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Ore Genesis and Geodynamic Setting of Laochang Ag-Pb-Zn-Cu Deposit, Southern Sanjiang Tethys Metallogenic Belt, China: Constraints from Whole Rock Geochemistry, Trace Elements in Sphalerite, Zircon U-Pb Dating and Pb Isotopes

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Abstract: The Laochang Ag-Pb-Zn-Cu deposit, located in the southern margin of the Sanjiang Tethys Metallogenic Belt (STMB), is the typical Ag-Pb-Zn-Cu deposit in this region. Its orebodies are hosted in the Carboniferous Yiliu Formation volcanic-sedimentary cycle and occur as stratiform, stratoid and lenticular. Whether or not the stratabound ore belong to the volcanogenic massive sulfide (VMS) deposit remains unclear and controversial. In this paper, the whole rock geochemistry, trace elements in sphalerite, U-Pb zircon chronology and Pb isotopes were investigated, aiming to provide significant insights into the genesis and geodynamic setting of the Laochang deposit. Lead isotope ratios of pyrite and sphalerite from the stratabound ore are 18.341 to 18.915 for 206 Pb/ 204 Pb; 15.376 to 15.770 for ²⁰⁷Pb/²⁰⁴Pb; and 38.159 to 39.200 for ²⁰⁸Pb/²⁰⁴Pb—which display a steep linear trend on Pb-Pb diagrams. This indicates a binary mixing of lead components derived from leaching between the host volcanic rock and mantle reservoir. Sphalerite from stratabound ores is relatively enriched in Fe, Mn, In, Sn, and Ga-similar to typical VMS deposits. Moreover, the Carboniferous volcanic rock hosting the stratabound Ag-Pb-Zn-Cu ores has a zircon U-Pb age of 312 ± 4 Ma; together with previous geochronological and geological evidences, thus, we consider that the stratabound mineralization occur in the Late Paleozoic (~323–308 Ma). Collectively, these geologic, geochemical, and isotopic data confirm that the stratabound ores should be assigned to Carboniferous VMS mineralization. In addition, volcanic rocks hosting the stratabound ore exhibit elevated high field strength elements (HFSEs, Nb, Ta, Zr and Hf) abundance, slight enrichment of light rare earth element (LREE), and depletion of Ba and Sr with obvious Nb-Ta anomalies. Such characteristics suggest that their magma is similar to typical oceanic island basalt. In addition, the oceanic island basalt (OIB)-like volcanic rocks were formed at Late Paleozoic, which could be approximately synchronous with the VMS mineralization at Laochang. Thus, it is suggested that the Laochang VMS mineralization was generated in the oceanic island setting prior to the initial subduction of the Changning-Menglian Paleo-Tethys Ocean.

Keywords: trace elements in sphalerite; U-Pb dating; geodynamic setting; Sanjiang Tethys Metallogenic Belt; Laochang Ag-Pb-Zn-Cu deposit



1. Introduction

The Sanjiang Tethys Metallogenic Belt (STMB), one of the premier polymetallic belts in China (Figure 1A), is located within the eastern Himalayan-Tibetan Orogen. Numerous ore deposits of diverse genetic types and metal speciation, including volcanogenic massive sulfide (VMS), porphyry-skarn Cu-Mo, Cu, and Cu-Au, orogenic Au, and Mississippi Valley-type (MVT) Pb-Zn deposits, were formed from Paleozoic to Cenozoic. These different genetic types of ore deposit formation are closely associated with the tectonic evolution in the Sanjing region [1–5].

The Laochang Ag-Pb-Zn-Cu deposit is located at the southern part of the STMB, and has a proven reserve of 866,000 t Pb at 4.5%, 336,000 t Zn at 3.3%, 1700 t Ag at 155 g/t, 116,000 t Cu at 0.5–0.9%, 2.84 Mt Pyrite and accompanying 0.8 t Au [6–8]. It is the largest Ag-Pb-Zn-Cu deposit at the Changning-Menglian Suture and has been mined since the Yongle Period of the Ming Dynasty (1404 AD) [9]. Over the past four decades, several studies have been carried out on the Laochang Ag-Pb-Zn-Cu deposit, most of which were published in Chinese. However, many issues, especially its ore genesis, are still controversial. The orebodies generally show stratigraphic control and the bulk chemical and Nd-Pb isotopic data suggest that the basalt hosting the stratabound orebodies exhibit an oceanic island basalt (OIB) signature [10,11]. Thus, a great number of authors consider it is a syngenetic VMS deposit [12–14]. In contrast, with recent mining exposures at Laochang deposit, the Cenozoic concealed porphyry intrusion has been discovered in depth, which is spatially related to the stratabound ores. Consequently, several authors have regarded it as a magmatic-hydrothermal deposit [6,15-17]. The former hypothesis suggests that the deposit is syngenetic and generated by submarine synvolcanogenic processes [18,19], whereas the latter model considers that it is epigenetic and related to concealed porphyry intrusion [20,21]. There has not been, until now, a complete understanding of the relationships between the stratabound Ag-Pb-Zn-Cu mineralization, host volcanic rock and porphyry intrusion.

In this paper, we present a comparative geochronology study (U-Pb dating using zricon) for stratabound ores hosting volcanic rocks and previous studies obtained the timing of stratabound mineralization to assess their temporal relationship. We further analyze trace elements of sphalerite and Pb isotopic composition of sulfides (pyrite and sphalerite) from stratabound ores and ore-hosting volcanic rocks to constrain its ore origin. Lastly, we use the major and trace element of ore-hosting volcanic rocks and zircon U-Pb dating to provide insights into the geodynamic setting of Laochang Ag-Pb-Zn-Cu deposit.

2. Geological Setting

The Changning-Menglian Suture forms part of the STMB (Figure 1B). It has a complex history that reflects a Proto-Tethys Ocean opened during the Neoproterozoic and closed in the late Early Paleozoic [4,11,22], followed by the development of the main Paleo-Tethys Ocean. The Paleo-Tethys Ocean opened during the Middle Devonian, as recorded by the Middle Devonian deep water marine cherts, *Eoalbaillella lilaensis radiolarians* and ophiolite complex with the zircon U-Pb ages of 349–331 Ma for gabbros [23,24], and the Changning-Menglian Tethys Ocean was subducted underneath the Simao block, forming the Yunxian-Jinggu Arc in ca. 306–265 Ma [4,25–31]. During the Middle Permian-Middle Triassic, the collision and amalgamation of the Baoshan and Simao terranes resulted in the S-type Lincang granitic batholith with zircon U-Pb ages of 234–219 Ma [27,32,33] and the coeval bimodal mafic-felsic volcanic rocks with zircon U-Pb ages of 231–210 Ma located at the east of the Lincang batholith [33,34]. Since the Late Triassic Period, the generation of the peraluminous granites was most likely related to post-collisional extension, including the Bulangshan and Mengsong granitoids, and the Lincang biotite granites/monzogranites [31–36].

The Changning-Menglian Suture is an N-S trending strip 300 km long and 15–50 km wide, sandwiched between the Simao block to the east and the Baoshan block to the west (Figure 1C). The overall stratigraphic succession is dominated by a Proterozoic basement complex that unconformably overlain Paleozoic to Quaternary sediments. The basement comprises upper Proterozoic epimetamorphic

rock series. The oldest rock, Devonian in age, are deep oceanic sediments comprised by siliceous rock, silica mudstone and greywacke unconformably overlain by Carboniferous shallow marine limestone intercalated by volcanic rocks. The volcanic rocks are mostly regarded as sea-mounts and/or oceanic islands in origin [37,38]. The Permian series consist of up to 730 m of massive detrital and bioclastic limestone and dolomite, followed by Triassic bathyal facies clastic sedimentary sequence of argillaceous slate, radiolarian bedded chert and vitric tuff [39]. The Jurassic sediment is composed of purple sand conglomerate, quartz sandstone, siltstone and mudstone, which is capped by Paleogene sand conglomerate and mudstone, and Quaternary unconsolidated sediments [10]. More details on the geology of the Changning-Menglian Suture can be found in Li et al. [11] and Deng et al. [40].



Figure 1. (**A**) Geotectonic framework map of China showing the location of the Sanjiang Orogen; (**B**) Geologic map of the Southwest Sanjiang Tethys metallogenic belt that shows the porphyry and volcanogenic massive sulfide (VMS) deposits (modified after Li et al. [8]); (**C**) The Lancang river zone showing the distribution of the major tectonic units, igneous rocks and location of the Laochang Ag-Pb-Zn-Cu deposit (modified after Deng et al. [3,4]).

3. Geology of the Laochang Deposit

3.1. Strata

The Laochang deposit (22°45′ N, 99°44′ E) is located about 30 km northwest of Lancang City (Figure 1C). The exposed strata in the Laochang deposit consist of Devonian, Carboniferous, Permian and Quaternary (Figure 2). The Devonian strata comprise clastic and siliceous rocks and are overlain by Carboniferous volcanic-sedimentary rocks, limestone and dolomite. The Lower Permian strata are composed of limestone, and the Quaternary is mainly red-clay sediment [41].

The stratabound Ag-Pb-Zn-Cu ore is mainly hosted in the Carboniferous Yiliu Formation, which comprises volcanic rocks (45.3 vol%; e.g., basalt, andesite and trachyte), volcaniclastic rocks (43.3 vol%; e.g., andesitic, basaltic-andesitic, basaltic, trachytic, trachyandesitic tuff-breccia and agglomerates) and small number of siliceous rocks and limestone lenses, with a total thickness of up to 870 m [8]. From bottom to top, Yiliu volcanic-sedimentary cycles can include as follows (1) andesitic tuff, andesitic breccia, basaltic breccia and basaltic tuff-breccia, >20 m thick; (2) basaltic breccia, basaltic tuff, 60–130 m thick; (3) andesite, andesitic agglomerates and andesitic breccia tuff, 60–130 m thick; (4) andesitic breccia tuff with sandstone, bioclastic limestone and tuffite, 0–120 m thick; (5) trachybasaltic, andesitic tuff with banded siliceous rocks, carbonaceous shale, and marble, 80–160 m thick; (6) massive basalt with trachybasaltic, andesitic tuff, 55–160 m thick; and (7) trachyandesitic, trachytic tuff with sand shale, siltstone and limestone, >150 m thick [41,42]. The Yiliu Formation is composed of two lava-agglomerates-breccia-tuff-sedimentary basic groups, which are divided into two-small volcanic-sedimentary cycles according to comparison of the profile of the regional volcanic rocks and Laochang drills [8].

3.2. Structure

The orefield is characterized by a set of N- to NW-trending, steeply east dipping thrust faults that control the distribution of volcanic rocks and mineralization (Figure 2). They were reactivated later, especially in the Cenozoic India-Asia collision [3,4,43] and controlled the concealed porphyry emplacement [8].



Figure 2. Geological map of the Laochang deposit (modified from Long [41]).

3.3. Porphyry Intrusion

Excavations in the Laochang mine resulted in the discovery of concealed porphyry intrusion, and numerous drillings have encountered granitic porphyry intrusion in the Carboniferous volcanic-sedimentary cycles (Figure 3). The granitic porphyry is grey-greyish white with porphyritic texture, which contains phenocrysts of K-feldspar (15–20 vol%, up to 15-mm diameter), quartz (10–15 vol%, 2–5 mm diameter, rounded or embayed shape), plagioclase (10–15 vol%, 2–8 mm diameter, altered by sericite and carbonate), and biotite (2–5 vol%). The groundmass comprises quartz and orthoclase. The granite porphyry show high SiO₂, K₂O and low MgO, CaO, FeO, P₂O₅ contents, and they belong to alkaline series [41], which is similar to the large and super large Cenozoic porphyry Cu-Au-Mo deposit in STMB. SHRIMP zircon U-Pb dating has shown that the granitic porphyry was emplaced at 44.6 \pm 1.1 Ma [44]. In addition, 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 [45].



Figure 3. Geologic cross-section (**A**,**B**) showing the mineralization in the Laochang deposit (modified from Li et al. [8]).

3.4. Sulfide Mineralization

Stratabound ores are situated in the Carboniferous Yiliu Formation (Figure 4) and show distinctive metal zonation from bottom to top [11]. The orebodies are divided into two layers vertically, which formed mainly at the top of the first and second volcanic cycles [7,42]. In each ore cluster, numerous sulfide orebodies are stacked upwards and largely overlap in the vertical projections (Figure 3). Metal zonation from Fe-Cu to Cu-Zn-Pb and then to Ag-Pb-Zn is present in both ore cluster and single orebody [44].

Ore cluster No. I consisting of 48 orebodies occurs in the top sequences of andesitic-trachyandesitic tuff interlayered with limestone and carbonaceous chert within the first volcanic cycle (Figure 4). These orebodies are stratiform, stratoid and lenses, which consistent with the host strata. The largest orebody No. I_{1+2} , located in the north part of this ore cluster, is stratiform and accounts for approximately 90.6% of the sulfide ore reserve of ore cluster No. I and 30% of Ag reserve of the total deposit. It is 875 m in length, 50 to 258 m in width with an average of 129 m and 3 to 23 m in thickness with an average of 7 m and has estimated metal reserves of 88,400 t Pb at 4.5%, 70,300 t Zn at 3.8% and 368.67 t Ag at 199.4 g/t [41]. Most of the high-grade Ag-Zn-Pb ores are distributed in the upper part of this orebody, and gradually grades into sparse disseminated sulfides and finally into pyrite-dominant sulfides downward (Figures 3 and 4). Other orebodies of ore cluster No. I occurring as lenses and sacks are mainly distributed in andesitic tuff, which are higher in metal grade, but smaller in size. In the northern part of this ore cluster, underneath the semi-horizontal stratiform Fe-Zn-Pb orebodies are a vertical stringer zone (Figure 5B). The replacement sulfides typically surround and occur outboard of the stringer zone, which were formed by widespread hydrothermal flow surrounding and originating from the stringer veins. In addition, in ore cluster No. I, the hanging wall of this orebody, lacks mineralization and has steep contact with the orebody. A commonly thin layered carbonaceous-sulfidic chert characterized by an exhalative-sedimentary structure was observed on top of the stratiform sulfide lenses [9].

Ore cluster No. II consists of 37 orebodies occurs mainly on the top of second volcanic-sedimentary cycle of the Carboniferous (Figures 3 and 4). Most sulfide orebodies occur as stratoid and lenticular, paralleling to the host volcanic rocks. All orebodies of cluster No. II, expect for the II₁, II₂, II₄ and II₅ orebody, are small in size. The largest orebody No. II₁ of ore cluster No. II is 260 m in length, 40 to 215 m in width with an average of 124 m and 1.8 to 16.3 m in thickness with an average of 6 m and contains 34,900 t Pb at 7.3%, 24,300 t Zn at 5.1% and 119.87 t Ag at 250.3 g/t [41,46]. The stringer and disseminated sulfides with low Zn-Pb and high Fe-Cu grade, appear locally beneath

the semi-horizontal stratiform sulfides. It is common that the content of the Pb, Zn and Ag in the lenses are high with an upward increase trend, yet the Cu content is mostly below the cutoff grade (\sim 0.5%) displaying a downward progressive increase. A laminated carbonaceous chert, similar to the ore cluster No. I, is present locally on top of the sulfide lenses [8]. In addition, compared with the ore cluster No. I, the pyrite-dominant ores are much less common in the ore cluster No. II.

Stratigraphy		Lithology	Volcanic cycle	Description		Pebbles,sand and clay
Quat	ernary			0-90m, Pebbles, sand and clay		Micrite and dolomite
Per	mian			260-420m, massive biomicrite and thick-bedded lime- stone in the upper part and dolomitic limestone inter- calated with limestone in the lower part		Biomicrite and limestone
				For madium to thick hadded earal limestance contai		Limestone lens
				ning fossils: Triticites, Schwagerina, Sp		Pelitic strip
				310-430m, micrite interclated with pelitic stripin the u- pper part, dolomite intercalated with micrite and oolit- ic limestone in the middle and micrite interclatted with		Shale
				silicate and shale in the lower part		Clastic and siliceous rocks
		X	308±5 Ma	0-150m, tuff, brecciated tuff, tuffite intercalated with shale,sandy shale and lenticular limestone. Most ore bodies of the cluster II occur at the top		Carbonaceous- sulfidic silicalite
niferous		Z,	¥312±4 Ma	50-160m, tuff, brecciated tuff, tuffite intercalated with basaltic tuff, and a thin layer of basaltic breccia in the lower part. Some orebodies of the cluster II occur at		Tuff with clastic rocks
rboi		Y.		the top		Basalt with tuff
Ca	nation		2323.6±2.8 Ma 2320.8±2.7 Ma	80-160m, trachyandestitic tuff, basitic tuff, carbonac- eous sulfidic silicalite, shale intercalated with silicite		Andesite
	iu Forn			top	* _* *	Volcanic agglomerate
	Yili	•	st	0-120m, trachyandesitic tuff and breccia intercalated with tuffite and limestone		Trachyandesitic tuff
				60-130m, andesitic agglomerate and breccia intercal- ated with andesite, and a thin layer of shale at the base	4 A A A A	Volcanic breccia
				50-130m, massive alkali basalt, basaltic breccia and tuff	****	Cenozoic granite
				>20m, trachyandesitic tuff with breccia		Massive sulfides
Devonian				>400m, quartz sandstone and thin-bedded silicite in the upper part and medium- to thick-bedded feldspa- thic quartz sandstone intercalated with silicite at the base		(Pb,Zn and Ag) Massive sulfides (Fe and Cu)

Figure 4. Lithostratigraphic column of the Laochang deposit. Note that the Carboniferous volcanic-sedimentary cycles comprise eight lithologic layers that formed during two volcanic cycles. (modified from Mo et al. [13] and Ye et al. [42]).

3.5. Hydrothermal Alteration

Widespread sericite-quartz-pyrite hydrothermal alteration were observed in the immediate footwall of the sulfide lenses [11]. The andesitic and basaltic tuff-dominant footwall rocks contain abundant fine-grained sericite, quartz and pyrite, whereas fine-grained sericite, quartz and pyrite are extremely rare in stringer and disseminated sulfide zones. Sericite is the most common alteration mineral. The chloritization in the footwall underneath the stratiform ore is generally weak with slight increase downward. There is no alteration in the hanging wall, which suggest that ore-forming hydrothermal activity occurred prior to the deposition of the hanging wall sequence.

In addition, low-grade metamorphic alteration in region, primarily for epidote, chlorite, serpentine, albite and calcite, has widespread influence on the Carboniferous intermediate-mafic volcanic rocks.

3.6. Ore Texture and Paragenesis

Primary sulfide minerals include pyrite, sphalerite, galena and chalcopyrite (Figure 5A,C–E), with minor arsenopyrite, pyrrhotite and tetrahedrite. Gangue minerals include quartz, calcite, and minor sericite and chlorite [11]. The presence of abundant gypsum, cerussite and covellite near the surface is interpreted as secondary.

Mineralization dominantly occurs in banded ores (Figure 5A), vein (Figure 5B,D), laminated ores (Figure 5C) and massive ores (Figure 5E,F–I).



Figure 5. Photographs showing occurrences and texture of the stratabound ores at Laochang deposit. (A) Banded sulfide ore in 1650 m mining tunnel. (B) Tuff in 1700 mining tunnel crosscuts by vein and veinlet sulfide ore. (C) The metal zonation from top to bottom: Pb-Zn ore to Fe-(Cu) ore from stratabound ores 1700 level. (D) Pyrite-sphalerite-galena vein filling in the fracture of tuff in 1650 m mining tunnel. (E) Galena-calcite vein crosscuts the stratiform ore in 1700 mining tunnel. (F) Massive coarse-pyrite ore in 1700 mining tunnel. (G) Massive sulfide ore composed of pyrite, sphalerite and minor chalcopyrite. (H) The clear contact boundaries between the tuff and massive sulfide ore from 1650 mining tunnel. (I) The clear contact boundaries between the dolomite and massive sulfide ore in 1750 mining tunnel. Mineral abbreviations: Q = quartz, Py = pyrite, Sp = sphalerite, Gn = galena.

The principal ore textures are euhedral-subhedral granular, colloform, veinlet-vein filling, cataclastic texture and metasomatic relict. Pyrite is the predominant mineral of this deposit, which usually occurs as medium-coarse grain euhedral aggregates (Figure 5G–I). It also occurs in metasomatic relict (Figure 6A,B,D–F), colloform masses with recrystallized texture (Figure 6A,B) and cataclastic texture (Figure 6H). Galena is the main carrier mineral of Ag, e.g., Ag content of galena from ore cluster No. II exceed 6900 ppm by electron microprobe analysis [43]. They are euhedral-subhedral granular and vein, which fill in the edge of pyrite (Figure 6G), sphalerite or dissolution and replacement the euhedral pyrite (Figure 6D–F). In addition, independent Ag minerals, such as argentite wrapped in the galena, are observed [11]. Sphalerite is characteristically fine-grained,

euhedral-subhedral granular (0.02–10 mm), which is replaced by galena (Figure 6D) or replaces galena and pyrite (Figure 6A,B,F). The chalcopyrite replaces pyrite (Figure 6B) or fills in fracture of pyrite (Figure 6F). Arsenopyrite, pyrrhotite and tetrahedrite are mainly fine-grained anhedral and intergrow with other sulfides (e.g., pyrite, sphalerite and galena) [11,47].



Figure 6. Mineral assemblages and textures of the stratabound ores. (A) Colloform pyrite replaced by sphalerite and galena. (B) Colloform pyrite replaced by sphalerite, chalcopyrite and galena. (C) Euhedral coarse grain pyrite crosscuts by quartz and calcite. (D) Euhedral pyrite replaced by sphalerite and galena, and chalcopyrite fills the fractures of pyrite. (E) galena and sphalerite replaced by pyrite. (F) Chalcopyrite filling in fracture of pyrite. (G) Coarse-grain pyrite crosscut by galena vein. (H) Chalcopyrite veinlets filling cracks in subhedral pyrite. (I) Interstitial filling of galena and sphalerite in subhedral pyrite. All microphotographs were taken under reflected plane-polarized light. Mineral abbreviations: Cal = calcite, Py = pyrite, Sp = sphalerite, Gn = galena, Cp = chalcopyrite, Cal = calcite, Q = quartz.

Based on field and microscope observation of crosscutting relationships, together with previously published geological data [8], the hydrothermal mineralization process of Laochang deposit can be divided into four stages (Figure 7), as follows: The hydrothermal stages I, II, III and IV. Abundant colloform pyrite (Py₁) was observed in hydrothermal stage I (Figure 6A,B). Hydrothermal stage II contains coarse-cubic pyrite (Py₂), black sphalerite (Sp₁), galena (Gn₁) and minor chalcopyrite (Cp₁) and quartz (Figure 6A–I). Stage III is represented by minor auhedral pyrite (Py₃), sphalerite (Sp₂), galena (Gn₂), chalcopyrite (Cp₂), quartz and minor arsenopyrite, pyrrhotite and tetrahedrite (Figure 6C,F,H). In stage IV, calcite filled in the fracture of galena and pyrite (Figure 6D) and quartz (Figure 6C).

Stages

Stage I

Minerals

Colloform pyrite Coarse-grain pyrite

Seafloor hydrothermal stage											
Stage II	Stage III	Stage IV									

Sphalerite				
Galena				
Chalcopyrite				
Quartz		<u> </u>		
Arsenopyrite				
Pyrrhotite				
Tetrahedrite				
Calcite				
Chlorite				
Sericite				
Main		– Minor –	Loc	ally occuring

Figure 7. Mineral paragenesis in the Laochang Ag-Pb-Zn-Cu deposit.

4. Sample and Analytical Methods

The volcanic rock hosting the stratabound Ag-Pb-Zn-Cu collected for zircon U-Pb dating were collected under the upper orebodies layers (1840 m mining tunnel). The basalt samples used for Pb isotope analysis were collected from the mining adit at 1650, 1725, and 1840 m. The stratabound ores used for sulfide separation were collected from the mining adit at 1650 m and 1700 m, respectively. Representative sulfide samples were crushed to 40–80 mesh, and sphalerite, pyrite, and galena were handpicked under a binocular microscope for Pb isotope analysis. In addition, sphalerite from stratabound ores were used for trace element analysis.

Zircon grains for geochronology were separated by conventional heavy liquid and magnetic techniques, then handpicked under a binocular microscope, and mounted in epoxy. The mount was polished to expose the interior of the grains. The grains were photographed using transmitted and reflected light, and following gold coating, cathodoluminescence (CL) images were obtained on a scanning electron microscope (SEM) in order to select the initial analytical sites. U-Pb isotopic ratios were measured on the Sensitive High-Resolution Ion Microprobe (SHRIMP II) at the Beijing SHRIMP Center, Chinese Academy of Geological Sciences, Beijing following procedures outlined in Williams [47]. The intensity of the primary O^{2-} ion beam was 4–5 nA and primary beam size was 30 µm. Each analytical site was rastered for 2–3 min prior to analysis to remove any common Pb on the surface. Five scans through nine mass stations were made for each analysis. Standards used were SL13, with U content of 238 ppm, and TEMORA 1, with a ²⁰⁶Pb/²³⁸U age of 417 Ma [47,48], provided by the Australian National University. Data processing was carried out using the SQUID and ISOPLOT programs [49], applying the ²⁰⁴Pb correction based on the measured values. BR266 (with an age of 559 Ma and U content of ~903 ppm) and TEMORA (417 Ma, with variable U contents) zircon fragments [48], were used as the calibration standards. Uncertainties on individual analyses are based mainly on the counting statistics and are quoted at the 1δ level, whereas uncertainties on weighted mean ages at 95% confidence level (2δ).

For whole-rock analyses, samples were crushed to 200-mesh using an agate mill. Abundances of major elements were determined using an X-ray fluorescence spectrometer (XRF) on glass disks at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), following analytical procedures described by Goto and Tatsumi [50,51]. A pre-ignition was used to determine the loss on ignition (LOI) prior to major element analyses. Analytical uncertainties for the majority of major elements analyzed

were estimated at less than 1% from repeatedly analyzed USGS standards BHVO-2, MRG-1 (basalt) and W-2 (diabase). The measured values of international standards are in satisfactory agreement with the recommended values. Whole-rock trace element data were obtained by ELAN DRC-e inductively coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer, Québec, QC, Canada) at the IGCAS. The powders (~50 mg) were dissolved in distilled HF-HNO₃ in Savillex screw top Telfon vials at 150 °C for four days. More details for the ICP-MS analytical procedures could see Liu et al. [52].

Trace element analysis of sphalerite was carried out on a Finngian MAT ICP-MS (Finnigan MAT, Bremen, Germany) at the National Geological Analytical and Testing Center, Chinese Academy of Geological Sciences, Beijing, using the method of Qi et al. [53] for sample preparation. About 50 mg of powdered sample was dissolved by 1 mL of HF and 1 mL of HNO₃ in a PTFE bomb; then the sealed bombs were heated to 190 °C in an electric oven for about 36 h. After cooling, the bombs were placed on a hot plate to evaporate to dryness. 500 ng of Rh was added as an internal standard, and then 2 mL of HNO₃ and 4 mL of ultrapure water were added. The bomb was again sealed and heated to 140 °C for about 5 h in an electric oven to dissolve the residue. After cooling, the final dilute factor is about 3000 for ICP-MS measurements. GSR-5 was used as the external standard, with an analytical precision of better than 10%. Minimum LOD were usually 1 ppm for the trace elements (Fe, Mn, Cu and Cd) and 0.1 ppm for In and Ag. In addition, LOD of the trace elements (Co, Ni, Ga, Ge, Sn, Sb, Pb and Bi) better than 0.01 ppm analyzed by ICP-MS.

Pb isotope composition analysis was carried out using the GV Isoprobe-T thermal ionization mass spectrometer (TIMS) at the Analytical Laboratory Beijing Research Institute of Uranium Geology (ALBRIUG). The analytical procedure involves dissolution of the sample using HF and HClO₄ in a crucible, followed by treatment with a basic anion exchange resin to purify the Pb. The analytical results for the standard NBS-981 are 206 Pb/ 204 Pb = 16.937 ± 0.002 (2 δ), 207 Pb/ 204 Pb = 15.457 ± 0.002 (2 δ), and 208 Pb/ 204 Pb = 36.611 ± 0.004 (2 δ). Detailed analytical procedures are described by Belshaw et al. [54].

5. Results

5.1. Major and Trace Elements of Volcanic Rocks

Major and trace element data for basalts and basaltic tuff in this study are given in Table 1. The collected samples in this study exhibit slightly higher LOI (>1.75%), suggesting that these rocks might have undergone low-grade metamorphism during post-magmatic events [10,11]. Thus, this study mainly focuses on high field strength elements (HFSEs), rare earth elements (REEs), and transitional elements (e.g., V and Sc) for rock classification and petrogenetic discussion of the Laochang samples. All the whole-rock major element data used in the following discussion are normalized to an anhydrous basis. The Laochang basalts and basaltic tuff in this study plot in or near the fields of alkali basalt series based on the Zr/TiO_2 vs. Nb/Y diagram (Figure 8).

Rock Type				Bas	salt		Basaltic Tuff							
Sample	06LC54	06LC79	1650-31	1650-34	1725-11	1725-21	LC1650-7	LC1840-51	LC09-29	ZK09-41	ZK09-24	ZK09-36	ZK09-44	
SiO ₂	44.01	43.38	44.51	45.20	46.67	45.39	45.65	48.97	48.20	47.69	48.34	46.76	48.06	
Al_2O_3	12.76	12.24	12.97	11.99	13.81	13.00	12.33	13.98	12.86	15.26	18.06	15.31	17.22	
FeO (Total)	15.14	15.54	12.12	11.23	10.40	11.39	15.46	11.9	12.48	12.21	10.46	11.75	11.97	
MgO	9.70	9.86	10.46	13.01	9.73	10.12	10.39	8.09	1.77	2.56	2.00	2.29	1.75	
CaO	8.53	8.12	8.57	9.69	7.55	8.86	8.25	8.56	14.22	12.35	9.34	13.97	8.85	
Na ₂ O	1.59	2.54	0.65	0.28	1.58	1.45	1.12	0.9	2.15	3.07	3.78	3.08	3.54	
K ₂ O	3.17	3.15	4.88	4.83	5.58	5.21	4.19	3.93	3.57	2.67	2.68	2.33	3.68	
MnO	0.17	0.15	0.14	0.13	0.12	0.11	0.14	0.15	0.2	0.22	0.16	0.24	0.13	
P_2O_5	0.77	0.58	1.40	0.85	1.29	0.71	0.12	0.17	1.03	1.37	1.46	1.06	1.23	
TiO ₂	4.16	4.44	4.30	2.79	3.26	3.75	2.35	3.35	3.52	2.6	3.72	3.21	3.57	
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	
LOI	13.38	10.09	1.75	8.80	7.81	6.36	6.29	2.92	15.17	11.69	9.90	15.91	8.26	
Sc	29.17	31.68	26.42	21.28	23.52	22.62	17.10	23.40	17.60	10.30	17.30	12.30	15.80	
V	388	390	334	252	344	242	251	281	204	149	233	209	235	
Rb	102.7	100.7	419.5	244.4	330.4	188.3	358.0	222.0	104.0	50.9	57.6	44.6	78.1	
Ba	123.5	104.3	136.2	128.4	197.3	103.6	799	362	267	1120	427	301	262	
Th	3.68	4.02	6.72	6.06	7.37	6.65	9.33	4.95	5.57	6.02	8.06	6.32	7.68	
U	0.77	1.11	1.47	2.16	2.82	1.57	1.54	3.02	9.19	1.49	1.54	1.14	0.95	
Nb	40.72	43.78	73.96	55.51	74.21	70.62	105.00	64.70	56.10	65.40	85.60	68.20	81.80	
Та	2.36	2.51	3.96	2.89	3.86	3.72	6.57	4.08	3.39	4.27	5.69	4.44	5.43	
La	28.32	30.64	64.37	46.28	63.61	53.82	74	50.9	71.9	76.3	73.7	60.9	71.9	
Ce	63.71	65.98	133.70	90.95	133.40	118.80	163.00	109.00	126.00	103.00	162.00	116.00	152.00	
Sr	413.4	432.5	398.9	288.0	354.4	91.4	182.0	105.0	132.0	439.0	342.0	453.0	371.0	
Nd	34.43	34.14	66.38	41.80	64.16	57.67	69.70	59.90	59.60	75.00	74.50	55.50	68.10	
Sm	7.63	7.07	12.80	8.01	12.32	10.60	13.00	11.60	11.40	14.00	15.40	10.90	13.70	
Zr	231	254	305	199	288	275	356	220	247	295	378	296	360	
Hf	5.09	5.44	5.79	3.81	5.42	5.1	7.29	5.06	5.20	5.88	8.04	7.26	7.86	
Eu	3.01	2.41	4.37	2.38	4.12	3.63	4.51	4.39	6.23	4.57	4.79	3.62	4.27	
Gd	8.25	6.84	11.13	7.49	10.8	9.44	11.35	10.69	10.23	13.48	13.22	9.80	12.01	
Dy	6.50	5.13	7.26	5.03	6.73	5.99	7.31	6.69	7.19	8.89	9.99	7.37	8.94	
Y	29.30	23.56	30.29	22.95	28.42	25.32	32.83	29.72	37.23	43.67	45.71	31.65	40.34	
Yb	2.29	1.88	2.11	1.65	1.95	1.84	2.3	1.87	2.25	3.18	3.54	2.35	3.25	

Table 1. Bulk rock composition of major (wt %) and trace elements (ppm) of Laochang basalt and basaltic tuff.

Tabl	e 1.	Cont.

Rock Type				Ba	salt		Basaltic Tuff						
Sample	06LC54	06LC79	1650-31	1650-34	1725-11	1725-21	LC1650-7	LC1840-51	LC09-29	ZK09-41	ZK09-24	ZK09-36	ZK09-44
Lu	0.33	0.26	0.29	0.23	0.27	0.25	0.33	0.27	0.31	0.44	0.51	0.33	0.46
(La/Sm) _N	2.40	2.80	3.25	3.73	3.34	3.28	3.68	2.84	4.08	3.52	3.09	3.61	3.39
(Gd/Yb) _N	2.98	3.01	4.36	3.75	4.58	4.24	4.08	4.73	3.76	3.51	3.09	3.45	3.06
(La/Yb) _N	8.87	11.70	21.89	20.13	23.41	20.99	23.09	19.53	22.93	17.22	14.94	18.60	15.88





Figure 8. Bulk-rock compositions of the Laochang volcanic rocks in a Zr/Ti versus Nb/Y.

The Laochang basalt samples have SiO₂ of 43.38–48.97%, MgO of 8.09–13.01%, CaO of 7.55–9.69%, Al₂O₃ of 11.99–13.98%, TiO₂ of 2.35–4.44% and P₂O₅ of 0.12–1.40%. In primitive-mantle normalized trace element patterns (Figure 9A), they are characterized by enrichment of HFSEs, such as Nb, Ta, Zr, and Hf, and most large ion lithophile elements (LILEs), such as Rb, Th, U, and light REE, but show Ba and Sr depletion. Chondrite normalized REE patterns (Figure 9B) show weakly fractionated light rare earth element (LREE) patterns, with $(La/Sm)_N = 2.40-4.08$, $(Gd/Yb)_N = 2.98-4.73$, $(La/Yb)_N = 8.87-23.41$.

The basaltic samples have SiO₂ of 46.76–48.34%, MgO of 1.75–2.65%, CaO of 8.85–14.22%, Al_2O_3 of 12.86–18.06%, TiO₂ of 2.60–3.72% and P_2O_5 of 1.03–1.46%. In primitive-mantle normalized trace element patterns and chondrite normalized REE patterns (Figure 9A,B), it has geochemical compositions similar to those of basalt from the Laochang.

Additionally, the trace elements and REE patterns of the basalt and basaltic tuff are almost identical, resembling those of the OIB reservoir formed by oceanic hotspot volcanism [55,56].



Figure 9. Primitive mantle-normalized trace element diagrams. (**A**) and chrondrite-normalized rare earth element (REE) patterns (**B**) for the Laochang basalt and basaltic tuff. The primitive mantle and chrondrite values are from Sun and McDonough [57].

5.2. Zircon U-Pb Geochronology

Data for U-Pb zircon chronological analyses are given in Table 2. Zircon grains from a basaltic tuff samples (LC09-102) display 74.6–1950 ppm Th and 58.63–557.77 ppm U, with Th/U ratios ranging from 1.29 to 3.52. Zircons from this sample show weak oscillatory zoning (Figure 10). Nine analyses are concordant. Our U-Pb zircon dating yielded the 206 Pb/ 238 U concordia age from 303 Ma to 316 Ma with a weighted mean 206 Pb/ 238 U age of 312 ± 4 Ma (MSWD = 1.02). Three spots from three zircon cores have relatively old 206 Pb/ 238 U age from 741 ± 15 Ma to 712 ± 17 Ma, which are interpreted to be inherited components.



Figure 10. Zircon SIMS U–Pb Concordia diagram (**A**,**B**) for the dated volcanic rocks (LC09-102) from the Early Carboniferous Yiliu Formation in Laochang district.

5.3. Trace Elements in Sphalerite

The trace elements in sphalerite from stratabound ores are summarized in Table 3. The ranges in absolute concentration for selected elements are shown in Figure 11.



Figure 11. Histogram of trace elements for sphalerite of the stratabound Ag-Pb-Zn-Cu ores from the Laochang deposit.

The concentrations of trace elements in the various sphalerite samples are relatively homogeneous, except for Cu, Sn, Sb, Bi, and Ag, which vary widely, ranging from 788~7161 ppm, 4.44~702.30 ppm, 3.85~90.19 ppm, 0.84~278.30 ppm, and 11.3~311.0 ppm, respectively. In general, sphalerite from stratabound ores has the following characteristics: (1) Enrichment of Fe, Cd and Mn contents, for which the concentration ranges are 98,800~132,500 ppm (average 111,750 ppm), 3813~4993 ppm (average 4243 ppm), and 1971~4594 ppm (average 3133 ppm), respectively; (2) relative enrichment of In and Ga contents, for which the concentration ranges are 192.1~1576.0 ppm (average 521.8 ppm) and 8.15~45.40 ppm (average 28.10 ppm), respectively; (3) relatively low Co and Ni contents, with concentrations ranging from 0.17~6.53 ppm, with an average of 1.70 ppm, and 1.13~26.68 ppm, with an average of 5.50 ppm; and (4) low Ge, Pb and As contents, with concentrations ranging from 0.41~1.30 ppm, 0.07~2.30 ppm and 34.72~589.60 ppm, with an average of 0.7 ppm, 0.9 ppm and 213.8 ppm, respectively. Collectively, sphalerite of the stratabound ores is characterized by enriched Fe, Mn, Cd, In, and Ga, and depleted Co, Ni, Ge, and Pb. Moreover, the contents of Fe, Mn, Cd, In, Ga Co, Ni, Ge, and Pb are relatively consistent, whereas Sn, Sb, Cu, and Bi show a wide range.

Analysis	1	Element	(ppm)		Isotopic Ratio						Age (Ma)					
1111119010	²³² Th	²³⁸ U	²³² Th/ ²³⁸ U	²⁰⁷ Pb/ ²⁰⁶ Pb	$\pm 1\delta$	²⁰⁷ Pb/ ²³⁵ U	$\pm 1\delta$	²⁰⁶ Pb/ ²³⁸ U	$\pm 1\delta$	²⁰⁶ Pb/ ²³⁸ U	18	²⁰⁸ Pb/ ²³² Th	1δ	²⁰⁷ Pb/ ²⁰⁶ Pb	1δ	
LC09-10-1	391	742	1.96	0.0518	17	0.35	17	0.05	2.4	311.0	7.4	307	13	278	390	
LC09-10-2	286	568	2.05	0.0571	12	0.39	12	0.05	1.8	309.5	5.4	302.8	9.2	494	270	
LC09-10-3	420	793	1.95	0.0511	11	0.34	11	0.05	1.6	304.3	4.9	296.7	7.8	243	260	
LC09-10-4	558	1950	3.61	0.051	6.3	0.35	6.5	0.05	1.6	315.5	4.8	309.5	5.9	243	150	
LC09-10-5	495	1688	3.52	0.0564	5.3	0.39	5.5	0.05	1.6	316.5	5.0	307.8	6.2	470	120	
LC09-10-6	177	407	2.38	0.0649	14	0.43	14	0.05	2.1	303.0	6.1	293	13	772	300	
LC09-10-7	72	90	1.29	0.058	18	0.96	19	0.12	3.9	730.0	27	655	53	523	400	
LC09-10-8	301	592	2.03	0.0577	9.5	0.39	9.7	0.05	1.8	308.1	5.3	308.7	8.9	520	210	
LC09-10-9	419	1209	2.99	0.0513	13	0.36	13	0.05	1.7	316.0	5.3	306.3	7.4	254	290	
LC09-10-10	59	75	1.31	0.0677	6.9	1.09	7.3	0.12	2.5	712	17	708	34	858	140	
LC09-10-11	115	173	1.56	0.067	9.8	1.13	10	0.12	2.1	741	15	738	31	839	200	
LC09-10-12	359	769	2.21	0.0568	9.6	0.39	9.8	0.05	1.7	316.7	5.2	310.0	7.9	483	210	

Table 2. SHRIMP zircon U-Pb isotopic data for basaltic tuff of the Laochang.

Table 3. Trace elements in sphalerite from stratabound ores of Laochang deposit.

Sample Na.	Zn	Fe	Mn	Со	Ni	Cu	Ga	Ge	As	Ag	Cd	In	Sn	Sb	Pb	Bi
Lcs75	49.79	112,000	4026	1.57	6.61	4912	30.32	0.64	88.74	15.0	4250	633.2	35.79	8.56	0.37	0.84
Lcs67	48.96	110,500	2768	3.14	1.64	1079	24.48	0.86	34.72	64.1	4993	941.7	19.58	53.34	2.30	0.87
Lcs76	50.66	110,500	3258	4.09	4.36	7161	30.65	0.47	105.80	27.2	4201	1576.0	25.7	19.79	1.19	1.31
Lcc5	49.59	98,800	1971	1.49	12.67	5058	21.31	1.30	80.76	48.7	3859	696.6	12.21	30.51	1.69	2.60
Lcs68	50.57	132,500	4594	1.84	2.92	2765	45.40	0.64	90.46	16.4	4186	849.4	702.3	11.86	0.63	2.74
Lcs69	48.72	117,800	2785	1.12	1.43	2398	26.55	0.62	62.35	11.3	4420	558.2	13.10	6.97	0.46	4.78
Lc117	48.47	100,400	3154	2.27	2.17	1053	19.29	0.58	43.45	13.8	4717	192.1	12.52	10.08	0.51	6.21
Lcb5	48.95	110,800	2562	6.53	1.13	788	8.15	0.41	543.30	17.6	3867	217.4	4.44	3.85	0.07	12.28
Lcs73	51.14	92 <i>,</i> 550	3211	1.10	26.68	3307	36.90	1.13	54.93	67.3	4690	289.5	15.84	13.75	0.96	27.30
Lcc27	49.81	123,100	3168	0.17	4.80	2887	44.44	0.67	543.60	78.7	4303	502.0	514.4	25.26	0.40	39.06
Lcc9	51.58	112,600	3052	0.87	5.89	4129	30.81	0.99	46.10	43.7	4424	532.0	20.20	22.80	1.77	59.02
Lcc16	48.66	102,400	2977	0.20	1.28	1321	28.56	0.65	429.40	43.8	3914	308.8	21.51	8.60	0.29	72.71
Lcc28	48.77	123,600	3278	0.93	2.39	1584	23.56	0.55	411.50	311.0	3874	353.3	12.49	22.08	0.92	131.30
Lcs48	50.52	121,100	2820	0.31	5.26	6720	12.90	0.41	82.53	82.5	3813	871.3	50.92	90.19	1.31	174.80
Lk16	50.44	107,600	3377	0.21	3.05	1096	38.44	0.90	589.60	126.0	4126	356.1	32.98	20.27	0.82	278.30
Min	48.47	98,800	1971	0.17	1.13	788	8.15	0.41	34.72	11.3	3813	192.1	4.44	3.85	0.07	0.84
Max	51.58	132,500	4594	6.53	26.68	7161	45.40	1.30	589.60	311.0	4993	1576.0	702.30	90.19	2.30	278.30
Mean	49.8	111,750	3133	1.70	5.50	3084	28.10	0.70	213.80	64.5	4243	591.8	99.60	23.20	0.90	54.30
S.D.	3.11	34,500	2623	6.36	25.55	6373	37.25	0.89	554.88	299.7	1180	1383.9	697.96	86.34	2.23	277.46

Notes: Zn is expressed in wt % and trace element contents are expressed in ppm, and S.D. stand for standard deviation in this table.

5.4. Pb Isotopes

Lead isotope data for the volcanic rock, granitic porphyry and sulfide samples from stratabound mineralization are listed in Table 4. The seven volcanic samples have whole-rock 206 Pb/ 204 Pb ratios of 18.595 to 18.918, 207 Pb/ 204 Pb ratios of 15.597 to 15.749, and 208 Pb/ 204 Pb ratios of 38.852 to 39.112, which are characterized by high radiogenic Pb isotopic composition. The lead isotope ratios of galena, pyrite, and sphalerite from stratabound ores are 18.341 to 18.915 for 206 Pb/ 204 Pb, 15.376 to 15.770 for 207 Pb/ 204 Pb, and 38.159 to 39.200 for 208 Pb/ 204 Pb.

Xu et al. [58] and Zhao et al. [59] reported lead isotope composition of concealed granitic porphyry, which is relatively homogeneous: ${}^{206}Pb/{}^{204}Pb = 17.988$ to 18.621, ${}^{207}Pb/{}^{204}Pb = 15.586$ to 16.663, ${}^{208}Pb/{}^{204}Pb = 38.246$ to 38.910 (Table 4).

Sample No.	Sample Na.	Sample Location	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	References
E-51	Granitic porphyry	ZK14827–998.5 m	18.205	15.586	38.405	
E-67	Granitic porphyry	ZK14827–214.8 m	18.426	15.601	38.623	
E-73	Granitic porphyry	ZK14827-302.8 m	18.564	15.62	38.774	Zhao et al. [59]
E-82	Granitic porphyry	ZK14827–389 m	18.621	15.663	38.910	
E-84	Granitic porphyry	ZK14827–412 m	18.283	15.628	38.524	
88061	Granitic porphyry	ZK15007–355 m	18.561	15.614	38.695	
88088	Granitic porphyry	ZK15006-427 m	17.988	15.652	38.246	Xu et al. [58]
88090	Granitic porphyry	ZK15006-440 m	18.552	15.661	38.766	
LC091700-27	Pyrite	1700 mining tunnel	18.601	15.659	38.835	
LC091700-41	Pyrite	1700 mining tunnel	18.623	15.646	38.823	
LC091700-45	Pyrite	1700 mining tunnel	18.657	15.682	38.935	This study
LC091700-49	Sphalerite	1700 mining tunnel	18.651	15.643	38.880	This study
LC091700-53	Sphalerite	1700 mining tunnel	18.449	15.487	38.423	
LC091700-54	Sphalerite	1700 mining tunnel	18.452	15.528	38.396	
Lc1925-3	Galena		18.736	15.758	39.09	
Lc1925-5	Galena		18.700	15.732	39.100	Va at al [12]
Lc1925-12	Galena		18.748	15.77	39.197	ie et al. [42]
Lc1925-13	Galena		18.716	15.729	39.087	
Ly017	Galena		18.500	15.480	38.380	
Ly020	Galena		18.510	15.500	38.410	
Ly016	Galena		18.590	15.600	38.68	
Lc-3G	Galena		18.726	15.761	39.200	Listal [9]
Lc-9G	Galena		18.657	15.700	38.973	Li et al. [o]
Lc-12G	Galena		18.726	15.762	39.200	
Lc-4P	Pyrite		18.676	15.699	39.000	
Lc-9P	Pyrite		18.709	15.763	39.191	
1700-23	Basalt	1700 mining tunnel	18.668	15.597	38.852	
1725-27	Basalt	1725 mining tunnel	18.595	15.672	38.867	
1700-5	Basalt	1700 mining tunnel	18.619	15.672	38.905	This study
1650-19	Basalt	1650 mining tunnel	18.612	15.657	38.901	
1700-6	Basalt	1700 mining tunnel	18.751	15.668	39.112	
87-B8	Basalt		18.661	15.709	38.902	Vu et al [50]
8725_1	Volcanic rock		18.918	15.749	39.037	Au et al. [56]

Table 4. Pb isotope data of rock and sulfides from the Laochang deposit.

6. Discussion

6.1. Age of Stratabound Mineralization

Zircon grains from the Carboniferous volcano-sedimentary sequence (Yiliu Formation) in Laochang deposit show morphological and compositional features typical of magmatic zircons (Figure 10, Table 1). The precise SHRIMP zircon U-Pb age (312 ± 4 Ma) present here provides a tight constraint on the eruption timing of Yiliu Formation basaltic tuff in 1840 m mining tunnel. This age is much younger than previous studies (320.8 ± 2.7 Ma by LA-ICP-MS, Deng et al. [17]; 323.6 ± 2.8 Ma by SHRIMP, Chen et al. [60]), which either reflect multistage magmatic eruption at Laochang or different analytical protocols used by those authors. Our field observations and drill core logging identify that the Yiliu Formation is composed of two lava-agglomerates-breccia-tuff-sedimentary basic groups.

Thus, it is suggested that the different ages have more likely resulted from multiple volcanic activities which have occurred at Laochang deposit in Carboniferous.

As mentioned above, the stratabound ores host in the top of the two volcanic cycles (Figure 4). Li et al. [11] and our view infer that at least two main stages of mineralization occurred in stratabound ores, i.e., at the first dormant period of volcanic activity and at the second intermittent period of volcanism marked by the sediment influx. Liu et al. [61] obtained a Re-Os isochron age of 308 ± 5 Ma on galena and sphalerite from upper stratabound ores (1930 m mining tunnel), which is slightly younger than a SHRIMP zircon U-Pb age of 312 ± 4 Ma for the footwall basaltic tuff from 1840 m mining tunnel. This result demonstrated that the ages of upper stratabound mineralization are approximately similar/slightly younger than the footwall volcanic rocks in 1840 m mining tunnel [18]. In constrast, the timing of lower stratabound ores is still unclear. Chen et al. [60] obtained a SHRIMP zircon U-Pb age of 323.6 \pm 2.8 Ma for the footwall tuff from 1725 m mining tunnel. More importantly, the geologic cross section shows that the orebodies are in conformity with the host volcanic rocks, occurring in bedded or bed-like form, lenticular and intercalated with sedimentary rocks, e.g., black shale, shallow marine, tuffite and siliceous rock, massive bioclastic limestone and biological fossils [62], which show the synvolcanogenic orgin. The presence of sulfide orebody underlying volcanic rocks place a maximum age for the lower stratabound mineralization (Figure 4). The timing of upper stratabound ore is considered as the minimum mineralization age (Figure 4). Therefore, the emplacement of stratabound mineralization is likely between ~323 Ma and 308 Ma. A similar age has been proposed for the Laochang stratabound mineralization by Hou et al. [2] and Deng et al. [40].

6.2. Source of Metals

The spatial relationship between the stratabound orebodies and the Cenozoic porphyry intrusion, coupled with the hydrothermal alteration assemblages, has led many authors to propose a genetic connection between the stratabound mineralization and the granitic porphyry magmatism [12,15–17]. They argue that the stratabound orebodies are a shallow product of the concealed porphyry-skarn Mo system. However, the significant difference between the Pb isotope signatures of stratabound ores and granitic porphyry (Figure 12A,B), together with very wide Pb isotope variation of stratabound ores, does not support a genetic relationship with the porphyry intrusion. Additionally, the data of trace elements in sphalerite and Y/Ho ratio reported by Ye et al. [63], which basically preclude the ore-stage metals were derived from Cenozoic porphyry magmatism.

Interestingly, on the Pb-Pb diagrams (Figure 12A,B), the Pb isotope signature of stratabound ore samples present good linear arrays (206 Pb/ 204 Pb vs. 207 Pb/ 204 Pb, correlation coefficient R² = 0.943; 207 Pb/ 204 Pb vs. 208 Pb/ 204 Pb, correlation coefficient R² = 0.984), which are identical to those reported for the Dapingzhang and Keketale VMS deposits in China [64,65], as well as VMS deposits in the other parts of the world [66,67]. Moreover, the Pb isotope signatures define a well-correlated trend, which suggests a mixing of two distinct source components characterized by different Pb isotope compositions, i.e., the radiogenic Pb-rich endmember and the nonradiogenic Pb-rich reservoir. As mentioned above, volcanic rocks are reflected by high radiogenic Pb isotopic composition, and a portion of the Pb isotope signature of sulfide samples are similar to that of the host volcanic rocks (Figure 12A,B), thus, we consider that the radiogenic Pb-rich metal stem from the host volcanic rocks. Moreover, Zhang et al. [68] demonstrate that the mantle reservoir of western Yunnan district is relatively enriched in low 208 Pb/ 204 Pb and 207 Pb/ 204 Pb, and another small fraction of sulfide samples fall into that area in Pb-Pb diagrams (Figure 12A,B). Therefore, a likely interpretation for the linear arrays of Pb isotope signatures show a mixed source, respectively, for leaching the volcanic rocks of the Yiliu Formation and mantle reservoir.

In summary, the Pb isotope compositions of sulfide samples from stratabound ores support that the host volcanic rocks of Yiliu Formation and the mantle reservoir were the main source of Pb in the Laochang district. Conversely, no Pb appears to have been sourced in the spatially associated Eocene granitic porphyry, as their Pb isotope compositions are significantly different from those of the sulfide samples.



Figure 12. Pb isotopic compositions of granitic porphyry, volcanic rocks, and stratabound ore from the Laochang deposit. (**A**) Plots of 206 Pb/ 204 Pb vs. 207 Pb/ 204 Pb. (**B**) Plots of 208 Pb/ 204 Pb vs. 207 Pb/ 204 Pb. Data are listed in Table 4.

6.3. Trace Element Constraints

Trace element contents in sphalerite from different genetic type of deposit are diagnostic, under the assumption that no overprint has occurred [69–73]. The skarn deposits feature high Co and Mn; their distal character is reflected by low In. The syngenetic massive sulfides deposit is characterized by elevated In, Sn and Ga, whereas the MVT deposits are typically enriched in Ge, Cd, Tl, and As [71]. Thus, the measured trace elements in sphalerite likely show promise as tracer for genetic type of mineral deposit. The genetic type of stratabound deposit can, to a large extent, be determined by comparing the trace element concentration in sphalerite.

Sphalerite from stratabound orebodies is characterized by low Co, Ni and Ge, which differs from the distal skarn deposits (Co > 200 ppm, In < 10 ppm), MVT and sandstone-hosted Pb-Zn deposits (Ge > 20 ppm, Mn < 100 ppm), and they also contrast markedly with the magmatic-hydrothermal deposits of the Middle-Lower Yangtze River Valley metallogenic belt, China [63]; the sphalerite is relatively enriched in Fe, Mn, In and Ga, which show strong similarities with VMS deposits (In > 50 ppm and Mn > 1000 ppm) of southern China [69,71], as well as VMS deposits elsewhere in the world [70,73]. Furthermore, on trace discrimination diagrams of Fe-In, Mn-Fe, Mn/Fe-In, In/Cd-Fe, Fe-In/Ge, Mn-Co, and In-Mn (Figure 13), the samples from stratabound orebodies plot within the VMS deposits field (Sauda, Western Norway; Kaveltorp and Marketorp, South-Central Sweden; Cook et al. [70]) and are distinct from the epithermal deposits (Baia de Aries, Rosia Montana and Magura, SE Europe; Cook et al. [70]), magmatic hydrothermal vein type deposit (Jinbao, China; Zhou et al. [74]) and distal skarn deposit (Luziyuan and Hetaoping, China; Ye et al. [71]). In addition, they are also different from MVT (East Tennessee district, USA; Tres Marias mine, Mexico; Limei, Yutang, Niujiaotang, Mengxing, Huize, Nayongzhi and Tianbaoshan deposits, China; Cook et al. [70]; Ye et al. [71,75]; Wei et al. [76]) and sandstone-hosted Pb-Zn deposits (Jinding, China; Ye et al. [71]).



Figure 13. Binary plots of Fe vs. In (**A**), Mn vs. Fe (**B**), Fe vs. In/Ge (**C**), Mn vs. Co (**D**), Fe vs. In/Ge (**E**), Mn vs. Co (**F**) and Mn vs. In (**G**) in sphalerite from the Laochang stratabound ores and Mississippi Valley-type (MVT), volcanogenic massive sulfide (VMS), epithermal, distal skarn, Sandstone-hosted, magmatic hydrothermal vein-type Pb-Zn deposits in China, NE Europe, Canada, Mexico and Japan. Note: Plots are based on data from Cook et al. [69], Ye et al. [71,75], Zhou et al. [74] and Wei [76].

Collectively, the trace element characteristic of the fifteen sphalerite samples from the stratabound ores are similar to that of the VMS deposits rather than magmatic-hydrothermal deposits, which exclude the Cenozoic concealed granitic porphyry as potential source rocks.

6.4. Implications for Ore Genesis of Stratabound Ores

Genesis of the stratabound ores in volcanic rocks at Laochang has been debated for many years [13,14,17,77,78]. Some authors interpreted the genesis of stratabound ores to be magmatic-hydrothermal deposit [13,14] based on a limited database. Others hold the opinion that the stratabound

ores is of syngenetic volcanogenic origin [17,77]. If the stratabound ores were genetically related to the concealed porphyry and thus interpreted as a magmatic-hydrothermal deposits, it should be characterized by: (a) Fault-controlled orebody showing clearly epigenetic origin; (b) timing of mineralization approximately contemporaneous with the emplacement age of granitic porphyry; (c) the majority of the metal derived from the coeval granitic porphyry. However, the stratabound ores is distinct from the magmatic hydrothermal deposit in: (a) The stratabound ores hosted in the top of two volcanic cycles, similar to the Tongchangjie and Dapingzhang VMS deposit in STMB, which would indicate that mineralization occurred at the intermittent stage of volcanic activity; (b) orebodies occurred mostly stratiform, stratoid, as lens or intercalated within sedimentary and volcano-sedimentary rocks like black shale, tuffite and siliceous rock, massive bioclastic limestone and biological fossils [62]; (c) abundant recrystallized colloidal pyrites with formation of atoll structures from colloform pyrite aggregates (Figure 6A,B), similar to that described from the Kuroko-style VMS deposits in Japan [79]; (d) the Pb isotopic compositions of sulfide samples from strataound ores is significantly different from the hidden granitic porphyry. In addition, the trace element in sphalerite from stratabound ores is enriched in Fe, Mn, Cd, In and Ga, which is significantly distinct from those of magmatic-hydrothermal deposit.

In summary, newly obtained zircon SHRIMP U-Pb geochronology, trace element in sphalerite and Pb isotopes, together with ore deposit geology and mineralogy, suggest stratabound ores should be classified as a VMS deposit.

6.5. Tectonic Setting and Geodynamic Setting of VMS Deposit

The Changning-Menglian Suture zone has experienced opening of the Changning-Menglian Paleo-Tethys, subduction of the oceanic plate, terrane-continent collision, and post-collisional uplift [80–82]. The presence of 349–331 Ma gabbros of ophiolite complex and the Middle Devonian deep water marine cherts, Eoalbaillella lilaensis radiolarians [23,24] suggest that opening of the Changning-Menglian Paleo-Tethys occurred during the Middle Devonian then spread, evolving into the one segment of the Paleo-Tethys main ocean [4,83]. Previous studies consider that subduction-related magmatism in Changning-Menglian Suture zone mainly occurred during the Late Carboniferous-Middle Permian [83–85]. Jian et al. [28] considered that the subduction of the Paleo-Tethys oceanic plate was generated in the middle Permian, as recorded by the meta-gabbros from the Damoguanfang supra-subduction zone (SSZ-type) ophiolites $(267.1 \pm 3.1 \text{ Ma by zircon U-Pb})$. The Changning-Menglian Paleo-Tethys oceanic plate underneath the Simao block has resulted in the formation of Nanlinshan and Banpo mafic-ultramafic intrusions, which were emplaced at 298–292 Ma [27,86] and 295–286 Ma [28,86], respectively. Subduction is further evidenced by the presence of the subduction -related intrusive rock with SHRIMP U-Pb age of tonalite, microgabbro, plagioclase hornblendite and diabase from 306 to 281 Ma in the north of this suture [28,86]. All evidences suggest that the initial subduction of the Changning-Menglian Paleo-Tethys oceanic plate was at Late Carboniferous (~306 Ma).

Laochang district is located in the South Changning-Menglian suture, and the volcanic rocks in this study exhibit typical OIB-like geochemical signature, such as elevated HFSEs (Nb, Ta, Zr and Hf) abundance, slight enrichment of LREE and depletion of Ba and Sr with obvious Nb-Ta anomalies $((Nb/La)_N = 0.87-1.11)$. Such characteristics suggest that the magma source is similar to typical oceanic island basalt [57]. In the Ce/Nb vs. Th/Nb and Th/Yb vs. Nb/Yb discrimination diagrams (Figure 14 A,B), all samples plot in or near the field of OIB, and in the Ti/50–V–5 × Sc and Ti/50–V–50 × Sm diagrams (Figure 14C,D), they plot in the fields of OIB [87,88]. Moreover, the OIB-like volcanic rocks intercalated with sedimentary rocks, e.g., black shale, siliceous rock, massive bioclastic limestone and fossils [62] and the continental substance were not observed in the overlying Carboniferous limestone and dolomite [89]. Thus, this suggest that the basalt were generated in the oceanic island setting (Figure 15A,B) [90]. Moreover, the OIB-like volcanic rocks were formed between ~323 Ma and 312 Ma, which could be approximately synchronous with the VMS mineralization at Laochang

(Figure 15B). Thus, this suggest that the timing of stratabound mineralization precedes the earliest record for subduction of the Paleo-Tethys oceanic plate.



Figure 14. Discrimination diagrams of mantle source for the Laochang volcanic rocks. (**A**) Th/Yb vs. Ce/Nb diagram from Sandeman et al. [91] and Taylor and Martinez [92]; (**B**) Nb/Yb vs. Th/Nb diagram. Discrimination fields of oceanic arcs, continental arcs, Mariana Trough back-arc basin basalts (BABBs) and mid-ocean ridge basalt (MORB)—oceanic island basalt (OIB) mantle array are from Pearce [93–95]. (**C**) Ti/50–50 × Sm–V ternary diagram and (**D**) Ti/50–50 × Sm–V ternary diagram from Vermeesch et al. [87,88].

Collectively, all geochemical and geochronological evidences confirm that the Laochang VMS mineralization generated in oceanic island setting prior to the subduction of Changning-Menglian Paleo-Tethys Ocean, corresponding with the VMS mineralization associated with submarine volcanism around the world [18,96].



Figure 15. (**A**) General sketch shows the tectonic setting of the Laochang ore deposit. (**B**) Proposed genetic model for the Laochang Ag-Pb-Zn-Cu deposit. High temperature, high salinity, metal-charged (Fe, Cu, Pb, Zn, and Ag) and H₂S-rich fluids were degassed directly from the shallow (sub-volcanic) fractionating magma chamber, and subsequently ascended and combined with the infiltration of seawater leaching metals from host volcanic rocks; then metal-rich hydrothermal fluid mixed with cold seawater causing the precipitation of stringer, disseminated and massive sulfide ores.

7. Conclusions

To briefly summarize our main findings in the Laochang Ag-Pb-Zn-Cu deposit, we have shown the following:

- 1. Newly geochronological data show the basaltic tuff (SHRIMP zircon U-Pb = 312 ± 4 Ma), combined with previous studies (zircon U-Pb = 323.6 ± 2.8 Ma, Chen et al. [60]; galena and sphalerite Re-Os = 308 ± 5 Ma, Liu et al. [61]), we consider that the stratabound mineralization occur in the Late Paleozoic (~323-308 Ma).
- 2. The trace element in sphalerite from stratabound ores is characterized by elevated Fe, In, Sn, and Ga, similar to typical VMS deposit; and Pb isotope ratios in sulfides display a steep linear trend, indicating the Pb originated from multiple sources via the mixing effect of leaching between the host rock and mantle reservoir.
- 3. The combined evidence of geology, Pb isotope, trace elements in sphalerite, along with the geochronology suggested that the stratabound ores formed in Carboniferous at Laochang deposit would be better attributed to a VMS deposit.

4. The volcanic rocks hosting the stratabound ore show elevated HFSEs (Nb, Ta, Zr and Hf) abundance, slight enrichment of LREE and depletion of Ba and Sr with obvious Nb-Ta anomalies. Such characteristics suggest that their magma is similar to typical oceanic island basalt, which suggests that Laochang VMS mineralization was generated in the oceanic island setting preceding the initial subduction of the Paleo-Tethys oceanic plate.

Author Contributions: C.W., L.Y. and Z.H. proposed and organized the project; C.W., Z.H. and W.G. discussed and designed and performed the experiment; C.W., Y.H. and Z.L. analyzed and interpreted the data; C.W. wrote the main manuscript; Z.H., L.Y. and J.Z. revised the main manuscript. All the authors discussed the study.

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