

# Re–Os and U–Pb geochronology of the Laochang Pb–Zn–Ag and concealed porphyry Mo mineralization along the Changning–Menglian suture, SW China: implications for ore genesis and porphyry Cu–Mo exploration

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**Abstract** Numerous polymetallic volcanogenic massive sulfide (VMS), vein, and replacement deposits are distributed along the Changning–Menglian suture zone in Sanjiang Tethyan metallogenic province, SW China. Laochang is the largest Pb–Zn–Ag vein and replacement deposit in this area, with a proven reserve of 0.51 Mt Pb, 0.34 Mt Zn, and 1,737 t Ag. Its age and relationship to magmatic events and VMS deposits in the region, however, have long been debated. In this paper, we present pyrite Re–Os and titanite U–Pb ages aiming to provide significant insights into the timing and genesis of the Pb–Zn–Ag mineralization. Pyrite grains in textural equilibrium with galena, sphalerite, and chalcopyrite from stratabound Pb–Zn–Ag and Cu-bearing Pb–Zn–Ag orebodies have a Re–Os isochron age of  $45.7 \pm 3.1$  Ma ( $2\sigma$ , mean square weighted deviation (MSWD)=0.45), whereas titanite grains intergrown with sulfide minerals yield a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $43.4 \pm 1.2$  Ma ( $2\sigma$ ,  $n=8$ ). A Mo–

mineralized granitic porphyry intersected by recent drilling below the Laochang Pb–Zn–Ag ores yields a zircon U–Pb age of  $44.4 \pm 0.4$  Ma ( $2\sigma$ ,  $n=12$ ). Within analytical uncertainties, the ages of the Pb–Zn–Ag deposit and the concealed Mo-mineralized porphyry are indistinguishable, indicating that they are products of a single magmatic hydrothermal system. The results show that Laochang Pb–Zn–Ag deposit is significantly younger than the host mafic volcanic rock (zircon U–Pb age of  $320.8 \pm 2.7$  Ma;  $2\sigma$ ,  $n=12$ ) and Silurian VMS deposits along the Changning–Menglian suture zone, arguing against its origin as a Carboniferous VMS deposit as many researchers claimed. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio ( $0.540 \pm 0.012$ ) obtained from the pyrite Re–Os isochron suggests that metals were likely derived from the granitic porphyry that formed from a hybrid magma due to mixing of crustal- and mantle-derived melts, rather than from the mafic volcanic host rocks as previously thought. Our results favor that the Laochang Pb–Zn–Ag deposit is the shallow product of a porphyry Mo system. Thus, there is potential for discovery of porphyry Mo or Cu–Mo deposits below Laochang and similar Pb–Zn–Ag deposits in the Changning–Menglian suture zone.

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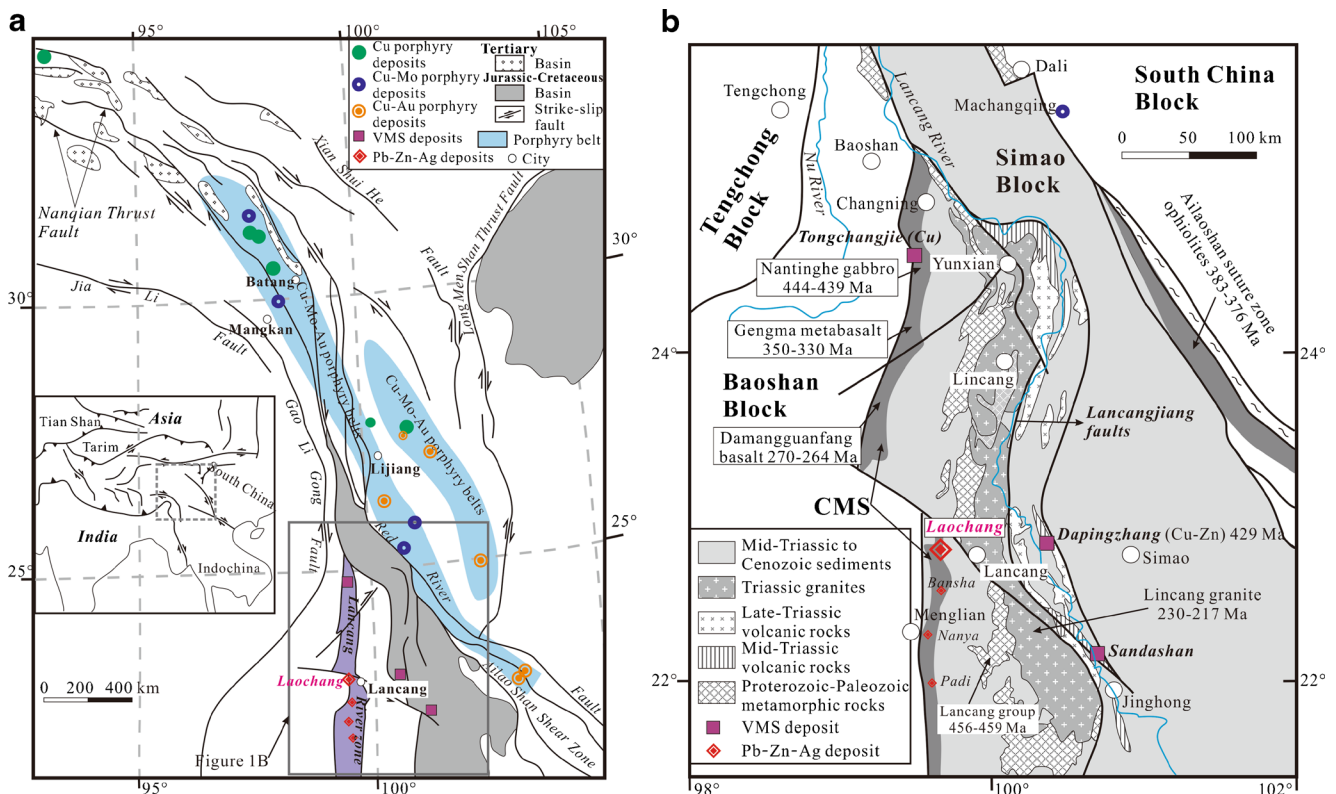
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**Keywords** Geochronology · Stratabound Pb–Zn–Ag mineralization · Porphyry Mo deposits · Changning–Menglian suture

## Introduction

The Sanjiang Tethyan metallogenic province (STMP) in the eastern Tibetan plateau is a well-endowed part of the giant eastern Tethyan metallogenic belt (Fig. 1a; Hou et al. 2007). Numerous porphyry Cu, Cu–Mo, and Cu–Au deposits define two sub-parallel porphyry belts in the STMP (Fig. 1a; Hou et al. 2006; Deng et al. 2014; Mao et al. 2014). These



**Fig. 1** Geologic map of the Sanjiang Tethyan metallogenic province (**a**) and Lancang river zone (**b**) showing the location of Laochang Pb–Zn–Ag deposit and other Eocene porphyry and Silurian VMS deposits. Geologic maps adapted from ECSGM (1986) and YBGMR (1990). Igneous rock

porphyry deposits have molybdenite Re–Os ages ranging from  $40.1 \pm 1.8$  to  $33.1 \pm 0.8$  Ma, indicating that they are related to subduction of the Indian oceanic plate below Eurasia and subsequent India–Eurasia continental collision (Wang et al. 2005; Hou et al. 2006, 2007; Zeng et al. 2006; He et al. 2013; Deng et al. 2014). Southwest of the two porphyry zones, a number of Pb–Zn–Ag vein and replacement deposits are distributed along the Changning–Menglian suture (CMS) zone, but whether the Pb–Zn–Ag mineralization is genetically related to a porphyry Cu–Mo system is not clear and has been a prolonged debate, as porphyry Cu–Mo (Au) deposits are generally absent in this area (Fig. 1b).

Laochang Pb–Zn–Ag deposit in the CMS of southwestern STMP (Fig. 1a) has been mined since the fifteenth century (Yang and Mo 1993). Some researchers proposed that Laochang and other Pb–Zn–Ag deposits in this district are shallow manifestations of Eocene porphyry systems (Xue 1989; Wang 2007; Long et al. 2008; Li et al. 2010a). This interpretation is supported by recent deep drilling that has revealed Mo mineralization in concealed granitic porphyry. Others, in contrast, claimed that Laochang is a volcanogenic massive sulfide (VMS) deposit related to the Carboniferous volcanic rocks (Fan 1985; Yang and Mo 1993; Yang et al. 1999; Hou et al. 2007; Li et al. 2015). The host volcanic rocks at Laochang yielded a

zircon U–Pb age of  $324 \pm 3$  Ma (Chen et al. 2010), which is significantly younger than Cu-dominated VMS deposits (e.g., Tongchangjie, 444–439 Ma; Fig. 1b; Wang et al. 2013) in northern CMS and Cu–Pb–Zn VMS deposits (e.g., Dapingzhang,  $429 \pm 3$  Ma; Lehmann et al. 2013) on the eastern side of this belt (Fig. 1b). The different models place Laochang into two different geologic settings: one related to Carboniferous mafic alkali volcanism in a continental rift setting and the other related to Eocene felsic plutonism in a continental collision setting.

In this paper, we present pyrite Re–Os and titanite U–Pb ages for the Laochang Pb–Zn–Ag deposit. In combination with zircon U–Pb ages of the host volcanic rocks and concealed Mo-mineralized granitic porphyry, these ages provide tight constraints on the timing of Pb–Zn–Ag mineralization and its relation to the host volcanic sequence and the hidden granitic porphyry. Our data provide convincing evidence that the Pb–Zn–Ag mineralization is the shallow product of a hidden porphyry Mo–(Cu) system. This finding has important implications for regional porphyry Mo and Cu–Mo deposit exploration.

### Geological setting

The STMP in the eastern Tibetan plateau is composed of a mosaic of accreted terranes and blocks (Mo et al. 2001;

Burchfiel and Chen 2012; Metcalfe 2013). It has a complex history that reflects the opening and closure of the paleo-Tethys Ocean basin (Mo et al. 2001; Metcalfe 2013). The Lancang river zone in the southwest of STMP (Fig. 1a) is an amalgamation of four continental blocks (South China, Simao, Baoshan, and Tengchong blocks; Fig. 1b). The Simao block was separated from the South China block in Devonian (Zhong 1998; Jian et al. 2009a), whereas the Tengchong and Baoshan blocks were separated from the NE Gondwana in the early Permian (Metcalfe 2006). All these blocks were amalgamated in the Late Triassic during closure of the paleo-Tethys Ocean and intruded by the 300-km-long Lincang batholith (Fig. 1b; Metcalfe 2006; Hennig et al. 2009).

The Simao block is covered by Middle Triassic limestones and Cenozoic terrestrial sedimentary rocks and exhibits one magmatic zone (Yunxian-Jinghong) and two suture zones (Fig. 1b). The Yunxian-Jinghong magmatic zone is dominated by the north trending Lincang batholith (locally called Lincang granite), which is surrounded by metamorphosed volcanic rocks. The Lincang batholith is composed of monzonite, granite, and granodiorite (Heppie et al. 2007), which were emplaced between 230 and 217 Ma (Hennig et al. 2009; Yang et al. 2014). To the west of Lincang batholith, the Lancang Group is dominated by blue schist and amphibolite facies metamorphic rocks (Fig. 1b) consisting of meta-sandstones, sericite-quartz schists, chlorite schists, and amphibole-epidote-bearing metavolcanic rocks (Zhang et al. 1993). Previous Sm–Nd and Rb–Sr isochron ages on metavolcanic rocks in the Lancang Group were between 2.0 and 1.3 Ga (Zhai et al. 1990; Zhong 1998). Recent zircon U–Pb dating, however, indicates that volcanism occurred between 459 and 456 Ma (Nie et al. 2015). The  $^{40}\text{Ar}/^{39}\text{Ar}$  and K–Ar ages show that the Lancang Group underwent metamorphism at 279–214 Ma (Zhang et al. 1993; Zhong et al. 2000; Heppie et al. 2007). To east of the Lincang batholith, the volcanic sequences are dominated by Permian mafic–ultramafic complexes and Triassic rhyolites and basalts (Fig. 1b), with minor Silurian rhyolite–dacite–andesite volcanics exposed in tectonic windows through the Middle Triassic to Cenozoic sedimentary sequence (Lehmann et al. 2013). The Silurian volcanics formed in a back-arc setting (Jian et al. 2009b; Lehmann et al. 2013).

The marginal areas of the Simao block are defined by two suture zones (Fig. 1b). The Ailaoshan suture zone on the eastern margin is marked by gabbro, anorthosite, and MORB, with zircon U–Pb ages of 383–376 Ma (Jian et al. 2009a). The CMS zone along the western margin is mainly composed of Paleozoic sedimentary and volcanic rocks (Fig. 1b). The sedimentary rocks include the Devonian cherts, sandstones and shales, and Late Carboniferous to Early Permian dolomites and dolomitic limestones. In the northern part of the CMS, volcanic rocks consist mainly of Early Silurian Nantinghe gabbro and meta-basalts (444–439 Ma; Wang et al. 2013), early Carboniferous Gengma meta-basalts

(350–330 Ma; Zhang and Duan 2001), and Late Permian Damangguanfang basalts (270–264 Ma; Jian et al. 2009a). In the southern part of the CMS, volcanic rocks are dominated by the early Carboniferous Yiliu Group (Yang and Mo 1993), which has a zircon U–Pb age of  $324\pm 3$  Ma (Chen et al. 2010). Several Pb–Zn–Ag deposits occur within the Yiliu Group (Fig. 1b).

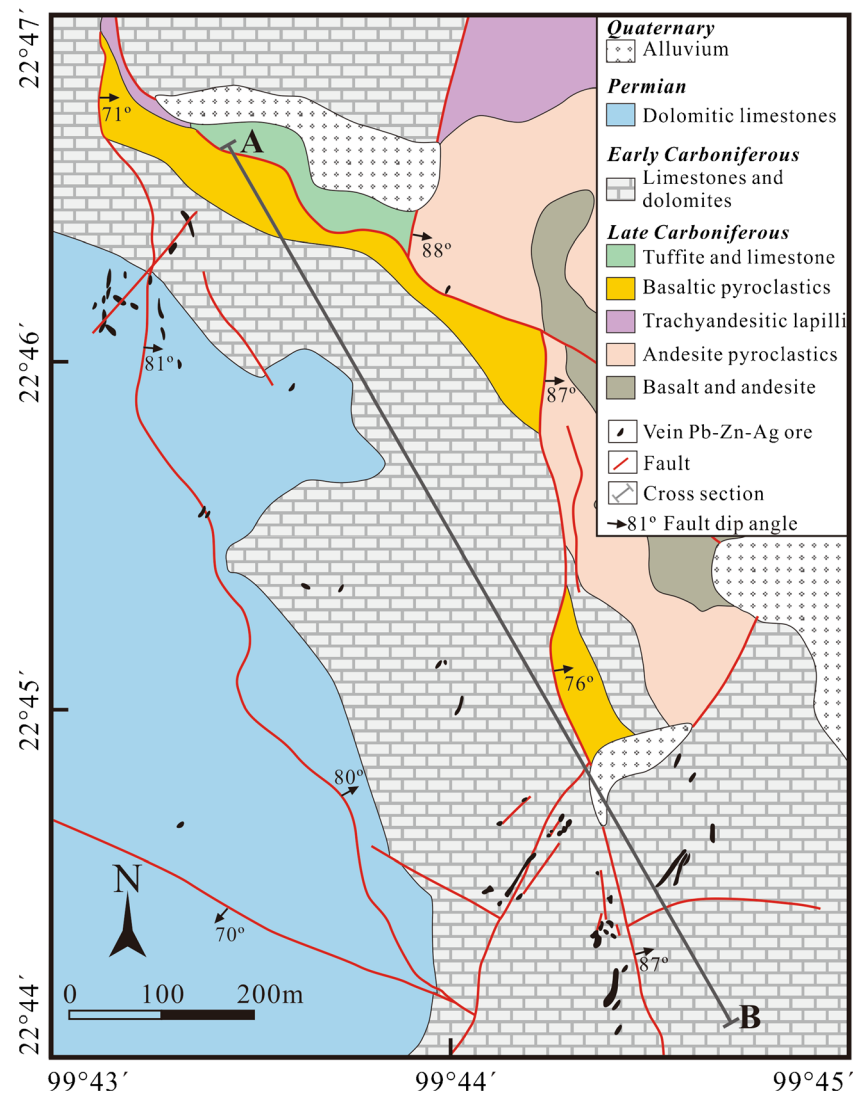
### Geology of the Laochang Pb–Zn–Ag deposit

The Laochang deposit ( $22^{\circ} 45' \text{ N}$ ,  $99^{\circ} 44' \text{ E}$ ) is located about 30 km northwest of Lancang City (Fig. 1). It is the largest Pb–Zn–Ag deposit at the CMS and has a proven reserve of 1,737 t Ag (57.5–635 g/t), 0.51 Mt Pb (1.2–8.9 wt%), 0.34 Mt Zn (2.9–5.1 wt%), and 0.1 Mt Cu (0.1–0.8 wt%) (Li et al. 2010a). Below the Pb–Zn–Ag orebodies, there is a recently discovered porphyry and skarn Mo resource containing 117,800 t Mo with a grade of 0.041–0.171 wt% (Li et al. 2010a). The Laochang deposit is hosted in early Carboniferous volcanic rocks (Yiliu Group) and Late Carboniferous to Early Permian marine carbonate rocks (Figs. 2 and 3). The early Carboniferous volcanic succession includes, from bottom to top (Fig. 2), (1) massive basalt to basaltic andesite and amygdaloidal andesite, 60–160-m thick; (2) andesitic pyroclastics with intercalated sandstone, shale, and limestone lenses, 0–20-m thick; (3) trachyandesitic lapilli and tuff with intercalated shale and limestone lenses, >22-m thick; (4) basaltic pyroclastics to massive flows, 55–160-m thick; and (5) tuffite and calcareous siltstone and limestone, 5–150-m thick (Yang and Mo 1993; Feng 2002). The volcanic sequence was conformably overlain by widespread Late Carboniferous to Early Permian limestones and dolomitic limestones (Fig. 2), with a total thickness of 570–900 m. The mining area and surroundings are variably mantled by colluvium or regolith. The volcanic rocks are fault-bounded by N- to NW-trending, steeply east dipping thrust faults (Fig. 2). Numerous secondary and higher order NE- or W-trending faults in carbonate rocks served to localize the Pb–Zn–Ag veins (Fig. 2).

Recent drill holes have encountered granitic porphyry at >300–900 m below the surface (Fig. 3; Li et al. 2010a). The porphyry is gray and contains phenocrysts of K-feldspar (10–15 vol%; up to 15-mm diameter), plagioclase (~10 % vol%; An=10–20; altered by sericite and carbonate), quartz (~10 vol%; rounded or embayed shape), and biotite (~5 vol%; replaced by chlorite, pyrite, and iron oxides). Groundmass is aplitic (10–200  $\mu\text{m}$ ) and composed of orthoclase and quartz. Geochemical data indicate that the felsic magma was produced by partial melting of mafic lower crust with input of minor amounts of mantle-derived melts (Yang et al. 2012). SHRIMP zircon U–Pb dating indicates that the porphyry was emplaced at  $44.6\pm 1.1$  Ma (Li et al. 2010a).

Five types of sulfide mineralization are present in the Laochang deposit, which are, from top to bottom, vein Pb–

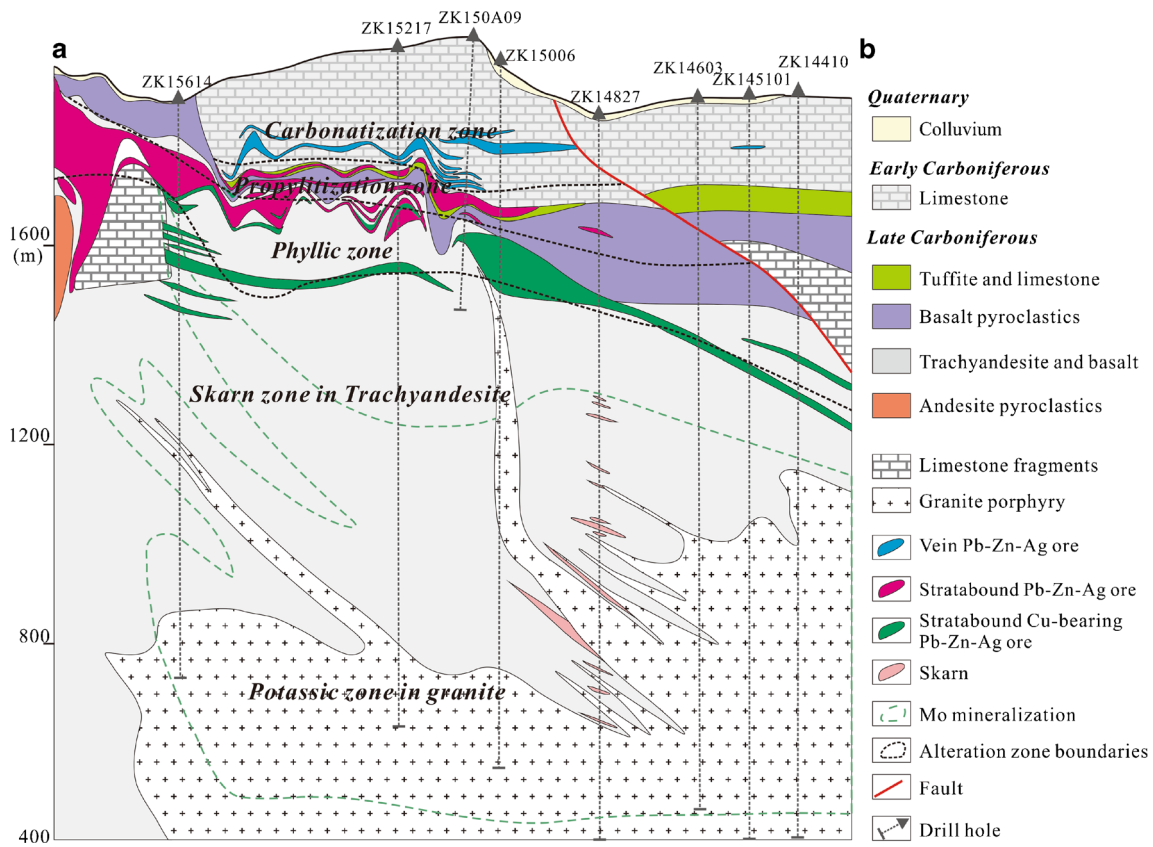
**Fig. 2** Geologic map of the Laochang Pb–Zn–Ag deposit showing the distribution orebodies in Late Carboniferous to Permian carbonate rocks and the location of the cross section in Fig. 3 (after Li et al. 2010a)



Zn–Ag (0–300 m below the surface), stratabound Pb–Zn–Ag (100–400 m), stratabound Cu-bearing Pb–Zn–Ag (400–700 m), skarn Mo (600–1,000 m), and porphyry Mo stockwork (>800 m) mineralization (Fig. 3; Li et al. 2010a). The Pb–Zn–Ag veins ranging from 0.3- to 15-m wide have the highest grades with 1.83–20.34 wt% Pb, 1.41–8.92 wt% Zn, and 96–635 g/t Ag. They mainly occur in Late Carboniferous to Early Permian marine carbonate and commonly follow stratigraphic intervals, fracture zones, and faults (Figs. 2 and 3). Hydrothermal alteration on both sides of individual Pb–Zn–Ag veins is dominated by calcite, ankerite, and rhodochrosite. These carbonate minerals commonly occur as fracture-infillings of a few millimeter to several centimeter width. Galena, sphalerite, and pyrite are the main sulfide phases, locally coexisting with minor amounts of chalcocopyrite, aramayoite, and siderite. The stratabound Pb–Zn–Ag and Cu-bearing Pb–Zn–Ag orebodies are lenticular in shape, hosted in early Carboniferous volcanic rocks, and exhibit replacement textures. The stratabound Pb–Zn–Ag ores contain 0.88–

10.16 wt% Pb, 0.85–4.97 wt% Zn, 59–217 g/t Ag, and 0.07–0.28 wt% Cu, whereas the Cu-bearing Pb–Zn–Ag ores have 0.18–5.26 wt% Pb, 0.40–2.18 wt% Zn, 20–167 g/t Ag, and 0.10–2.15 wt% Cu. The host volcanic rocks of stratabound Pb–Zn–Ag ores are intensely altered to epidote, chlorite, calcite, and clay (propylitic alteration), whereas those of Cu-bearing Pb–Zn–Ag ores are enveloped by sericite and quartz (phyllic alteration). Pyrite, Ag-bearing galena, and sphalerite are the main sulfide phases in stratabound Pb–Zn–Ag ores, with minor amounts of arsenopyrite, pyrrhotite, aramayoite, and native silver. The Cu-bearing Pb–Zn–Ag ores commonly consist of pyrite, galena, chalcocopyrite, and sphalerite, with minor pyrrhotite, native silver, and scheelite.

Skarn Mo mineralization mainly occurs in the Early Carboniferous trachyandesite and basalt, whereas porphyry Mo mineralization is mainly distributed within granitic porphyry (Fig. 3). The skarn Mo orebodies are irregularly distributed along the contact zones between the Early Carboniferous trachyandesite and Eocene granitic porphyry (Fig. 3). The



**Fig. 3** Geologic cross section **a, b** showing the distribution of alteration and mineralization in the Laochang deposit (after Li et al. 2010a)

skarn assemblages include prograde (e.g., diopside, garnet; Fig. 4a) and retrograde (e.g., epidote, actinolite, tremolite, chlorite, and vesuvianite) minerals. The main sulfide minerals include molybdenite, chalcopyrite, pyrite, and pyrrhotite, which are accompanied by minor amounts of oxide minerals such as scheelite and cassiterite. Porphyry Mo mineralization is characterized by quartz–sulfide veins, stockworks, and dense to sparse sulfide disseminations in altered granite, mostly at depths >800 m (Fig. 3). The ore-related alteration is dominated by K-feldspar, sericite, and quartz (Fig. 4b). Molybdenite is commonly intergrown with pyrite, chalcopyrite, and arsenopyrite.

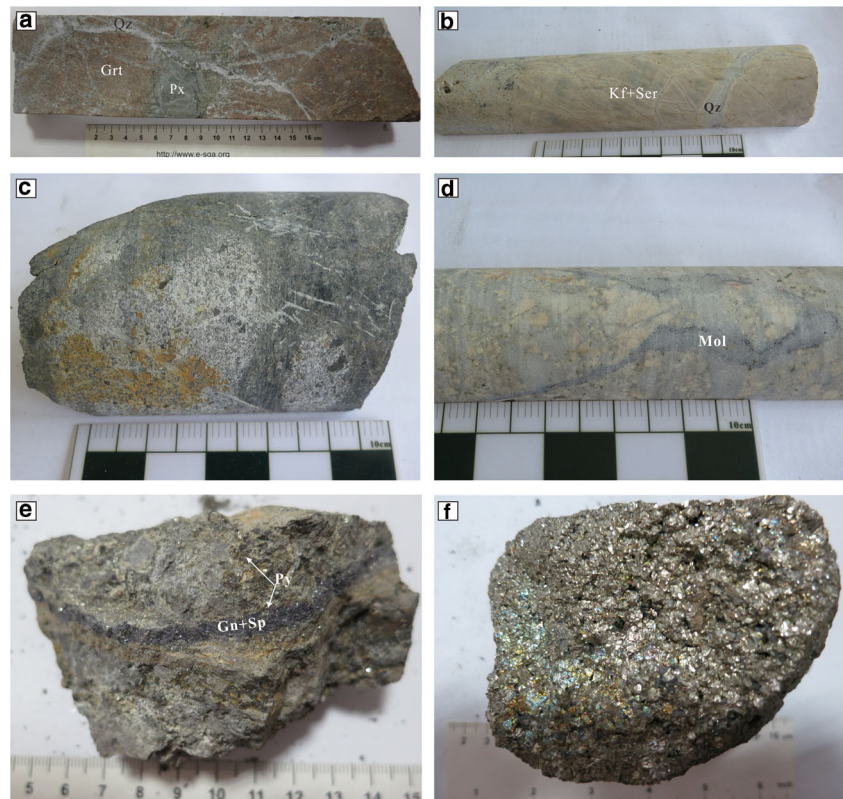
**Samples and analytical methods**

The volcanic rock (Fig. 4c) and granitic porphyry samples (Fig. 4d) used for zircon U–Pb dating were collected from the mining tunnel at 1,700 m elevation and ZK14830 drill core at 631 m elevation, respectively. The stratabound Pb–Zn–Ag ore used for titanite separation was also collected from the mining tunnel at 1,700 m elevation. Zircon and titanite grains were separated using conventional heavy liquid and magnetic methods and then handpicked under a binocular microscope. Mineral grains were mounted in epoxy containers and then polished to expose the interior of the minerals. The back-

scattered electron (BSE) and cathodoluminescence (CL) imaging is used to characterize the morphology and internal structure of these minerals, using a Quanta 450 FEG SEM equipped with a SDD Inca X-Max 50 and a MonoCL 4+ detector at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan.

Uranium–Th–Pb isotopes of zircon and titanite were analyzed using an Agilent 7500a ICP-MS apparatus equipped with a DUV 193 nm ArF-excimer laser (MicroLas, Germany) hosted at GPMR. Detailed analytical procedures and data reduction method follow those in Liu et al. (2010a, b) and are briefly summarized here. A spot size of 32 μm, a repetition rate of 5 Hz, and an energy density of 6 J/cm<sup>2</sup> were applied to all analyses. Argon was used as the make-up gas and mixed with helium as the carrier gas via a T-connector before entering the ICP. Nitrogen was added into the central gas flow (Ar + He) of the Ar plasma to decrease the detection limit and improve precision (Hu et al. 2008). Each analysis incorporated a background acquisition of 20–30 s (gas blank) followed by 50 s data acquisition. Zircon standard 91500 was used as a calibration standard for mass discrimination and U–Th–Pb isotope fractionation (Li et al. 2010b; Deng et al. 2015). Preferred U–Th–Pb isotopic ratios used for 91500 are from Wiedenbeck et al. (1995). The precision and accuracy of U–Th–Pb dating with this technique have been evaluated by

**Fig. 4** Photographs of hydrothermal alteration and samples used for geochronological studies. **a** Skarn assemblages consisting of garnet and pyroxene are cut by quartz vein. **b** Potassic alteration consisting of K-feldspar, sericite, and quartz. **c** Phyllically altered mafic volcanic host rock. **d** Mo-mineralized granitic porphyry. **e** Stratabound Pb–Zn–Ag ore. **f** Stratabound Cu-bearing Pb–Zn–Ag ore. Mineral abbreviations: *Grt* garnet, *Px* pyroxene, *Qz* quartz, *Kf* K-feldspar, *Ser* sericite, *Mol* molybdenite, *Gn* galena, *Sp* sphalerite, *Py* pyrite



comparison with zircon standard GJ-1 (Jackson et al. 2004). Uranium and Th contents were calibrated against the glass standard NIST SRM610 combined with internal standardization (Si). Off-line selection and integration of background and analyzed signals and time-drift correction and quantitative calibration for U–Th–Pb dating were performed by ICPMSDataCal (Liu et al. 2010b). Uncertainties of preferred values for the external standard 91500 were propagated into the final results of the samples. Concordia diagrams and weighted mean calculations were plotted using Isoplot/Ex\_ver3 (Ludwig 2003).

Stratabound Pb–Zn–Ag (Fig. 4e) and Cu-bearing Pb–Zn–Ag ores for pyrite separation (Fig. 4f) were collected from 1,700 and 1,600 m elevation tunnels, respectively. Detailed analytical procedures are described in Qi et al. (2010). Pure pyrite separates of 2 to 3 g were accurately weighed according to the analyzed Re concentrations and were digested in a 200-ml re-usable Carius tube using aqua regia with rhenium and osmium spikes at 200 °C for about 10 h (Qi et al. 2013). Osmium was separated from the matrix by distillation, and Re was separated from the remaining solutions using anion exchange resin. Rhenium contents were measured using a PR ELAN DRC-e ICP-MS, whereas Os isotopes were determined with a Bruker Auraro M90 ICP-MS due to the extremely low Os contents. Total blanks were 6.4 ± 1.1 pg for Re and 2.0 ± 0.4 pg for Os. Uncertainties in Re and Os mass spectrometer measurements, blank

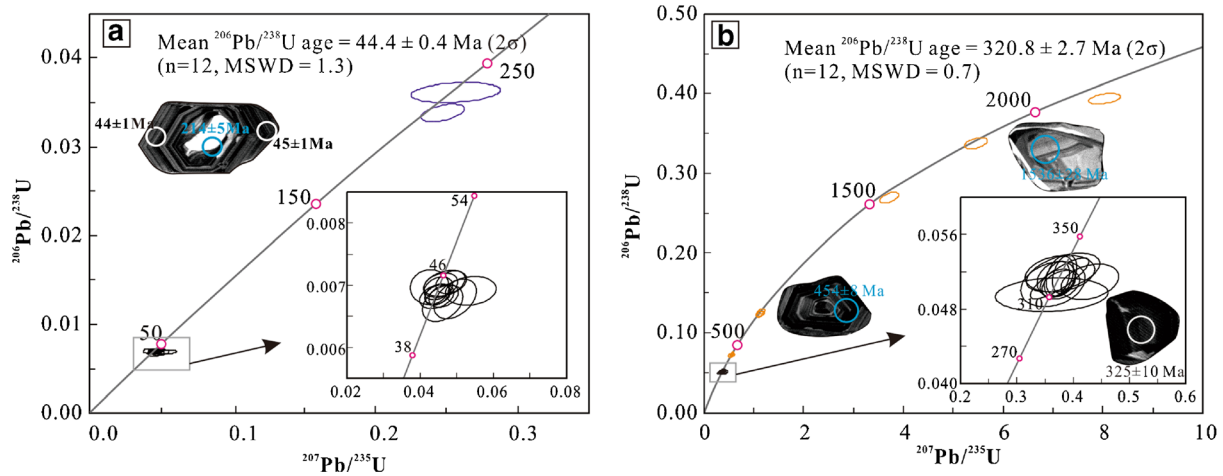
abundances, and spike calibrations were propagated into the final results.

## Results

### Zircon U–Pb age

Laser ablation ICP-MS titanite U–Pb dating results are summarized as Electronic Supplementary Material (ESM 1: Table S1). Zircon grains from Mo-mineralized granitic porphyry are colorless to pale brown and 50–350- $\mu$ m long, with length/width ratios of 2–4. In CL images, most grains exhibit bright cores with oscillatory zoned rims, typical of magmatic zircon (Fig. 5a). Zircon crystals have high U (577–2,528 ppm) and Th (117–1,164 ppm) contents, with Th/U ratios of 0.1–0.5 (ESM 1: Table S1). Twelve spot analyses on ten zircon grains yield concordant  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 43 ± 2 to 45 ± 1 Ma (ESM 1: Table S1 and Fig. 5a), with a weighted mean of 44.4 ± 0.4 Ma (2 $\sigma$ , mean square weighted deviation (MSWD)=1.3). Two spots from two zircon cores have relatively old  $^{206}\text{Pb}/^{238}\text{U}$  ages of 214 ± 5 and 229 ± 6 Ma, which are interpreted to be inherited components.

Zircon grains from the host volcanic rock can be classified into three types. Type 1 zircon grains are subhedral to anhedral, >100- $\mu$ m long, and exhibit irregular zoning in CL images. They have low U (182–



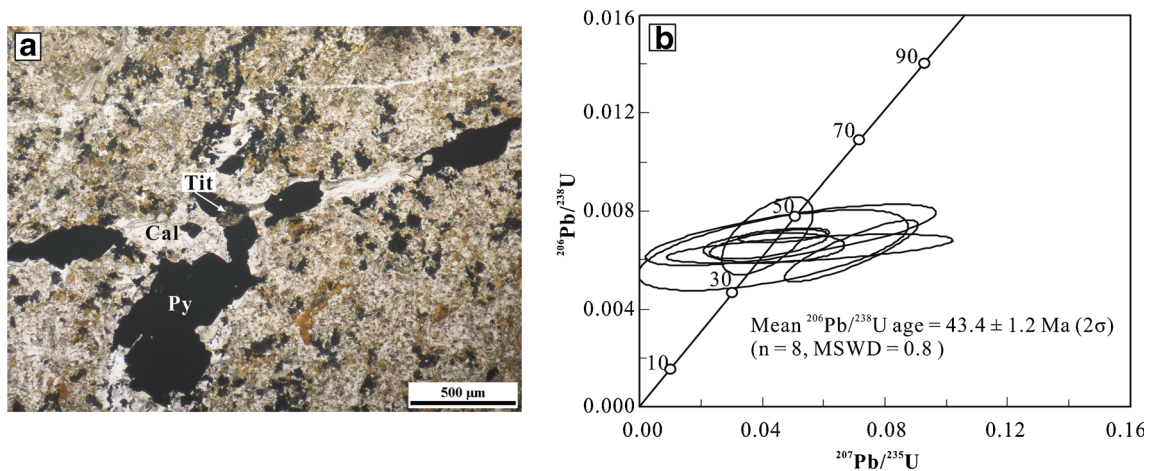
**Fig. 5** CL images and U–Pb concordia diagrams for zircon grains in granitic porphyry (a) and the host volcanic rock (b) from the Laochang deposit

535 ppm) and Th (57–353 ppm) contents, with Th/U ratios of 0.2–1.0 (ESM 1: Table S1). Six spot analyses on type 1 zircon yield relatively old U–Pb ages, ranging from 765±31 to 2,234±29 Ma (ESM 1: Table S1 and Fig. 5b). Type 2 zircon grains are dark to brown, subhedral, 50–150-μm long, and display irregular zoning in CL images (Fig. 5b). They have variable U (183–1,112 ppm) and Th (52–483 ppm), with Th/U ratios of 0.3–0.8 (ESM 1: Table S1). Five analyses yield  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 445±10 to 455±14 Ma, with a weighted mean of 449±4 Ma ( $2\sigma$ , MSWD=0.8). Type 3 zircon grains are subhedral to euhedral, 30–100-μm long, and have wide zoning bands in CL images (Fig. 5b). Uranium and Th concentrations are high but relatively variable, ranging from 125 to 3,127 ppm and 190 to 8,249 ppm, respectively (ESM 1: Table S1),

with Th/U ratios at 0.7–9.8. Twelve spots on type 3 zircon have  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 312±9 to 326±10 Ma (Fig. 5b), with a weighted mean age of 320.8±2.7 Ma ( $2\sigma$ , MSWD=0.7).

**Titanite U–Pb age**

Titanite grains extracted from stratabound Pb–Zn–Ag ore are subhedral and commonly intergrown with sulfide minerals and hydrothermal calcite (Fig. 6a). They have low but variable U (39–551 ppm) and Th (31–207 ppm), with Th/U ratios of 0.2–1.5 (ESM 1: Table S1 and Fig. 6b). Eight spot analyses on eight grains have reproducible  $^{206}\text{Pb}/^{238}\text{U}$  ages that range from 41±7 to 45±2 Ma (Fig. 6b), with a weighted mean of 43.4±1.2 Ma ( $2\sigma$ , MSWD=0.8).



**Fig. 6** a Photomicrograph of titanite grains intergrown with sulfide minerals and calcite in altered mafic volcanic rock from the Laochang Pb–Zn–Ag deposit. b U–Pb concordia diagram for titanite grains. Mineral abbreviations: *Tit* titanite, *Cal* calcite, *Py* pyrite

## Pyrite Re–Os age

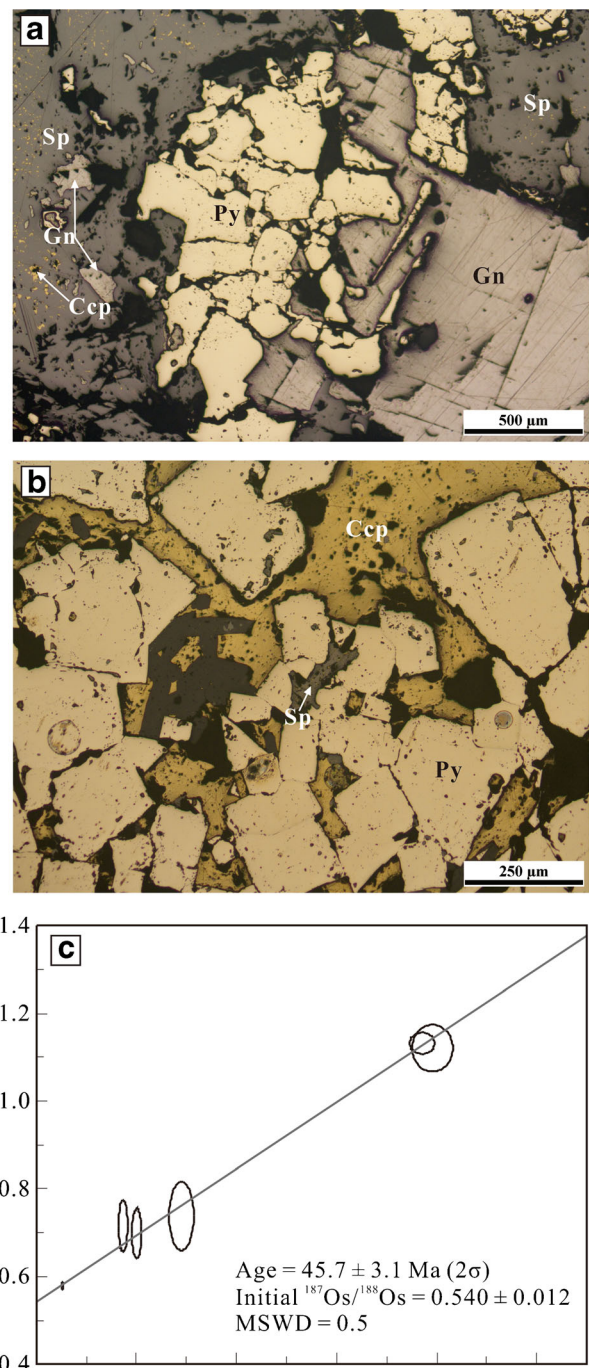
Pyrite grains from the stratabound Pb–Zn–Ag and Cu-bearing Pb–Zn–Ag ores are intergrown with sphalerite, galena, and chalcopyrite (Fig. 7a, b). All pyrite samples have relatively low total Re contents, ranging from 405 to 3,605 ppt with  $^{187}\text{Re}$  abundance of 253 to 2,257 ppt (Table 1). The abundance of  $^{187}\text{Os}$  in pyrite ranges from 0.72 to 4.41 ppt (Table 1). They contain high common Os ranging from 9.58 to 72.59 ppt and have  $^{187}\text{Re}/^{188}\text{Os}$  ratios between 52 and 791. All six samples yield an isochron age of  $45.7 \pm 3.1$  Ma (MSWD=0.45) on the  $^{187}\text{Re}/^{188}\text{Os}$  vs.  $^{187}\text{Os}/^{188}\text{Os}$  plot, with an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.540 \pm 0.012$  (Fig. 7c).

## Discussion

### Age of the volcanic rocks hosting Laochang Pb–Zn–Ag deposit

The age of the volcanic rocks hosting Laochang Pb–Zn–Ag ores has been controversial (Yang and Mo 1993; Chen 1995; Feng 2002). Abundant bivalve-fauna and radiolarian assemblages have been found within chert and limestone fragments entrained in volcanic sequences at Laochang and have been interpreted to be late Permian in age (Feng and Liu 1993; Feng 2002). Previous whole-rock K–Ar dating on the volcanic rocks defined two age groups of 245–195 and 51–38 Ma (Chen 1995), suggesting the volcanic rocks may have formed in the Early Triassic and then were thermally overprinted by extensive Eocene magmatism along the Sanjiang Tethyan tectono-magmatic belts.

Our zircon U–Pb results on the volcanic rocks define three age groups. The oldest group has U–Pb ages from  $2,234 \pm 29$  to  $765 \pm 31$  Ma (Fig. 5b), which most likely reflect inherited components from the Precambrian basement underlying this area and widely distributed over the South China block (Zhou et al. 2002, 2014; Li et al. 2014). The intermediate group has U–Pb ages of 455–445 Ma (Fig. 5b) that are interpreted to be inherited from meta-basalts (444–439 Ma, Wang et al. 2013; Fig. 1b) and/or metavolcanic rocks of the early Silurian Lancang Group previously dated at 459–456 Ma (Nie et al. 2015; Fig. 1b), which underlies the district. The youngest group has a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $320.8 \pm 2.7$  Ma (Fig. 5b), which we consider to be the best estimate for the eruption age of the host volcanic rocks. This view is confirmed by a SHRIMP zircon U–Pb age of  $324 \pm 3$  Ma (Chen et al. 2010) for volcanic tuff from the Laochang Pb–Zn–Ag deposit. Our new data are also consistent with U–Pb ages of meta-basalts in the Gengma area in the CMS (350–331 Ma; Zhang and Duan 2001; Fig. 1b). Together, our results demonstrated that the volcanic rocks hosting Pb–Zn–Ag mineralization at Laochang were erupted in the Early Carboniferous and



**Fig. 7** Photomicrographs of stratabound Pb–Zn–Ag (a) and Cu-bearing Pb–Zn–Ag (b) ore samples from the Laochang deposit showing pyrite intergrown with galena, sphalerite, and chalcopyrite. c Re–Os isochron diagram for pyrite from ore samples. Mineral abbreviations: *Gn* galena, *Sp* sphalerite, *Ccp* chalcopyrite, *Py* pyrite

thus are products of coeval mafic-intermediate magmatism that are widely distributed along the CMS.

Our U–Pb zircon data indicate that the ages inferred from the paleontological stratigraphy are problematic and



**Table 1** Re–Os isotope data for pyrite from the Laochang deposit

Sample	Re		<sup>187</sup> Re		<sup>187</sup> Os		Os <sub>com</sub>		<sup>187</sup> Re/ <sup>188</sup> Os		<sup>187</sup> Os/ <sup>188</sup> Os	
	ppt	1σ	ppt	1σ	ppt	1σ	ppt	1σ	1σ		1σ	
LC1700-01	590	15	369	9	0.77	0.04	9.58	0.48	290	16	0.738	0.052
LC1700-03	809	5	506	3	4.41	0.08	72.59	1.83	52	1	0.579	0.006
LC1700-05	482	6	302	4	1.02	0.04	13.10	0.41	173	6	0.716	0.039
LC1600-08	3,605	56	2,257	35	2.92	0.05	22.01	0.32	771	16	1.131	0.016
LC1600-09	2,872	65	1,798	41	2.25	0.02	17.09	0.44	791	27	1.121	0.035
LC1600-17	405	9	253	6	0.72	0.04	9.49	0.20	201	6	0.698	0.038

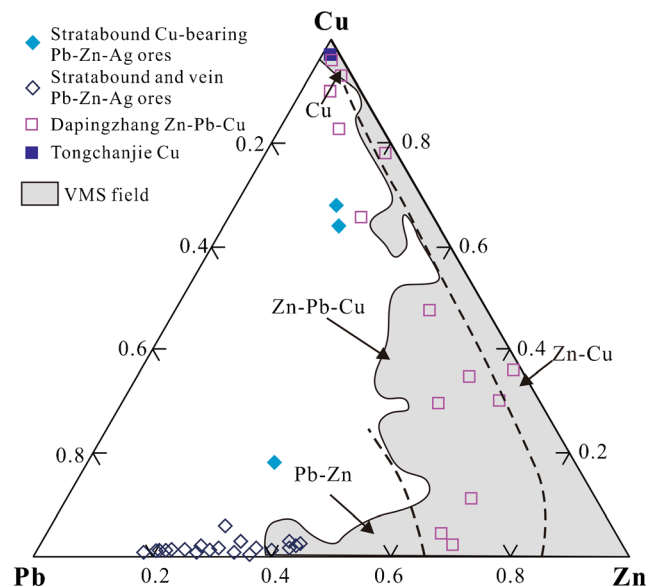
unreliable when interpreted as the formation age of the volcanic rocks. We suggest that the fossil-bearing Late Permian sedimentary rocks are extraneous in origin as partly indicated by the fact that they are in structural contact with the volcanic sequences along thrust faults (Fig. 3; Feng 2002; Li et al. 2010a; Lehmann et al. 2013). The Triassic K–Ar ages (245–195 Ma; Chen et al. 1995) are consistent with the 250 to 200 Ma high-T/low-P metamorphism of the Lancang Group (Zhang et al. 1993; Zhong et al. 2000; Hepepe et al. 2007), whereas the Eocene K–Ar ages (51–38 Ma; Chen et al. 1995) are evidence of a paleothermal anomaly related to the hidden granitic porphyry (44.4±0.4 Ma; Fig. 5a). Collectively, the volcanic rocks hosting the Laochang Pb–Zn–Ag deposit formed in the early Carboniferous and then were subsequently disturbed in Triassic metamorphic and Eocene magmatic events.

**Age of mineralization**

The Laochang deposit is dominated by shallow stratabound Pb–Zn–Ag and deep stockwork Mo mineralization. Previous Pb–Pb model ages on the Pb–Zn–Ag orebodies define three age groups at 351–336 Ma (Fan 1985), 147–98 Ma (Xue 1989), and 87–66 Ma (Ouyang and Xu 1991) that do not agree with dates obtained by other methods and are, therefore, geologically meaningless. In contrast, the previous Rb–Sr isochron age of 45 ±4 Ma (Long et al. 2008) on sphalerite and pyrite from the Pb–Zn–Ag orebodies agrees with our Re–Os date on ore-related pyrite of 45.7±3.1 Ma (Fig. 7c) and U–Pb date on hydrothermal titanite of 43.4±1.2 Ma (Fig. 6b). The Eocene ages on the stratabound Pb–Zn–Ag ores are consistent with the zircon U–Pb emplacement age of the hidden granitic porphyry (44.4±0.4 Ma; Fig. 5a) and the Re–Os age of stockwork molybdenite veins within it (43.4±0.8 Ma; Li et al. 2010a). Together, these results confirm that the Pb–Zn–Ag mineralization at shallow levels was within error contemporaneous with porphyry Mo mineralization at deeper levels.

**Implications for ore genesis and regional exploration**

Genesis of the stratabound Pb–Zn–Ag and Cu-bearing Pb–Zn–Ag orebodies in volcanic rocks at Laochang has long been debated (Fan 1985; Xue 1989). Previous studies have proposed that the Laochang Pb–Zn–Ag deposit is of VMS origin formed coevally with the host volcanic rocks (Fan 1985; Yang and Mo 1993; Yang et al. 1999; Hou et al. 2006; Li et al. 2015). If this model is correct, one would expect that Cu-mineralized pipes and stringer zones, typical of VMS deposits, would be present below the Pb–Zn–Ag ores as is the case in the Tongchangjie and Dapingzhang VMS deposits in the Sanjiang Tethyan metallogenic province (Li et al. 2010a; Lehmann et al. 2013). Our new geochronological results, however, demonstrate that the Pb–Zn–Ag mineralization is not of VMS origin in association with the volcanic rocks in the mine. This view is partly confirmed by geochemical features of the Pb–Zn–Ag ores. The Pb/Zn ratios of the Laochang



**Fig. 8** Cu–Pb–Zn ternary diagram from Franklin (1996) that compares Laochang ore samples to those from the Dapingzhang and Tongchangjie VMS deposits

Pb–Zn–Ag ores (1.2–4.5; Li et al. 2010a) are significantly higher than those typically found in VMS deposits ( $Pb/Zn < 1$ ; Franklin et al. 2005). In the Cu–Pb–Zn ternary diagram (Franklin 1996), samples from the Tongchangjie and Dapingzhang VMS deposits in the Sanjiang Tethyan metallogenic province plot within the VMS field, whereas samples from Laochang deviate this diagnostic area (Fig. 8).

Geological and geochronological data confirm that the Laochang Pb–Zn–Ag ores are genetically related to the hidden granitic porphyry with porphyry and skarn Mo mineralization. These ores are typically localized in permeable volcanic units, fractures, and/or Late Carboniferous to Permian carbonate rocks and exhibited conspicuous replacement textures (Figs. 2, 3, and 4). These features are consistent with polymetallic vein and replacement deposits associated with porphyry intrusions widely recognized in the world (e.g., Titley 1993; Plumlee et al. 1995; Mao et al. 2009, 2011). The lateral and vertical alteration patterns (Fig. 3; Li et al. 2010a), consisting predominantly of potassic (stockwork Mo mineralization), garnet–diopside (skarn Mo mineralization), phyllic (stratabound Cu–bearing Pb–Zn–Ag ores), propylitic (stratabound Pb–Zn–Ag ores), and Fe–Mn carbonatization (vein Pb–Zn–Ag ores), confirm that the Laochang hydrothermal system was initiated by a porphyry intrusion, as observed in other porphyry-epithermal systems (Simmons et al. 2005; Sillitoe 2010; Cooke et al. 2011).

The initial  $^{187}Os/^{188}Os$  ratio ( $0.540 \pm 0.012$ ) obtained from the pyrite Re–Os isochron (Fig. 5c) is between that of typical crustal ( $\sim 1.0$ – $1.5$ ) and mantle ( $\sim 0.12$ – $0.13$ ) sources (Shirey and Walker 1998) and thus indicating a hybrid igneous source for the ore fluids and other components in the fluids. The initial Os isotopic ratio of pyrite is consistent with previous geochemical studies demonstrating that the granitic porphyry formed by the mixing of mantle- and crustal-derived magmas (Xu and Ouyang 1991; Yang et al. 2012), but it is inconsistent with the mantle origin of the mafic volcanic rocks (Chen et al. 2011; Li et al. 2015). We therefore infer that metals and hydrothermal fluids were derived from granitic porphyry, rather than from mafic volcanic rocks. This interpretation is supported by the initial  $^{87}Sr/^{86}Sr$  ratio obtained from the pyrite and sphalerite Rb–Sr isochron of  $0.70977 \pm 0.00034$  (Long et al. 2008), which is similar to the value of granitic porphyry ( $0.71127 \pm 0.00047$ ; Ouyang and Xu 1991) but much higher than the early Carboniferous mafic volcanic rocks ( $0.70001$ ; Long et al. 2008). In summary, the textural, geochemical, and isotopic evidence confirms that the Laochang Pb–Zn–Ag mineralization is spatially, temporally, and genetically related to the concealed Mo-mineralized porphyry.

Several other Pb–Zn–Ag deposits with propylitic and phyllic alteration halos similar to Laochang occur in early Carboniferous volcanic rocks along the CMS (Fig. 1b; Wang 2007). If they are related to concealed granitic porphyries, then the CMS may potentially become the third porphyry

Cu–Mo–Au belt in the STMP (Fig. 1). This concept will have important implications for future exploration strategy in this giant metallogenic belt.

## Conclusions

Pyrite intergrown with galena and sphalerite from the Laochang stratabound Pb–Zn–Ag and Cu-bearing Pb–Zn–Ag ores has a Re–Os isochron age of  $45.7 \pm 3.1$  Ma, whereas titanite grains coexisting with sulfide minerals from the stratabound Pb–Zn–Ag ores yield a weighted mean U–Pb age of  $43.4 \pm 1.2$  Ma. Both ages are consistent with a zircon U–Pb age ( $44.4 \pm 0.4$  Ma) of a concealed Mo-mineralized granitic porphyry and a molybdenite Re–Os isochron age of  $43.4 \pm 0.8$  Ma on stockworks within this porphyry. The initial  $^{187}Os/^{188}Os$  ratio of pyrite ( $0.540 \pm 0.012$ ) allows that Os and, by inference, other melts in the hydrothermal ore fluids were sourced from the hidden granitic porphyry that formed by mixing of crustal and mantle-derived magmas revealed in previous studies. Meanwhile, the mafic volcanic rocks hosting the Pb–Zn–Ag mineralization have a zircon U–Pb age of  $320.8 \pm 2.7$  Ma, significantly older than the ores. Results from this study confirm that the Laochang stratabound and vein Pb–Zn–Ag ores are not parts of a Late Paleozoic VMS deposit as previously thought, rather they represent shallow expressions of a porphyry Mo system, both forming an important part of the giant Cenozoic Sanjiang Tethyan metallogenic province. We infer that similar Mo or Cu–Mo porphyry deposits may be present below other Pb–Zn–Ag deposits along the CMS that may be within reach of drilling.

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