



# Article Geological and Geochemical Characteristics and Genesis of the Laoyingqing Zinc Deposit in Northeastern Yunnan

Jinhang Lu<sup>1</sup>, Hongsheng Gong <sup>1,2,\*</sup>, Peng Wu<sup>1,2,\*</sup> and Changqing Zhang <sup>3</sup>

- <sup>1</sup> Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China; 18789491716@163.com
- <sup>2</sup> Southwest Institute of Geological Survey, Geological Survey Center for Non-Ferrous Metals Resources, Kunming 650093, China
- <sup>3</sup> Ministry of Natural Resources (MNR) Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China; zcqchangqing@163.com
- \* Correspondence: 20070088@kust.edu.cn (H.G.); wupeng8104@163.com (P.W.)

Abstract: The Laoyingqing zinc deposit is located in the Pb-Zn deposit concentration district in northeastern Yunnan, with a geotectonic location on the southwestern edge of the Yangtze block. This deposit occurs in the interlayer fracture zone of the Huangcaoling Formation slate in the Middle Proterozoic Kunyang Group. In this deposit, zinc is significantly enriched compared to lead, and the sulfur isotopic composition of sphalerite shows  $\delta^{34}S_{CDT}$  close to negative values. These characteristics are different from the common Pb-Zn deposits that occur in Sinian and Carboniferous carbonate rocks in northeastern Yunnan. The genesis of this deposit and its similarities to and differences from other Pb-Zn deposits hosted in carbonate rocks in the Sichuan-Yunnan-Guizhou Pb-Zn metallogenic triangle area (SYGT) need further research. This article selects typical rock (ore) samples for fluid inclusion, trace element, and H–O isotope analyses. The results show that (1) the homogenization temperature of the fluid inclusions is 130~306.5 °C, the salinity is 7.17 wt%~20.67 wt% NaCleq, and the density of the ore-forming fluids is 0.86–1.07 g/cm<sup>3</sup>. Overall, these ore-forming fluids belong to medium-low-temperature, medium-low-salinity, and medium-low-density ore-forming fluids, and they have reducibility. The fluid pressure is 36.3~85.6 Mpa, and the mineralization depth is 1.34~3.17 km. (2) The ore-forming fluids mainly came from deep-source metamorphic water and basin brine containing organic matter. (3) The ore-forming materials mainly came from the surrounding rocks (Kunyang Group). (4) The trace element characteristics of this deposit are different from sedimentary-exhalative type, magmatic hydrothermal type, and skarn type of Pb-Zn deposits, and have little difference from MVT Pb-Zn deposits. Based on the comprehensive analysis, this deposit is classified as a medium-lowtemperature hydrothermal vein-type zinc deposit unrelated to magmatic activity. This study extends the ore-bearing surrounding rocks of Pb-Zn deposits in the SYGT to the slate of the Kunyang Group, enriching the regional Pb-Zn deposit mineralization theory and providing new ideas for mineralization prediction.

**Keywords:** fluid inclusions; H–O isotope; trace elements; source of ore-forming materials; Laoyingqing zinc deposit; Sichuan–Yunnan–Guizhou Pb-Zn metallogenic triangle area (SYGT); medium–low-temperature hydrothermal vein-type zinc deposits

## 1. Introduction

Different scholars have proposed different viewpoints on the genesis of Pb-Zn deposits in the SYGT. The viewpoints of most scholars are that they are the Mississippi Valley type (MVT) and the strata-bound type dominated by sedimentation [1–3]. By contrast, Han Runsheng et al. [4] proposed they are the Huize type (HZT).



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The Laoyingqing zinc deposit is about 19 km in horizontal distance from Huize County, Yunnan Province, with a geotectonic location on the southwestern edge of the Yangtze block. Previous research on this deposit mainly includes the following: (1) Yang Xiaoxia [5] and Bian Shantao et al. [6] believed that the ore body is controlled by fault fracture zones, and the genesis of this deposit is a fracture-filling vein-type Pb-Zn deposit, whereas (2) Gong et al. [7] studied the composition of Pb and Sr isotopes and believed that the ore-forming metals mainly came from surrounding rocks (Kunyang Group).

The Laoyingqing zinc deposit is hosted in the slate of the Huangcaoling Formation of the Kunyang Group, and zinc is significantly enriched compared to lead in this deposit. Being unlike other common Pb-Zn deposits hosted in Sinian and Carboniferous carbonate rocks in northeastern Yunnan, the genesis of this deposit and its similarities to and differences from other Pb-Zn deposits hosted in carbonate rocks in the Sichuan–Yunnan–Guizhou Pb-Zn metallogenic triangle area (SYGT) need further research. Previous comprehensive research on this deposit is relatively weak, with unclear sources of ore-forming fluids and unclear ore-forming mechanisms. Due to the limitations of analysis and testing methods, current understanding of the genesis of this deposit and other issues is relatively vague and controversial. This article selects typical sulfide minerals and wall rock minerals from the Laoyingqing zinc deposit, and uses fluid inclusion temperature measurement, trace element analysis, and H–O isotope analysis to trace the characteristics and sources of ore-forming fluids, thereby determining the genesis of the deposit. The results of this study not only enrich the ore-forming theory of regional Pb-Zn deposits, but also provide a basis for deep and peripheral ore exploration of this deposit.

## 2. Metallogenic Geological Background

The SYGT is located on the western edge of the Yangtze platform (Figure 1a), with its layers mainly including basement and sedimentary cover. The Yangtze platform has a "double-layered basement" structure, and the crystalline basement is composed of the Archean Kangding Group. The folded basement is composed of the Middle Proterozoic Yanbian Group, the Huili Group, and the Kunyang Group [8]. The region is widely developed, with north–south-, northeast-, and northwest-trending faults and folds (Figure 1b). The Pb-Zn deposit concentration district in northeastern Yunnan is distributed within the "triangle area" enclosed by three deep and large faults: the north–south Xiaojiang Fault, the northwest Yadu–Ziyun Fault, and the northeast Mile–Shizong Fault. Almost all Pb-Zn deposits in the area are distributed along deep and large fault zones and secondary structures, with obvious structural ore-control effects.

The exposed strata in the mining area of the Laoyingqing zinc deposit include the Middle Proterozoic Kunyang Group Huangcaoling Formation  $(Pt_2h)$ , the Heishantou Formation  $(Pt_2hs)$ , the Sinian Dengying Formation  $(Z_2dn)$ , and the Quaternary System (Q). Among them, the lower section of the Middle Proterozoic Kunyang Group Huangcaoling Formation  $(Pt_2h_1)$  is the main ore-bearing layer, and the lithology of this section is thinto-medium-layered slate with a small amount of limestone and dolomite. There is no exposed magmatic rock in or around the mining area. The main ore-controlling faults in the mining area are  $F_1$  and  $F_2$ , among which  $F_1$  is a reverse fault with a fault occurrence of  $60 \circ \angle 86 \circ$  and a fault width of 1.6-16 m;  $F_2$  is a nearly vertical reverse fault with a fault occurrence of  $115 \circ \angle 86 \circ$  and a fault width of 1.5-7.5 m. Similar to  $F_1$ ,  $F_2$  is filled with breccia and fragmented slates containing sphalerite. The main wall rock alterations include silicification and carbonatization, which are distributed in the fault fracture zones and the surrounding rocks on the side of the ore bodies.

The  $V_1$  and  $V_2$  ore bodies in the mining area are strictly controlled by the Wuxing anticline and occur in the  $F_1$  and  $F_2$  fracture zones, respectively (Figure 2). The occurrence of these ore bodies is basically consistent with the faults. The  $V_1$  and  $V_2$  ore bodies belong to steeply inclined ore bodies. The controlled ore bodies are 302–371 m long and 3.10–3.56 m thick. The morphology of the ore bodies is irregular and locally swollen. The average thickness of the  $V_1$  ore body in a single engineering project is 3.56 m, with an average grade of 4.90%. The average thickness of the V<sub>2</sub> ore body in a single engineering project is 3.10 m, with an average grade of 5.36%. In the V<sub>1</sub> and V<sub>2</sub> zinc ore bodies, it is estimated that the 332 and 333 types of zinc resources are 657,500 tons, the total amount of zinc metals is 32,992.55 tons, and the average grade of Zn is 5.02%. Among them, the amount of zinc resources of the 332 type is 328,600 tons, the amount of zinc metals is 15,916.40 tons, and the average grade of Zn is 4.84%; the amount of zinc resources of the 333 type is 328,900 tons, the amount of zinc metals is 17,076.15 tons, and the average grade of Zn is 5.19%.



**Figure 1.** Structural sketch of Southwest China (**a**) and distribution map of main faults and mineral deposits in the SYGT (**b**). Base map data were obtained from [9].

The metal minerals in the ores of this deposit are mainly waxy-yellow and iron-black sphalerite, with low contents of galena, chalcopyrite, pyrite, and limonite. The metal minerals do not reach industrial grade, except for sphalerite. The gangue minerals mainly include calcite and quartz, followed by mica, dolomite, chlorite, and a small amount of feldspar. The ores have an idiomorphic or semi-idiomorphic granular texture, including texture with a block-like, disseminated, or fine vein-like structure. The natural type of the ores is mainly sulfide ore, while the industrial type is mainly sphalerite–quartz vein-like structural breccia, accounting for about 87.3%. The secondary type is sphalerite–quartz vein-like slate, accounting for about 12.7%.



**Figure 2.** Geological map of the Laoyingqing zinc deposit (**a**); geological sketch of the deposit (**b**); and geological profile of Exploration Line 12 in Laoyingqing Ore Block and geological profile of Exploration Line 104 in Laolongtian Ore Block (**c**) [7].

Based on the typical ore samples and microscopic observations, the deposit had undergone a hydrothermal mineralization period and a supergene period, with two main mineral associations formed during the hydrothermal mineralization period (Figure 3).

Sphalerite–quartz–carbonate combination: This combination is the main mineral combination of zinc ore in the mining area and is commonly seen. The main metal sulfide is sphalerite; the main gangue mineral is quartz, followed by calcite. This combination often exhibits strong zinc mineralization and a high zinc grade. Pyrite, quartz, and carbonate minerals such as dolomite formed in the earlier stage were metasomatized by sphalerite (Figure 4a–c). Based on the sequence of mineral formation shown in Figure 3, this mineral combination formed earlier and can be designated as the first stage of mineralization.



Figure 3. Mineral generation sequence of Laoyingqing zinc deposit.



**Figure 4.** Typical ore texture and structure photos of Laoyingqing zinc deposit: (**a**) brecciated ore; (**b**) block ore; (**c**) pyrite and sphalerite are metasomatized by quartz; (**d**) veined ore body; (**e**) veined ore body; and (**f**) sphalerite is metasomatized by quartz. Gn: galena; Py: pyrite; Sp: sphalerite; Qz: quartz; Dol: dolomite; Cal: calcite.

Sphalerite–galena–pyrite–quartz–carbonate combination: This combination is a secondary mineral combination in the mining area. The main metal sulfide is sphalerite, followed by galena and pyrite; the main gangue mineral is quartz, followed by calcite. Zinc mineralization is weak, and the zinc grade is low. Sphalerite was metasomatized by quartz and pyrite, and formed an "island" and "harbor" structure (Figure 4d–f). Based on the sequence of mineral formation shown in Figure 3, this mineral combination formed relatively later and can be designated as the second stage of mineralization.

In summary, sphalerite was mainly formed in the first stage of hydrothermal mineralization.

#### 3. Sampling and Testing Methods

#### 3.1. Sample Collection

The samples of ore and surrounding rocks were collected from different middle sections of the  $V_1$  and  $V_2$  ore bodies in the Laoyingqing zinc deposit. Microthermometry and laser Raman spectroscopic analysis were performed on fluid inclusions in 3 quartz and 3 sphalerite samples. Trace element analysis was performed on 7 sphalerite samples; rare-earth element analysis was performed on 6 sphalerite samples, 2 dolomite samples, 2 slate samples, and 1 structural breccia sample; and H–O isotope analysis was performed on 8 quartz samples.

#### 3.2. Analysis and Testing Methods

The microthermometry of fluid inclusions was completed at the Fluid Laboratory of the Southwest Geological Survey Institute of the Nonferrous Metals Geological Survey Center. The instruments used included a THMS 600 heating and freezing stage (Linkam co., Surrey, UK) and a standard microscope equipped with an imaging analysis system. Prior to the experiment, the heating and freezing stage was calibrated using the standard of international synthetic fluid inclusions. Under low-temperature (<0 °C) and high-temperature (>200 °C) conditions, the instrument errors were  $\pm 0.1$  °C and  $\pm 2$  °C, respectively.

The laser Raman spectroscopic analysis was completed using a Renishaw in Via confocal laser Raman spectrometer (Renishaw Inc., Gloucester, UK) at the Faculty of Land Resource Engineering Kunming University of Science and Technology. The laser power was 25 mW, the laser wavelength was 514.53 nm, and the spatial resolution was  $1-2 \mu m$ . The integration time was generally 30~60 s, and the peak was taken once in the entire wavelength range of  $1000 \sim 4000 \text{ cm}^{-1}$ . The laser beam spot diameter was about 1  $\mu m$ . The spectral resolution was  $1-2 \text{ cm}^{-1}$ .

The analysis of trace element and rare-earth element contents in sphalerite was completed at the Central South Mineral Resources Supervision and Testing Center of the Ministry of Land and Resources. The testing instrument was ICP-MS, and the accuracy of the standard sample analysis was better than 5%. The limit of detection was  $(0.n~n) \times 10^{-9}$  [10]. Please see Zhang Baoke et al. [11] for details regarding the analysis operation process.

The testing of rare-earth element composition in surrounding rocks was completed at the Northwest Mineral Geological Testing Center of Nonferrous Metals. The testing instrument was an ICP-MS, with an analysis accuracy of better than 2%, a temperature of 20 °C and a relative humidity of 30%. The main experimental parameters were as follows: carrier gas flow rate of 0.99 L/min; cooling air flow rate of 13.00 L/min; RF power of 1.35 KW; resolution of 300; and auxiliary air flow rate of 0.85 L/min. The instrument included a glass concentric atomizer; a glass mist chamber with water cooling; a membrane stripping injection device; and a nickel cone, with a pore size of 0.8 mm.

The H–O isotope testing was completed by Beijing Kehui Testing Technology Co., Ltd. The testing equipment used was a pyrolysis furnace (FlashEA, Thermo, Waltham, MA, USA) and a mass spectrometer (253 plus, Thermo, Waltham, MA, USA). The testing process and conditions were as follows: (1) hydrogen isotope testing of fluid inclusions: wrapping 40 to 60 mesh quartz single minerals in a tin cup, drying them, and then throwing them into a high-temperature (1420 °C) pyrolysis furnace. The generated H<sub>2</sub> and CO passed

through a chromatographic column and entered a mass spectrometer for determination of the isotopic ratio of the  $\delta D$  value of H<sub>2</sub>. The testing accuracy of the international standard substance (polyethylene, IAEA-CH-7,  $\delta D_{V-SMOW} = -100.3\%$ ) was better than 1‰ [12]. (2) Oxygen isotope testing: grinding the samples to 200 mesh, weighing 6 mg of pure quartz samples or silicate minerals with equivalent oxygen content, and then placing the samples in an oven at 105 °C for 12 h. The traditional BrF<sub>5</sub> analysis method [13] was used, and the analytical accuracy of the standard sample was better than ±0.2‰, with a relative standard of V-SMOW. The testing instrument was a 253 plus gas isotope ratio mass spectrometer.

## 4. Test Results

## 4.1. Fluid Inclusions

#### 4.1.1. Petrographic Characteristics of Fluid Inclusions

The fluid inclusions in the sphalerite and the quartz of this deposit are both primary fluid inclusions that are dispersedly distributed and irregularly shaped, including being approximate triangular, approximate rectangular, and approximate elliptical, with sizes ranging from  $10-40 \mu m$ . The fluid inclusion gas in quartz accounts for 5% to 35% of the total volume, while the fluid inclusion gas in sphalerite accounts for 5% to 20% of the total volume. In some fluid inclusions, in addition to gas- and liquid-phase components, there are also daughter minerals such as quartz and sphalerite. According to the classification scheme proposed by Lu Huanzhang et al. [14], these fluid inclusions could be classified as liquid inclusions (the liquid phase accounts for more than 50% of the fluid inclusion volume) and multiphase inclusions containing daughter minerals (Figure 5).



**Figure 5.** Microscopic image of fluid inclusions in the Laoyingqing zinc deposit: (**a**) smaller fluid inclusions in sphalerite; (**b**) smaller fluid inclusions in quartz; (**c**–**i**) gas–liquid two-phase fluid inclusions in quartz; and (**j**–**l**) gas–liquid two-phase fluid inclusions in sphalerite.

#### 4.1.2. Temperature and Salinity Measurement Results of Fluid Inclusions

The salinity and homogenization temperature of the primary gas–liquid two-phase fluid inclusions and primary multiphase inclusions containing daughter minerals in 54 quartz and 11 sphalerite samples were measured.

The homogenization temperature of fluid inclusions ranges from 130 °C to 306.5 °C, with an average of 207.8 °C. The salinity ranges from 7.17 wt% to 20.67 wt% NaCleq, with an average of 14.2 wt% NaCleq. The homogenization temperature of fluid inclusions in quartz ranges from 130 to 306.5 °C, with an average of 215.65 °C. The salinity ranges from 7.17 wt% to 19.6 wt% NaCleq, with an average of 13.61 wt% NaCleq. The homogenization temperature of fluid inclusions in sphalerite range from 132.5~216.5 °C, with an average of 169.25 °C (Figure 6). The salinity ranges from 12.39 wt%~20.67 wt% NaCleq, with an average of 17.21wt% NaCleq. From the histogram of homogenization temperature of fluid inclusions, it can be seen that the homogenization temperature of fluid inclusions is mainly concentrated between 130 °C and 280 °C. Overall, the ore-forming fluids exhibit medium–low temperature and medium–low salinity.



**Figure 6.** Histogram of homogenization temperature and salinity of fluid inclusions in Laoyingqing zinc deposit.

#### 4.1.3. Laser Raman Spectroscopy of Fluid Inclusions

The liquid component of the fluid inclusions in quartz is  $H_2O$  (Figure 7a), and the bubble component is  $H_2O$  (Figure 7b) with a small amount of CO (2143 cm<sup>-1</sup>) (Figure 7c). The liquid composition of the fluid inclusions in sphalerite is  $H_2O$  (Figure 7d), and the bubble composition is  $H_2O$  (Figure 7e,f).

#### 4.2. Trace Elements

The trace element analysis results of seven sphalerite samples (Table 1) show that the trace element composition of sphalerite in this deposit has the following characteristics:

Relatively enriched in Co, Ga, Ge, Hg, Ni, Sb, Cu, and Sn, with content ranges of 49.6~93.2, 48.6~171, 38.7~85.2, 39.5~60.4, 4.83~15.2, 29.4~120, 376~2500, and 3.15~10.3, and an average of 78.51, 108.71, 61.2, 49.71, 8.16, 60.8, 904.29, and 7.10 (n = 7; unit: μg/g);

2. The contents of Tl and Sr are extremely low and have a small range of variation. The maximum value of Tl in the samples is  $0.07 \ \mu g/g$ , and the minimum value is less than the detection limit ( $0.01 \ \mu g/g$ , n = 7). The variation range of Sr is  $0.91 \sim 2.16 \ \mu g/g$ , and the mean is  $1.33 \ \mu g/g$  (n = 7).



Figure 7. Laser Raman spectroscopy of fluid inclusions.

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Table L	Irace element	content of	sulfide in	Laoving	aino	zinc de	posit (	11m1t 1	10/	$\sigma$
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Sample Number	LYQ-1	LYQ-2	LYQ-3	LYQ-5	LYQ-6	LYQ-7	LYQ-8
Mineral	Sphalerite						
Cu	801	671	564	716	376	702	2500
Pb	914	24	12	300	11.2	15.8	72.8
Ni	9.98	15.2	7.05	6.34	7.18	6.52	4.83
Со	91	79.1	81.3	49.6	93.2	83.6	71.8
Cd	2140	1530	1680	1570	1700	1760	1510
Li	0.26	0.05	0.015	< 0.01	0.024	< 0.01	< 0.01
Rb	1.3	1.55	1.26	1.14	0.69	0.58	0.9
W	0.082	0.17	0.12	0.082	0.26	0.24	0.033
Мо	0.23	0.12	0.019	2.51	0.022	0.036	0.073
As	5.1	2	4.93	3.03	3.74	5.43	1.83
Sb	76.1	35	78	120	29.4	101	36.5

Sample Number	LYQ-1	LYQ-2	LYQ-3	LYQ-5	LYQ-6	LYQ-7	LYQ-8
Mineral	Sphalerite						
Hg	60.4	39.5	51.9	60.4	43.3	49.5	43
Sr	2.16	1.25	1.14	1.82	1.02	0.91	1.04
Sc	0.44	0.54	0.58	0.69	0.44	0.36	0.32
Nb	0.17	< 0.05	0.05	0.053	< 0.05	< 0.05	0.26
Zr	1.11	0.69	0.83	0.63	0.79	0.4	0.54
Hf	0.036	0.022	0.018	0.016	0.019	0.012	0.017
Ga	78.6	110	152	48.6	106	171	94.8
Sn	4.82	6.85	9.58	3.15	6.38	10.3	8.64
Ge	38.7	64.6	68.7	53	61.2	85.2	57
Tl	0.07	0.028	0.02	0.026	0.02	0.013	< 0.01
Ag	3.71	3.08	2.3	5.05	2.3	3.16	2.64
Ŭ	0.022	0.1	0.011	0.016	< 0.01	< 0.01	< 0.01
Th	0.12	0.12	0.12	0.13	0.058	0.044	0.092
Ti	732	7.88	40.8	9.7	8.59	7.17	141
Mn	18.1	20.3	16.4	38.2	19	13.4	22
Cr	5.14	5.23	5.76	5.99	3.44	3.43	2.77
Ba	3.03	3.64	3.57	3.71	8.68	5.95	1.95

Table 1. Cont.

#### 4.3. Rare-Earth Elements

The rare-earth element analysis results of seven samples of sphalerite, two samples of dolomite, two samples of slate, and one sample of tectonic breccia (Table 2) are as follows:

Table 2. Rare-earth element characteristics of Laoyingqing zinc deposit (unit:  $\mu g/g$ ).

Sample Number	LY-13-1	LY-13-2	LY-2-1	LY-1-1	LY-4	LYQ-1	LYQ-2	LYQ-3	LYQ-5	LYQ-6	LYQ-7
Mineral	Tectonic Breccia	Dolomite	Dolomite	Slate	Carbonaceous Slate	Sphalerite	Sphalerite	Sphalerite	Sphalerite	Sphalerite	Sphalerite
La	51.339	39.965	40.072	41.451	45.744	0.108	0.067	0.064	0.062	0.043	0.054
Ce	103.846	78.935	78.835	82.01	90.21	0.183	0.112	0.119	0.099	0.085	0.102
Pr	12.455	9.556	9.588	9.757	10.883	0.02	0.012	0.011	0.009	0.008	0.009
Nd	43.427	33.084	33.152	33.834	37.814	0.08	0.039	0.041	0.029	0.032	0.032
Sm	8.193	6.228	6.198	6.141	6.939	0.015	0.007	0.008	0.006	0.006	0.004
Eu	1.651	1.367	1.333	1.345	1.557	0.004	0.003	0.002	0.002	0.002	0.002
Gd	7.199	5.711	5.642	5.53	6.435	0.014	0.008	0.006	0.005	0.006	0.007
Tb	1.028	0.829	0.796	0.77	0.932	0.002	0.001	0.001	0.001	0.001	0.001
Dy	5.046	4.166	3.914	3.791	4.658	0.014	0.008	0.007	0.009	0.006	0.007
Ho	1.057	0.84	0.783	0.73	0.919	0.003	0.003	0.002	0.002	0.001	0.002
Er	3.203	2.573	2.399	2.296	2.869	0.009	0.005	0.005	0.006	0.004	0.006
Tm	0.501	0.392	0.363	0.344	0.44	0.001	0.001	0.001	0.001	0.001	0.001
Yb	3.078	2.373	2.256	2.217	2.703	0.008	0.006	0.006	0.006	0.004	0.004
Lu	0.522	0.415	0.395	0.375	0.451	0.001	0.001	0.001	0.001	0.001	0.001
Y	31.399	27.782	28.094	28.083	28.239	0.113	0.061	0.052	0.049	0.039	0.044
ΣREE	242.54	186.43	185.73	190.59	212.56	0.46	0.27	0.28	0.24	0.2	0.23
LREE/HREE	10.21	9.78	10.22	10.87	9.95	7.63	7.48	8.28	6.71	7.22	6.99
δEu	0.64	0.69	0.68	0.69	0.7	0.85	1.36	0.85	1.2	0.95	1.16
δCe	0.96	0.94	0.94	0.95	0.94	0.89	0.89	0.97	0.91	1.03	1.01
(La/Yb) <sub>N</sub>	11.25	11.36	11.98	12.6	11.41	9.3	7.71	7.32	7.42	7.29	9.51
(La/Sm) <sub>N</sub>	3.94	4.04	4.07	4.25	4.15	4.43	5.92	4.78	6.92	4.68	7.99
(Gd/Yb) <sub>N</sub>	1.89	1.94	2.02	2.01	1.92	1.43	1.1	0.86	0.74	1.17	1.52

The rare-earth elements in the sphalerite of this deposit are characterized by an enrichment of light rare-earth elements, with the LREE/HREE ratios ranging from 6.71 to 8.28 and a mean of 7.39. The  $\delta$ Eu values range from 0.85 to 1.36, with an average value of 1.06, indicating that the content of Eu element is close to chondrites and has no obvious enrichment or depletion characteristic. The  $\delta$ Ce values range from 0.89 to 1.03, with an average of 0.96, indicating that the content of Ce element is close to chondrites and has no obvious enrichment or depletion characteristics. The  $\lambda$ Ce values range from 0.89 to 1.03, with an average of 0.96, indicating that the content of Ce element is close to chondrites and has no obvious enrichment or depletion characteristics. The (La/Yb)<sub>N</sub> ratios are all greater than

1, ranging from 7.29 to 9.51, indicating a right-leaning feature of the rare-earth-element distribution curves. The  $(La/Sm)_N$  ratios range from 4.43 to 7.99, with an average of 5.79, and the  $(Gd/Yb)_N$  ratios range from 0.74 to 1.52, with an average of 1.14, indicating that the internal differentiation of heavy rare-earth elements is not significant, while the internal differentiation of light rare-earth elements is relatively strong.

The  $\Sigma REE$  of tectonic breccia is 242.54 µg/g, and the LREE/HREE ratio is 10.21, indicating the enrichment characteristics of light rare-earth elements. The \deltaEu value is 0.64, indicating a weak negative anomaly in Eu. The  $\delta$ Ce value is 0.96, indicating a weak negative anomaly in Ce. The  $(La/Yb)_N$  ratio is 11.25, indicating a right-leaning feature of the rare-earth-element distribution curve. The  $(La/Sm)_N$  ratio is 3.94 and the  $(Gd/Yb)_N$ ratio is 1.89, indicating that the internal differentiation of heavy rare-earth elements is not significant, while the internal differentiation of light rare-earth elements is relatively strong.

The  $\Sigma$ REE of dolomite ranges from 185.73 to 186.43 µg/g, with an average of 186.08 µg/g. The LREE/HREE ratios range from 9.78 to 10.22  $\mu$ g/g, with an average of 10  $\mu$ g/g, indicating the enrichment characteristics of light rare-earth elements. The  $\delta Eu$  values range from 0.68 to 0.69, with an average of 0.685, indicating a weak negative anomaly in Eu. The  $\delta$ Ce values are all 0.94, indicating a weak negative anomaly in Ce. The (La/Yb)<sub>N</sub> ratios range from 11.36 to 11.98, indicating a right-leaning feature of the rare-earth-element distribution curves. The  $(La/Sm)_N$  ratios range from 4.04 to 4.07, with an average of 4.055, and the  $(Gd/Yb)_N$  ratios range from 1.94 to 2.02, with an average of 1.98, indicating that the internal differentiation of heavy rare-earth elements is not significant, while the internal differentiation of light rare-earth elements is relatively strong.

The  $\Sigma$ REE of slate ranges from 190.59 to 212.56 µg/g, with an average of 201.56 µg/g. The LREE/HREE ratios range from 9.95 to 10.87  $\mu g/g,$  with an average of 10.41  $\mu g/g,$ indicating the enrichment characteristics of light rare-earth elements. The  $\delta Eu$  values range from 0.69 to 0.70, with an average of 0.695, indicating a weak negative anomaly in Eu. The  $\delta$ Ce values range from 0.94 to 0.95, with an average of 0.945, indicating a weak negative anomaly of Ce. The  $(La/Yb)_N$  ratios range from 11.41 to 12.60, indicating a right-leaning feature of the rare-earth-element distribution curves. The (La/Sm)<sub>N</sub> ratios range from 4.15 to 4.25, with an average of 4.20, and the  $(Gd/Yb)_N$  ratios range from 1.92 to 2.01, with an average of 1.965, indicating that the internal differentiation of heavy rare-earth elements is not significant, while the internal differentiation of light rare-earth elements is relatively strong.

#### 4.4. H–O Isotopes

The homogenization temperature of fluid inclusions in the Laoyingqing zinc deposit ranges from 130 °C to 306.5 °C, with an average of 207.8 °C. According to Clayton's [15] calculation formula, 1000lna =  $\delta^{18}O_{quartz} - \delta^{18}O_{water} = 3.38 \times 10^6/T^2 - 3.4$ , where T is taken as 207.8 °C. The calculation results of  $\delta^{18}O_{water}$  (Table 3) show that the  $\delta^{18}O_{water}$ values of the ore-forming fluids of this deposit range from 4.79‰ to 6.89‰ (average of 5.71‰).

Sample Number	Analysis Object	δ D‰	$\delta$ <sup>18</sup> O <sub>V-SMOW</sub> ‰
LYQ-1-3	quartz	-93.9	17.61

Table 3. H–O isotope composition in the Laoyingqing zinc deposit.

Sample Number	Analysis Object	δ D‰	$\delta$ <sup>18</sup> O <sub>V-SMOW</sub> ‰	$\delta^{18}O_{water}$ ‰
LYQ-1-3	quartz	-93.9	17.61	6.40
LYQ-2-3	quartz	-82.5	16.28	5.07
LYQ-3-3	quartz	-80.0	16.35	5.14
LYQ-4-3	quartz	-82.9	18.10	6.89
LYQ-5-3	quartz	-73.2	18.07	6.86
LYQ-6-3	quartz	-70.9	16.00	4.79
LYQ-7-3	quartz	-79.5	16.32	5.11
LYQ-8-3	quartz	-75.0	16.64	5.43

#### 5. Discussion

#### 5.1. Properties of Ore-Forming Fluids

## 5.1.1. Fluid Density

The density of ore-forming fluids can be obtained via the conversion of the homogenization temperature and salinity of fluid inclusions. According to the density formula [16], under low-salinity conditions (wt% (NaCleq)  $\leq$  25), the density of the ore-forming fluids in this deposit ranges from 0.86 to 1.07 g/cm<sup>3</sup>, with an average value of 0.96 g/cm<sup>3</sup>.

## 5.1.2. Ore-Forming Pressure

Based on the homogenization temperature and salinity of fluid inclusions, using the empirical formula for calculating fluid pressure by Shao Jielian [17],  $P = P_0 \times t_h/t_0(10^5 Pa)$  ( $P_0 = 219 + 2620 \times w$  and  $T_0 = 374 + 920 \times w$ ). In this formula, P is the ore-forming pressure,  $t_h$  is the homogenization temperature, and w is the salinity of the ore-forming fluids. The fluid pressure of the corresponding fluid inclusions was obtained. The results show that the fluid pressure range of the gas–liquid two-phase inclusions and multiphase inclusions containing daughter minerals in this deposit is 36.3~85.6 Mpa.

#### 5.1.3. Mineralization Depth

Using the empirical formula for mineralization depth [18],  $H = P \times 1/270$  (km), the corresponding burial depth range was calculated to be 1.34~3.17 km, with an average of 2.26 km.

According to W. Lingren's [19] classification, the temperature of mesothermal deposits is 300~200 °C, and the pressure is  $(1 \sim 5) \times 10^7$  Pa, with a mineralization depth of approximately 2~0.5 km; the temperature of a low-temperature hydrothermal deposit ranges from 200 to 50 °C, and the pressure is less than  $10^7$  Pa. The temperature, pressure, and depth of mineralization of this deposit are generally within the range of medium-temperature hydrothermal deposits. Therefore, this deposit is classified as a medium-low-temperature hydrothermal deposit.

#### 5.1.4. Comparison of Mineralization Temperatures

Compared to the main Pb-Zn deposits listed in Table 4 in the Sichuan–Yunnan– Guizhou Pb-Zn metallogenic triangle area (SYGT) and a typical MVT Pb-Zn deposit in Huayuan, western Hunan, the range of mineralization temperature of this deposit is wide, with the end-member being a high-temperature fluid. The salinity is also relatively high, and the range is relatively wide. Overall, the mineralization temperature of this deposit is consistent with the overall mineralization temperature of the SYGT and similar to the MVT Pb-Zn deposit in Huayuan, western Hunan.

**Table 4.** Comparison table of fluid inclusion temperature and salinity of main Pb-Zn deposits in the SYGT and a typical MVT Pb-Zn deposit in Huayuan, Western Hunan.

Mining Area	Temperature	Salinity	Source
Huize	164–355 °C	6-18 wt% NaCleq	[4,20]
Maoping	123–206 °C	6.7–13.8 wt% NaCleq	[20]
Maozu	153–248 °C	2.8–5.3 wt% NaCleq	[20]
Le Hong	165–229 °C	11.3-14.5 wt% NaCleq	[20]
Jinniuchang	165–274 °C	6.5–14.0 wt% NaCleq	[21]
Daliangzi	121–263 °C	3.87–14.04 wt% NaCleq	[22]
Tianbao Mountain	157–267 °C	12.4–20 wt% NaCleq	[23]
Chipu	130–250 °C	8.5–17 wt% NaCleq	[22]
Shanshulin	150–280 °C	<15 wt% NaCleq	[24]
Shaojiwan	115–170 °C	0.9–17.5 wt% NaCleq	[25]

Mining Area	Temperature	Salinity	Source
Tianqiao	150–240 °C	10 wt% NaCleq	[26]
Tuanjie (typical MVT Pb-Zn deposit in Huayuan, western Hunan)	110–317 °C	7.86–21.20 wt% NaCleq	[27]
Laoyingqing	130–306.5 °C	7.17–20.67 wt% NaCleq	this paper

Table 4. Cont.

#### 5.2. Trace Elements

MVT deposits are the main source of associated Ge worldwide [28]. Compared to the Pb-Zn deposits in the Mississippi Valley region of the United States, in which the w(Ge) content of sphalerite is mostly less than  $20 \times 10^{-6} \,\mu\text{g/g}$  [29], the Pb-Zn deposits in northeastern Yunnan generally have a high Ge content. Among them, the w(Ge) content in sphalerite of the Fule Pb-Zn deposit in Yunnan is  $170 \times 10^{-6} \,\mu\text{g/g}$  [30], and the maximum of w(Ge) in sphalerite of the Huize Pb-Zn deposit is  $520 \times 10^{-6} \,\mu\text{g/g}$  [30–32]. The average value of w(Ge) in the Laoyingqing zinc deposit is  $61.2 \times 10^{-6} \,\mu\text{g/g}$ , which is also in line with this observation.

The Cd/Mn ratio in sphalerite can determine whether there is magmatic activity involved in the mineralization process. Sphalerite related to magmatic activity often has a low Cd/Mn ratio (<5), while sedimentary or strata-bound deposits have a Cd/Mn ratio greater than 5 [33]. In addition, the content of Ge in sphalerite has indicative significance for mineralization, and the content of Ge in sphalerite deposits related to magmatic hydrothermal activity is usually less than  $3 \times 10^{-6} \,\mu g/g$  [34].

The Cd/Mn ratios in the sphalerite of this deposit range from 41.10 to 131.34 (mean 80.66). The content of Ge in the sphalerite of this deposit ranges from  $38.7 \times 10^{-6} \,\mu\text{g/g}$  to  $85.2 \times 10^{-6} \,\mu\text{g/g}$ . The above data indicate that the mineralization process of sphalerite in this deposit is not related to magmatic activity.

The content of Cd in this deposit is lower than the MVT Pb-Zn deposit in the Huayuan area of western Hunan [27], the MVT Pb-Zn deposit in Lehong, northeastern Yunnan [3], and the HZT (Huize-type) Pb-Zn deposit in Huize [20], but it is within the Cd content range of MVT Pb-Zn deposits.

Li Yungang et al. [35] compared the chemical analysis results of Cd and Fe contents in sphalerite from different Pb-Zn deposits in the Sichuan–Yunnan–Guizhou region, and found a negative correlation between Fe and Cd contents. A high Fe content in the fluid will inhibit Cd from entering the sphalerite lattice. The low Cd content in the sphalerite of this deposit suggests that the Fe<sup>2+</sup> content in the fluid is high, which suppresses Cd from entering sphalerite during the formation process of sphalerite.

In a study of different types of Pb-Zn deposits in southern China, Ye et al. [36] found that sedimentary-exhalative deposits have relatively high levels of Fe, Mn, and In, but lacking in Cd, Ge, and Ga, while distal skarn deposits are significantly enriched in Co and Mn, but lacking in In, Sn, and Fe. Magmatic hydrothermal deposits are enriched in Fe, Mn, In, Sn, and Co, but lacking in Cd, Ge, and Ga, while MVT Pb-Zn deposits are enriched in Ge, Cd, and Ga, but lacking in Fe, Mn, In, Sn, and Co. In addition to enriched Pb and Zn, the ores of HZT (Huize-type) Pb-Zn deposits are enriched in Ga and Ge, which is different from sedimentary-exhalative and magmatic hydrothermal Pb-Zn deposits. From the above, it can be seen that the mineralization process of this deposit is not related to magmatic activity, indicating that the genesis of this deposit is not a skarn type (Table 5).

Through further comparison, it can be seen that in the Ge–Mn and Mn–Cd relationship diagrams, the content of sphalerite of this deposit falls within the trace element range of MVT and HZT (Huize-type) deposits, while in the Ga–Ge relationship diagram, the content of sphalerite of this deposit falls within the range of MVT Pb-Zn deposits, which is different from HZT (Huize-type) Pb-Zn deposits. In the Sb–Cu and Ni–Co relationship diagrams, the content of sphalerite of this deposit shows some differences from MVT and HZT (Huize-type) Pb-Zn deposits (Figure 8).



**Figure 8.** Scatter plots of trace elements in different types of sphalerite: Huize [20,37]; Le Hong [20]; Huayuan, western Hunan [27]; and Huayuan, western Hunan [38].

			1	51	1				
Types of Pb-Zn Deposits	Cd/(10 <sup>-6</sup> )	Mn/(10 <sup>-6</sup> )	Cu/(10 <sup>-6</sup> )	Ga/(10 <sup>-6</sup> )	Ge/(10 <sup>-6</sup> )	In/(10 <sup>-6</sup> )	Sn/(10 <sup>-6</sup> )	Ag/(10 <sup>-6</sup> )	Cd/Mn
MVT	1296~5023 [39]	40.87~81.86 [39]	/	8.29~54.2 [39]	>10 [40]	0.45–1.55 [39]	0.79~9.51 [39]	/	26.52~122.90 [39]
	5333~12,260 [27]	5.65~104.3 [27]	19.78–118.1 [27]	3.54~47.9 [27]	4.59–102 [27]	/	0.44~4.21 [27]	0.19–11.2 [27]	83.57~1573.98 [27]
Huize type	894~4647 [36]	7.1–300 [36]	7.0~1188 [36]	0.05–21.1 [36]	1.4~107.5 [40]	0.003~5.6 [36]	0.07–27.4 [36]	6.00~76.80 [36]	13.45–155.56 [36]
Traille type	1053.97–3518.87 [20]	0.46~20.82 [20]	7.46~319.13 [20]	0.12-65.16 [20]	3.06~231.15 [20]	/	0.06–22.32 [20]	1.39–18.80 [20]	60.82~4170.22 [20]
Magmatic hydrothermal type (medium to high temperature)	2000~2400 [41]	1940–4030 [41]	/	310~530 [41]	/	35~268 [41]	/	159–179 [41]	0.60~1.03 [41]
Strata-bound type	1342–3942 [42]	48~888 [42]	/	25~531 [42]	/	2.60–19.40 [42]	/	/	1.51~34.96 [42]
ouuu oouuu ope	969–21300 [43]	48~888 [43]	/	3.4~534 [43]	/	0–19.4 [43]	28.70–101 [43]	17.10~164.5 [43]	1.51~34.96 [43]
Volcanic rock type	1950~3300 [44]	300~1800 [44]	/	7.70~83 [44]	/	3–136.8 [44]	/	/	1.83–11.33 [44]
Magmatic	1086~3971 [42]	2591~7528 [42]	/	2.34~39.90 [42]	<5 [40]	69~777 [42]	/	/	0.14~0.73 [42]
hydrothermal type	1826–2883 [45]	1036–1895 [45]	517-6506 [45]	2.62–11.6 [45]	0.065~0.341 [45]	4.87–257 [45]	/	/	1.09–2.37 [45]
Sedex type	1162–3837 [39]	6.90–149 [39]	/	14.70~73.40 [39]	/	0.05–1.17 [39]	1.35–108 [39]	/	20.97~254.93 [39]
	3465~9600 [46]	1715-4152 [46]	119~4852 [46]	2.3–117 [46]	0.18-15.1 [46]	58-566 [46]	2.23–185 [46]	4.8~522 [46]	/

Table 5. Trace element characterist	tics of sphalerite	in different ty	pes of deposits.

## 5.3. Rare-Earth Elements

Anomalies in  $\delta Eu$  and  $\delta Ce$  can be used to discuss the oxidation–reduction property of ore-forming environments. However, an anomaly in Eu is the result of a combination of temperature, pH, oxidation–reduction property, and pressure, and is mainly influenced by temperature [47-49]. An anomaly in Ce is determined by the oxidationreduction property, PH, and oxygen fugacity of ore-forming fluids [49]. Compared to situations referring to a single  $\delta Eu$  or  $\delta Ce$  anomaly, the authors believe that it is more objective to discuss the oxidation-reduction property of ore-forming environments synthesizing Eu anomaly,  $\Sigma REE$ , and  $\Sigma LREE / \Sigma HREE$  ratio. Zhou Jiaxi et al. [50] proposed that minerals often exhibit a negative Eu anomaly, a high  $\Sigma REE$ , and a low  $\Sigma LREE / \Sigma HREE$ ratio under relative oxidation conditions, whereas they exhibit a positive Eu anomaly, a low  $\Sigma REE$ , and a high  $\Sigma LREE / \Sigma HREE$  ratio under reduction conditions. In Table 6, the ore-forming fluids of the Huize [51], Daliangzi, and Tianbaoshan [52] Pb-Zn deposits exhibit reducibility. When compared to the Eu anomaly,  $\Sigma REE$ , and  $\Sigma LREE / \Sigma HREE$ ratio of the Laoyingqing deposit, the results indicate that the rare-earth element characteristics of this deposit are more reducible than the other deposits. Combined with the CO detected in the fluid inclusions, the results indicate that the ore-forming fluids of this deposit are reducible.

Table 6. Rare-earth element characteristics of sphalerite in major Pb-Zn deposits in the SYGT.

Mining Area	Huize	Daliangzi	Tianbao Mountain	Laoyingqing
mineral	sphalerite	sphalerite	sphalerite	sphalerite
$\Sigma \text{REE} (\mu g/g)$	1.6	4.68~5.61	4.54	0.28
LREE/HREE	30.31	5.00~5.27	3.89	7.39
δ Ευ	0.53	0.84~0.96	0.55	1.06
δCe	1.1	$0.74 \sim 0.78$	0.99	0.95
(La/Yb) <sub>N</sub>	430.7	8.02~10.35	3.16	8.09
(La/SM) <sub>N</sub>	1.85	1.20~1.32	1.2	5.79
(Gd/Yb) <sub>N</sub>	113.08	5.25~7.90	2.16	1.14
literature sources	[53]	[53]	[53]	this paper

The sphalerite and surrounding rocks (tectonic breccia, dolomite, and slate) in this deposit have similar rare-earth-element distribution patterns (Figure 9), suggesting that the surrounding rocks (Kunyang Group) of this deposit provide ore-forming materials for sphalerite. There is a large scale of Emeishan basalt exposed in the SYGT. Regarding the source of ore-forming materials in this area, there is a viewpoint that it is provided by the synergistic supply of carbonate rock strata and Emeishan basalt [9,54,55]. It cannot be completely ruled out that there is Emeishan basalt in the deep part of this deposit activated by ore-forming fluids, which provides a small amount of metallic elements for this deposit. This conclusion is consistent with the conclusion obtained by Gong et al. [7] through Pb and Sr isotope research.



**Figure 9.** The distribution pattern diagram of rare-earth elements standardized by chondrite from Laoyingging zinc deposit (the REE content of chondrite [56]).

The Y and Ho elements have the same valence state and ion radius, and their ion radii with eight co-ordination numbers are almost identical. Therefore, this pair of elements exhibit close consistency in most geochemical environments in terms of geochemical behavior [57]. Bau and Dulski [58] believe that there is no significant change in Y/Ho values in different types of magmatic rocks, sedimentary rocks, and chondrites. The Y/Ho ratios in chondrites range from 24 to 36. The Y/Ho ratios in the sphalerite of this deposit range from 20.60 to 33.20, and the Y/Ho ratios in the dolomite of this deposit range from 33.30 to 35.70, indicating that the surrounding rock (dolomite) in the mining area may provide ore-forming materials for sphalerite.

## 5.4. Source of Ore-Forming Fluids

Compared to a typical brine basin in North America (Illinois, California Basin) and the Sichuan Basin, the ore-forming fluids of this deposit have the characteristics of low  $\delta D$  and high  $\delta^{18}O_{water}$  values (Figure 10). The characteristic of the  $\delta D$ - $\delta^{18}O$  relationship diagram of gangue minerals in this deposit suggests that it may have mixed sources of magmatic water, metamorphic water, and organic fluids, and may have some atmospheric precipitation. However, the aforementioned trace element characteristic of Cd/Mn suggests that this deposit does not contain magmatic water. In the Kunyang Group of the mining area, deep-source metamorphic water mixed with basin brine containing organic matter, and then underwent water–rock reaction with surrounding rocks enriched in organic matter, resulting in low  $\delta D$  values. Deep-source metamorphic water rising, resulting in high  $\delta^{18}O$  values. This does not rule out the reaction between atmospheric precipitation and carbonate rocks in various layers during the atmospheric precipitation infiltration process, resulting in high  $\delta^{18}O$  values.





In summary, the ore-forming fluids of this deposit mainly came from a mixture of deep-source metamorphic water and basin brine containing organic matter. Based on the homogenization temperature and salinity test results of fluid inclusions and the ore-forming fluid properties mentioned above, it is believed that the ore-forming fluids have the characteristics of medium–low temperature, medium–low salinity, medium–low density, and reducibility.

## 5.5. Genesis and Metallogenic Model of Deposit

MVT Pb-Zn deposits mainly occur in carbonate rock (mainly dolomite) formations, especially dolomite and a small amount of associated sandy or muddy rocks [19]. There are also reports of occurrence in schist, marble, breccia [66], gravel rock [67], limestone, and shale [68]. There is a significant difference in the lithology and occurrence status of the ore body of this deposit and that of MVT Pb-Zn deposits. Based on a comprehensive analysis of temperature, salinity, and trace element characteristics, it is believed that this deposit is a medium–low-temperature hydrothermal vein-type zinc deposit.

Based on the research conclusions regarding rare-earth elements and H–O isotopes, combined with previous research results, the mineralization process of the Laoyingqing zinc deposit can be described as a collision between the Indosinian landmass and Yangtze landmass in the late Indosinian period (about 200 Ma), which led to the closure of the ancient Tethys Ocean and the formation of the Wuxing anticline [7]. The basin fluids underwent large-scale migration under the action of gravity, and a small amount of gypsum-salt layer sulfate from marine carbonate rocks of the Dengying Formation of the Sinian system was extracted. Under the tectonic driving forces, deep-source fluids migrated upwards along faults and major ore-forming metal ions, such as Pb and Zn, from the basement (Kunyang Group) were extracted. When the two types of fluids migrated to the interlayer-gliding fracture zones of the basement strata in the core of the Wuxing anticline, the thermal energy brought by the two types of fluids led to the pyrolysis of sulfur-containing organic matter in the surrounding rocks (Kunyang Group), and produced



the main reducing sulfur. Accompanied by changes in physical, chemical, and other mineralization conditions, the Laoyingqing zinc deposit was formed (Figure 11).

Figure 11. Metallogenic model map of the Laoyingqing zinc deposit.

## 6. Conclusions

The ore-forming fluids of the Laoyingqing zinc deposit are characterized by mediumto-low temperature, medium-to-low salinity, medium-to-low density, and reducibility. The fluid pressure ranges from 36.3 to 85.6 Mpa, and the ore-forming depth ranges from 1.34 to 3.17 km. The fluids mainly came from deep-source metamorphic water and basin brine containing organic matter. The main source of ore-forming minerals is the surrounding rocks of the deposit (Kunyang Group).

The characteristics of trace elements indicate that this deposit is different from exhalativesedimentary type, magmatic hydrothermal type, and skarn type of Pb-Zn deposits; its mineralization process is not related to magmatic activity and also shows some differences from the geological characteristics of MVT and HZT Pb-Zn deposits.

This deposit belongs to a medium–low-temperature hydrothermal vein-type zinc deposit unrelated to magmatic activity.

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