for the syn-ore stage, assuming hydrostatic conditions at Zhaiping); (4) hydrothermal fluid of medium to low salinities and temperatures below 375 °C; (5) a magmatic-hydrothermal origin for the ore-forming fluids (e.g., Baumgartner et al., 2009; Fontboté and Bendezú, 2009). However, some distinctions between Zhaiping and the Cordilleran-type vein deposits also exist. The differences include (1) the Cordilleran-type deposits commonly have a well-developed metal and alteration zonation in deposit scale (Fontboté and Bendezú, 2009), in contrast, there is no apparent metal and alteration zonation at Zhaiping; (2) a metal assemblage of Cu-Zn-Pb-Au-Ag-(Bi-Sb) in the Cordilleran-type deposits, in which Cu is an important and Au is a common metallic constitution (Kissin and Mango, 2014), whereas Zhaiping deposit contain Ag-Pb-Zn without Cu and Au; (3) the Cordilleran-type deposits commonly show the close spatial, temporal, and genetic relationship with porphyry system, however, this has not been observed at Zhaiping.

The Ag-Pb-Zn veins in the Zhaiping deposit also have some features similar to the Ag-Pb-Zn veins hosted in clastic metasedimentary rocks in some respects (Beaudoin and Sangster, 1992), including (1) the associations of ore (e.g. galena, sphalerite, and Ag-bearing sulfosalts) and gangue (e.g., quartz, calcite) minerals; (2) the occurrence of mineralized veins associated spatially with silicification and sericite alteration; (3) the structurally controlled orebodies. However, the Zhaiping deposit differs in many important respects from the veins defined by Beaudoin and Sangster (1992). These differences include: (1) commonly, these Ag-Pb-Zn veins hosted in Precambrian to Mesozoic metamorphic terranes, and they are generally linked to greenschist to amphibolite facies metamorphism, whereas, the Ag-Pb-Zn veins in Zhaiping are hosted in early Cretaceous volcanic and subvolcanic rocks, and these rocks have not underwent greenschist to amphibolite facies metamorphism during early Cretaceous; (2) the most significant different is the origin of the ore-forming fluids, the Ag-Pb-Zn veins hosted in clastic metasedimentary terranes typically show no spatial or genetic links with felsic intrusions, and their isotope characters suggest that the hydrothermal fluids and metals originated from their country rocks (Beaudoin and Sangster, 1992; Johnson et al., 1996; Paiement et al., 2012), whereas the Ag-Pb-Zn veins in Zhaiping show a close relationship to the igneous rocks, moreover, the H-O-C-S isotope data presented in this study show that the ore-forming fluids are magmatic in origin. Thus, the Zhiaping Ag-Pb-Zn veins could not be classified as "Ag-Pb-Zn deposit hosted in the clastic metasedimentary rocks" (Beaudoin and Sangster, 1992).

Fluid inclusions and stable isotopes data need to be interpreted in context with geologic relationships (both at regional and deposit scale), to develop a coherent genetic model. Mesozoic Au-Ag, Pb-Zn, and Mo deposits show a wide distribution in the South China Block, and they formed mainly during late Jurassic and early Cretaceous (Zeng et al., 2012; Mao et al., 2013; Wang et al., 2016a,b; Zhong et al., 2017). Southeast China, including the studied area, contains widespread late Mesozoic volcanic-intrusive rocks and belongs to the Mesozoic-Cenozoic NE-trending marginal belt of the Eastern Asia, where tectonism since the Mesozoic has been related mainly to the subduction of the paleo-Pacific plate (Wang and Zhou, 2002; Zhou et al., 2006; Li and Li, 2007; Jiang et al., 2015).

During the late Jurassic to early Cretaceous period, subduction of the paleo-Pacific beneath the South China Block caused large-scale volcanic events across SE China. Geochemical characteristic of intrusive and volcanic rocks, which are closely related to mineralization in the region, show higher $\varepsilon_{Hf}(t)$ and $\varepsilon_{Nd}(t)$ values than those of metamorphic basement rocks (Guo et al., 2012; Liu et al., 2014; Wang et al., 2016a,b). This is a result of the involvement of a juvenile composition in their origin (Guo et al., 2012; Liu et al., 2014). The identification of A-type and alkaline intrusive rocks (Wang et al., 2005; Li et al., 2007), and bimodal volcanic rocks (Chen et al., 2008; Wang et al., 2008), suggests that South China was in an extensional tectonic setting during late Jurassic to early Cretaceous (Wang et al., 2005; Li et al., 2007).

The timing of mineralization of different ore deposits in the costal area of the South China Block is documented by Ar-Ar and K-Ar dating of sericite and muscovite, Rb-Sr dating of sulfides, and Re-Os dating of molybdenite (Mao et al., 2013). These data indicate that interval of 120–80 Ma is important for epithermal Au-Ag-Cu, hydrothermal veintype Ag-Pb-Zn, and granite-related polymetallic W-Sn mineralization in the coastal area of South China (Mao et al., 2013; Zhong et al., 2017). Deposits of this age have similar δD and $\delta^{18}O$ data which support oreforming fluids of magmatic origin mixing with meteoric water (Fig. 11). Sulfur isotope data of these deposits also demonstrate a magmatic-hydrothermal origin for the ore-forming sulfur (Fig. 10).

A genetic model is proposed herein for the formation of the Ag-Pb-Zn veins in the Zhaiping deposit (Fig. 14). Mineralization in the region concided with large-scale lithospheric extension and crust-mantle interaction during the early Cretaceous (Zhou et al., 2006; Jiang et al., 2015). Asthenosphere upwelling initiated crustal thinning, reactivated structures, and provided a heat source to circulate fluids on regional scale. Crust-mantle interaction generated large bodies of metal-rich silicic magma associated with mineralization (Wang et al., 2016a,b). The process of magma crystallization evolved fluids rich in volatiles and metals. The hydrothermal fluids were in a relatively closed, reduced system and transported Ag, Pb and Zn as aqueous Cl⁻ complexes. During the evolution of the ore-forming fluids, the drop of temperature (cooling) of the ore-forming fluids provoked the deposition of the silver, lead and zinc. And fluid-rock interaction which caused phyllic alteration changed the physico-chemical parameters and also played an important role during the formation of the Zhaiping Ag-Pb-Zn deposit (Fig. 3G-H, J). These processes of ore precipitation are common in the region, where ore minerals deposited within extensional structures produced by regional tectonic events, and forming large deposits (e.g., Wang et al., 2013a,b; Li et al., 2018a,b).

7. Conclusions

(1) The Zhaiping deposit, located in the costal area of the South China



Fig. 14. An idealized genetic model for Ag-Pb-Zn vein formation at Zhaiping deposit.

Block, is hosted in early Cretaceous volcanic and subvolcanic rocks and structurally controlled by the extensional faults. The mineralization at Zhaiping deposit can be subdivided into three stages, i.e., the pre-ore quartz-pyrite stage, the syn-ore quartz-Ag-base metal sulfide stage, and the post-ore quartz-calcite-fluorite stage.

- (2) H, O, C, and S isotopic compositions obtained from the deposit demonstrate that the ore-forming fluids had a dominantly magmatic signature but with admixture of meteoric water at late stage.
- (3) Fluid cooling and water-rock interaction are suggested as the major factors controlling the ore precipitation. In addition, small scale fluid boiling did take place in some syn-ore stage quartz.
- (4) The Zhaiping Ag-Pb-Zn deposit is a typical mesothermal deposit and shares many similar features with those of Cordilleran-type vein deposits worldwide, and it was formed in an extensional environment related to early Cretaceous subduction of paleo-Pacific plate.

Competing interests

The authors declare that they have no competing interests regarding the publication of this paper.

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