

Article

Genesis of Caoziwa Pb–Zn Deposit in Tengchong Block, SW China: Constraints from Sulfur Isotopic and Trace Elemental Compositions of Sulfides

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Abstract: The Caoziwa Pb–Zn deposit is one of the typical vein-type Pb–Zn deposits in the western part of the Tengchong block. Due to limited research, the genesis of these deposits is unknown. In this study, the sulfur isotopic and trace elemental compositions of sulfides from the Caoziwa Pb–Zn deposit were analyzed to trace the sources of ore-forming materials, and to reveal the genetic type of this deposit. The results show that abundant Co, Ni, As, and Se, and less Cu, Zn, Ag, Cd, Sn, Sb, Te, Pb, and Bi could enter pyrite by isomorphic substitution. Elemental Mn, Fe, Cd, Co, and Ni could substitute Zn to enter sphalerite, while the contents of Ag, Sn, and Sb are mainly controlled by the Pb-rich inclusions in sphalerite. Elemental Bi, Sb, Cd, Sn, Ag, and Tl mainly enter the galena grains via an isomorphic substitution mechanism of $(\text{Bi, Sb})^{3+} + (\text{Cd, Sn})^{2+} + (\text{Ag, Tl})^+ \leftrightarrow 2\text{Pb}^{2+}$. Both sulfur isotopic compositions and trace elemental compositions indicate that the ore-forming materials and fluids of the Caoziwa Pb–Zn deposit mainly originate from magmatic hydrothermal fluid related to Paleocene granitic magmatism. Combined with the geological facts that some skarnizations developed in the northern part of the ore field near the Paleocene granite, the Caoziwa Pb–Zn deposit is suggested to be a magmatic hydrothermal vein-type deposit that probably belongs to a distal part of a skarn mineralization system developed by the intrusion of Paleocene granitic magmatism in the western part of the Tengchong block.

Keywords: Tengchong block; Caoziwa Pb–Zn deposit; sulfur isotope; trace elements; LA-ICP-MS



Citation: Cheng, Y.; Yang, C.; Deng, M.; Bai, F.; Chen, F. Genesis of Caoziwa Pb–Zn Deposit in Tengchong Block, SW China: Constraints from Sulfur Isotopic and Trace Elemental Compositions of Sulfides. *Minerals* **2024**, *14*, 82. <https://doi.org/10.3390/min14010082>

Academic Editor: Paolo Nimis

Received: 24 November 2023

Revised: 8 January 2024

Accepted: 8 January 2024

Published: 11 January 2024



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1. Introduction

The Tengchong–Lianghe metallogenic belt, located in the Tengchong block of the southern part of the Sanjiang region, hosts a large number of skarn-type polymetallic deposits, greisen-type Sn–REE deposits and vein-type Pb–Zn deposits, and is one of the most important Fe–Pb–Zn–Sn metallogenic regions in SW China [1–4] (Figure 1a). The mineralization in the Tengchong–Lianghe metallogenic belt exhibits obvious spatial zonation (Figure 1b). The skarn-type polymetallic mineralization mainly developed in the eastern part of the Tengchong block, and is represented by the Diantan Fe deposit, the Laochangpingzi Cu–Pb–Zn deposit, and the Jiaojiguan Fe–Cu–Pb–Zn deposit. The greisen-type Sn–REE mineralization mainly developed in the middle part of the Tengchong block, and is represented by the Xiaolonghe Sn deposit, the Xinqi Sn deposit, and the Lailishan Sn–REE deposit). Meanwhile, the vein-type Pb–Zn mineralization mainly developed in the western part of the Tengchong block, and is represented by the Caoziwa, Shizshan, and Erkun Pb–Zn deposits.

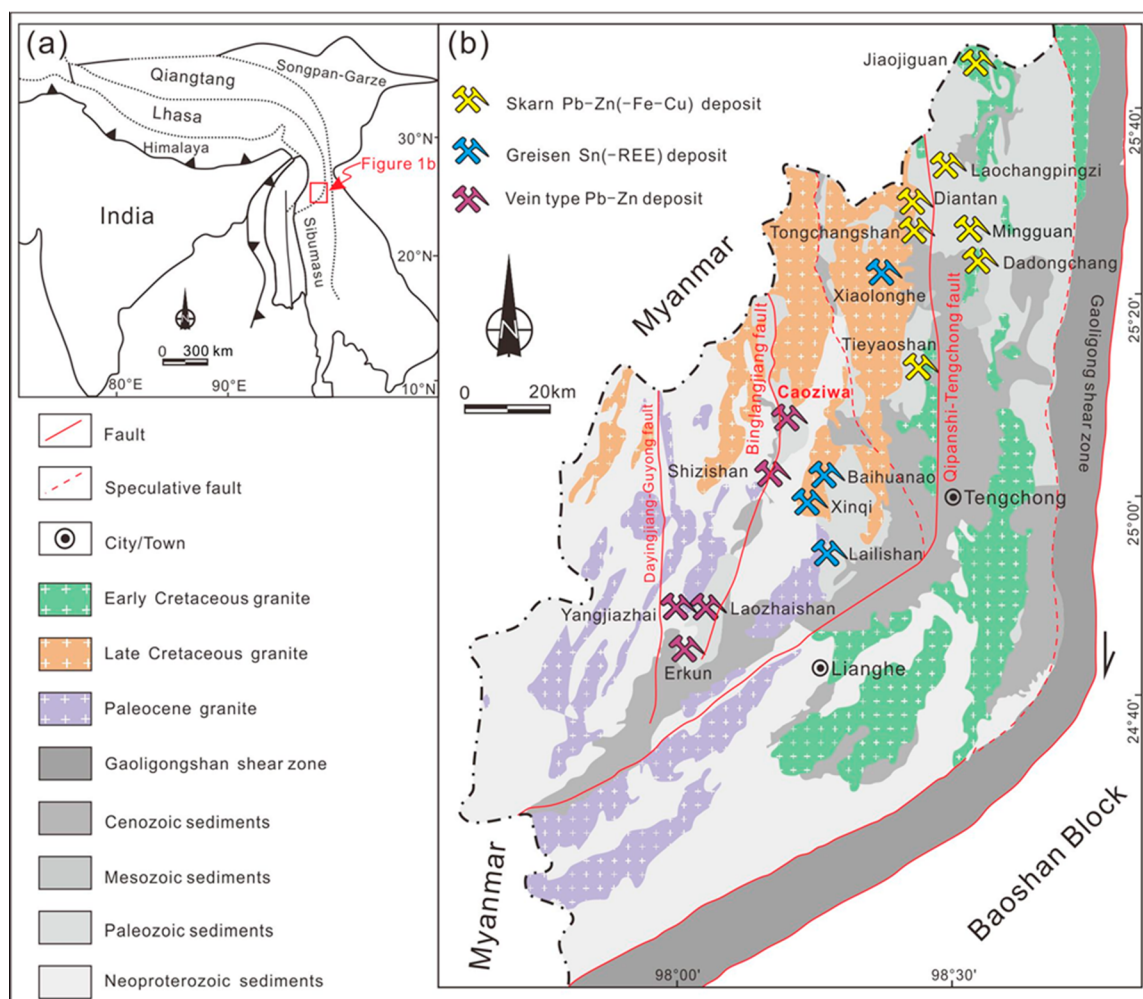


Figure 1. (a) Tectonic setting of the Tengchong block [1]; (b) simplified geological map of the Tengchong block [5–7].

For the skarn-type polymetallic mineralization in the eastern part and the greisen-type Sn–REE mineralization in the middle part of the Tengchong block, many previous research studies were conducted that mainly focused on the deposit geology [8–11], geochronology of mineralization [9,12–14], and ore-forming fluids [5,11]. These studies provided a lot of reliable evidence to reveal the genesis of skarn-type polymetallic mineralizations and greisen-type Sn–REE mineralizations. However, for the vein-type Pb–Zn mineralization in the western part of the Tengchong block, there is no relevant research. The source of ore-forming fluids, geochronology of mineralization, and mineralization process of these vein-type Pb–Zn deposits are still unclear, hindering our understanding of the genesis of these deposits and further exploration in the Tengchong block.

In this paper, we systematically provide new data on trace elemental and sulfur isotopic compositions of sulfides from the Caoziwa deposit, which is one of the typical vein-type Pb–Zn deposits found in the western part of the Tengchong block. The results effectively constrain the source of ore-forming materials and fluids, revealing the genesis of the Caoziwa Pb–Zn deposit.

2. Geological Setting

2.1. Regional Geology

The Tengchong block, located at the southeast edge of the Tibetan Plateau, is considered to be the southeastern extension of the Lhasa terrane [6,15] (Figure 1a). It is bounded by the Bangong–Nujiang suture zone to the east and the dextral Sagaing fault

zone to the west [3,7,16–18]. The basement of the Tengchong block is the Neoproterozoic to Paleozoic Gaoligongshan group, which is composed of granulite, gneiss, migmatite, and marble [1,5]. The Neoproterozoic to Paleozoic metamorphic basement was covered by Late Paleozoic to Cenozoic sedimentary rocks, including Devonian carbonate rocks, Carboniferous clastic rocks, Lower Permian carbonate rocks, Middle to Upper Triassic muddy limestone, Triassic to Middle Jurassic clastic rocks and limestone, and Cenozoic volcanic clastic rocks [19,20]. Under the influence of the India–Eurasia collision, three main faults (including the Binglangjiang fault, the Dayingjiang–Guyong fault, and the Qipanshi–Tengchong fault) in the Tengchong block are distributed in a nearly NS direction.

The granite exposed within the Tengchong block has an area of over 60%. From east to west, the ages of these granites transition from the Yanshan period to the Himalayan period. Based on the lithology and ages, the granites in the Tengchong block could be divided into three groups that are parallelly distributed in a nearly NS direction [7,19]. From east to west, the three groups include (1) the Early Cretaceous group comprising syenogranite, monzogranite, granodiorite, and granite porphyry, with zircon U–Pb ages of 130–108 Ma [21–23]; (2) the Late Cretaceous group, comprising plagiogranite, alkali-granite, syenogranite, monzogranite, and various granite porphyries, with zircon U–Pb ages of 77–64 Ma [7,21,24]; and the (3) Paleogene group, comprising biotite monzogranite, plagiogranite, and syenogranite, with zircon U–Pb ages of 56–51 Ma [21,24].

Multi-stage granitic magmatism and extensive tectonic activities in the Tengchong block have developed a large number of deposits, including skarn-type polymetallic mineralization, greisen-type Sn–REE mineralization, and hydrothermal vein-type Pb–Zn mineralization. The skarn-type polymetallic mineralization (e.g., Diantan Fe deposit, Laochangpingzi Cu–Pb–Zn deposits, Dadongchang Pb–Zn deposit), mainly distributed in the eastern part of the Tengchong block, has been considered to be related to the Early Cretaceous granitic magmatism [12]. The greisen-type Sn–REE mineralization (e.g., Xiaolonghe Sn deposit, Xinqi Sn deposit and Lailishan Sn–REE deposit), mainly distributed in the middle part of the Tengchong block, has been proven to be related to the Late Cretaceous granitic magmatism [5,25]. The vein-type Pb–Zn mineralization (e.g., Caoziwa Pb–Zn deposit, Shizishan Pb–Zn deposit, and Erkun Pb–Zn deposit) is mainly distributed in the western part of the Tengchong block. However, due to the lack of relevant research, the genesis of the vein-type Pb–Zn mineralization in the western part of the Tengchong block is still unknown.

2.2. Deposit Geology

The Caoziwa Pb–Zn deposit is located in the northwest of the Tengchong block, on the west side of the Binglangjiang fault (Figure 1b). It consists of the Dadoushan and Dahuadongshan ore zones (Figure 2a). The exposed sedimentary strata in the mining area are mainly composed of Upper Silurian dolomite, Lower Devonian Guanshang Formation slate, dolomite, limestone and sandstone, Middle Carboniferous Menghong group slate and sandstone, and Quaternary gravel sediments (Figure 2a). Among them, the the Lower Devonian Guanshang Formation is the ore-hosting strata. According to lithology, the Guanshang Formation can be divided into four sections. The first section of the Guanshang Formation is composed of dark gray carbonaceous slate in the upper part, blue-grey dolomite in the middle part, and light gray fine-grained metamorphic feldspar–quartz sandstone and siltstone in the lower part. This section is the main ore-bearing layer in the mining area, with a thickness of 241 m. The second section of the Guanshang Formation consists of dark grey limestone and light grey marble, with a thickness of 151–200 m. The third section of the Guanshang Formation consists of gray slate and argillaceous siltstone, with a thickness of 250–300 m. The fourth section of the Guanshang Formation is composed of light gray fine-grained feldspar–quartz sandstone and siltstone, with a thickness greater than 450 m.

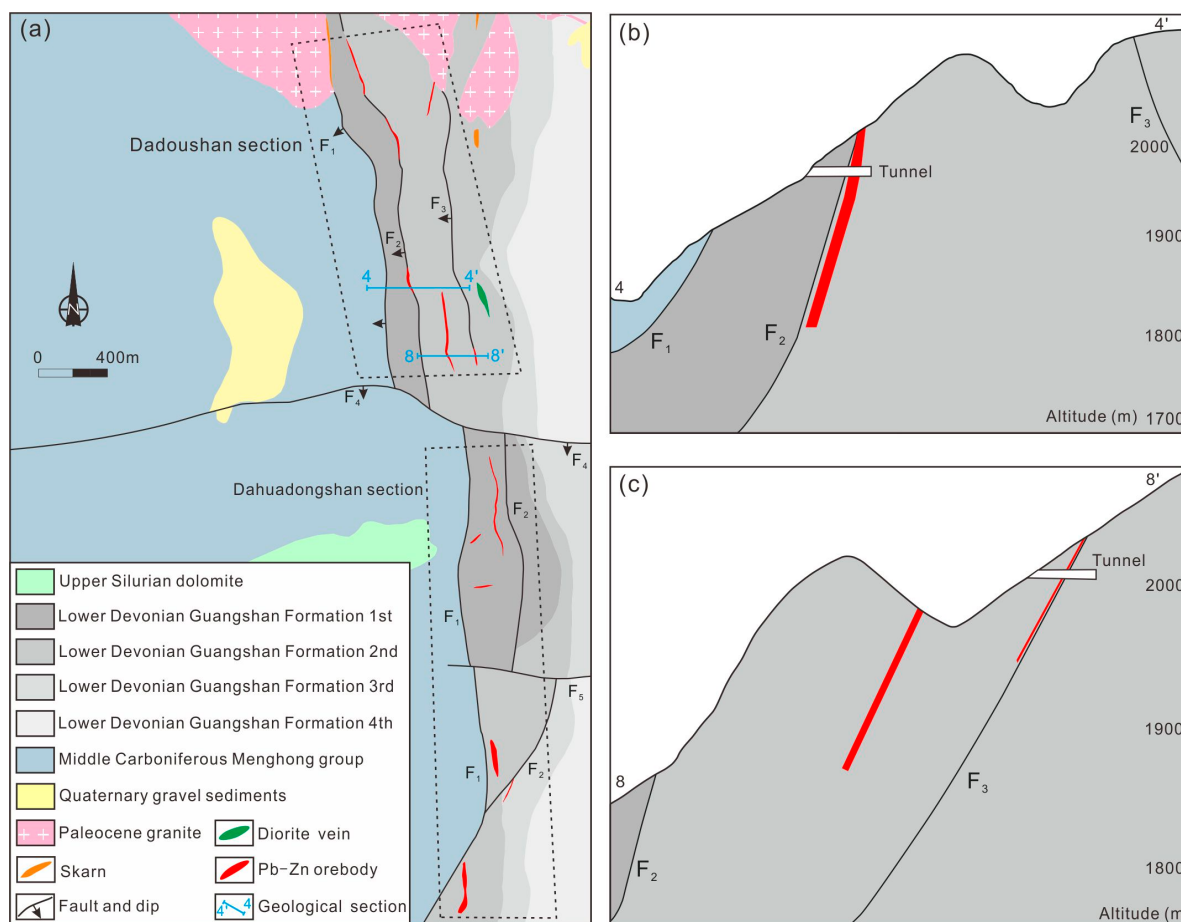


Figure 2. (a) Geological map of the Caoziwa Pb–Zn deposit; (b) cross-section (4–4') of the Caoziwa Pb–Zn deposit; (c) cross-section (8–8') of the Caoziwa Pb–Zn deposit.

Regional tectonic activities have led to the widespread development of faults in the mining area. There are five main faults in the Caoziwa mining area, named F1, F2, F3, F4, and F5 (Figure 2a). NS-striking F1 and F2 are located in the central part of the mining area. Both of them are staggered by the EW-striking F4 and F5 in the central and southern parts of the mining area, respectively. F3 is located in the northeast of the mining area, and is also NS-striking, distributed in parallel with F1 and F2 (Figure 2a). Among them, the NS-striking F1, F2, and F3 were considered to be the main ore-bearing structure in the Caoziwa mining area. Pb–Zn orebodies generally developed along the fracture zones of these faults (Figure 2b,c). However, the EW-striking F4 and F5 were considered to be post-mineralization faults.

The Pb–Zn mineralization in the Caoziwa deposit comprises abundant primary sulfide orebodies and a small number of oxidized orebodies. The orebodies are obviously controlled by the faults, which mainly developed along the fracture zones of NS-striking faults in the dolomite and marble of the first section of the Lower Devonian Guanshang Formation (Figure 3a,b). Moreover, some orebodies are massive and lenticular (Figure 3d). Caoziwa is a medium-scale Pb–Zn deposit. A total of six economic Pb–Zn orebodies have been identified, with an average thickness of 2.4 m, and an average grade of Pb = 2.14 wt.% and Zn = 8.79 wt.%. The ore minerals of the Caoziwa deposit include sphalerite, galena, smithsonite, hemimorphite, cerusite, limonite, pyrrhotite, pyrite, and a small amount of malachite. Gangue minerals mainly include calcite, dolomite, and quartz. The primary sulfide ores generally occur as massive and vein-like aggregates, while the oxidized ores generally occur as loose earthy aggregates. The wall-rock alteration in the Caoziwa Pb–Zn deposit mainly includes chloritization, silicification, and carbonatization (Figure 3a–c).

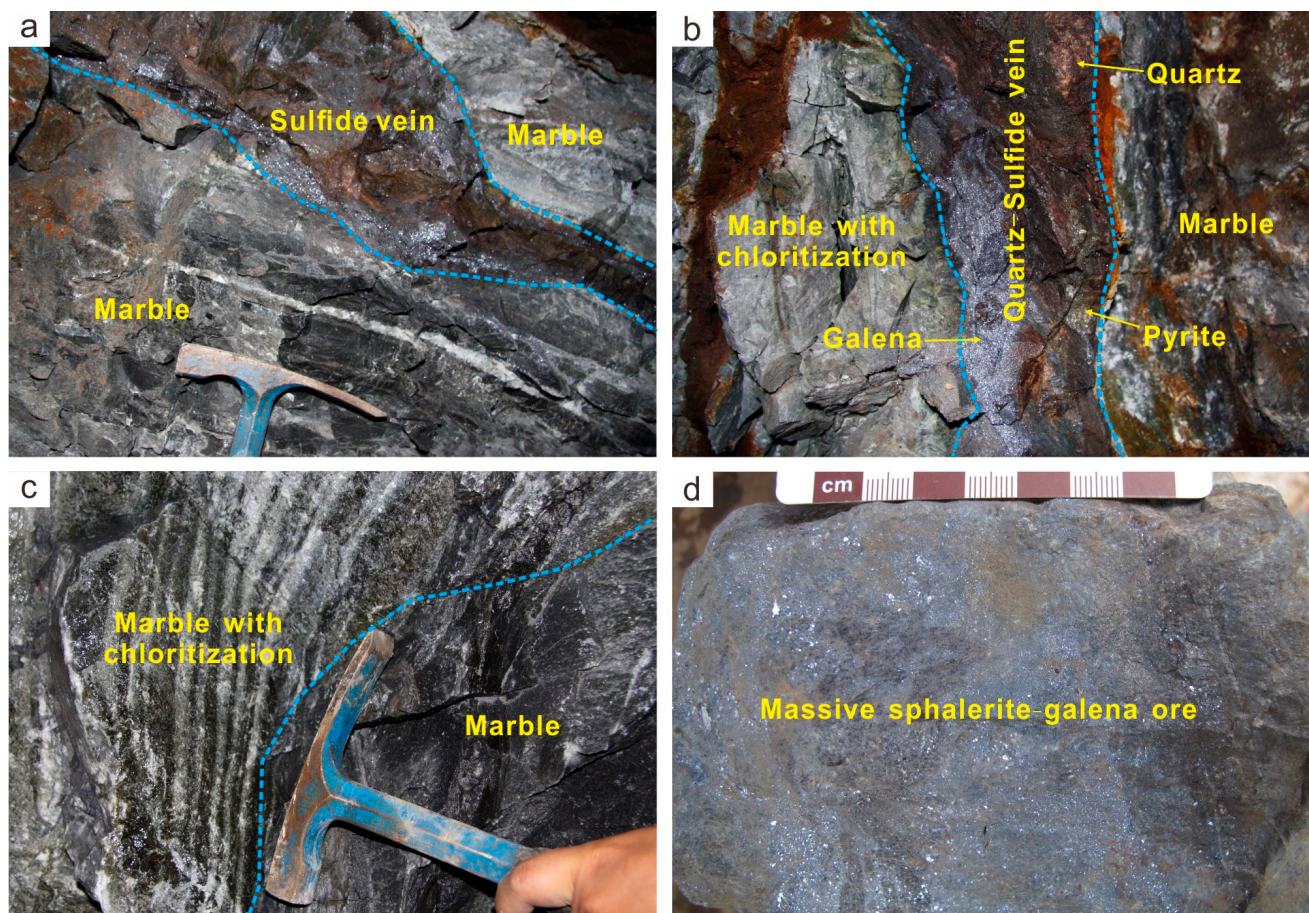


Figure 3. Representative photographs of orebodies. (a) Sulfide veins in marble. (b) Quartz-sulfide veins in marble, with obvious chloritization. (c) Marble near the orebodies is characterized by chloritization. (d) Massive sphalerite-galena ores.

Based on detailed field investigations and petrographic observations, three ore-forming stages have been identified (Figure 4). These three stages are (1) the syn-sedimentary stage: dolomite—calcite—pyrite (Py-I); (2) the hydrothermal stage: dolomite—calcite—pyrite (Py-II)—quartz—sphalerite—chalcopryite—galena—pyrrhotite and (3) the supergene stage: smithsonite—hemimorphite—cerussite—limonite—malachite—calcite—quartz.

The characteristics of the syn-sedimentary stage in the Caoziwa deposit are the extensive developments of coarse-grained euhedral Py-I, dolomite, and marble. The Py-I grains are commonly overprinted or crosscut by hydrothermal stage sulfides (Figure 5a,b). The hydrothermal stage is considered to be the main mineralization stage with abundant sulfides (Figure 5c–g). The sulfides are predominantly sphalerite and galena (Figure 5g) associated with euhedral Py-II, chalcopryite, and pyrrhotite (Figure 5e,h), and coexisting with dolomite, calcite, and quartz. Locally, the minerals in the hydrothermal stage were observed to overprint each other. For example, as shown in Figure 5f, pyrrhotite was replaced by Py-II, but Py-II was also overprinted by pyrrhotite (Figure 5i), so that they have been suggested to be co-genetic. The supergene stage is characterized by the development of ore-barren calcite and quartz with local oxidation of sulfides, which are generally crosscut earlier hydrothermal stage sulfides (Figure 5h,i). Oxidation processes transformed sphalerite into smithsonite and hemimorphite, galena into cerussite, chalcopryite into malachite, and pyrite into limonite.

Stage Mineral	Synsedimentary	Hydrothermal	Supergene
Dolomite			
Calcite			
Pyrite			
Quartz			
Sphalerite			
Chalcopyrite			
Galena			
Pyrrhotite			
Chlorite			
Smithsonite			
Hemimorphite			
Cerussite			
Limonite			
Malachite			

Figure 4. Paragenetic sequence of the Caoziwa Pb–Zn deposit.

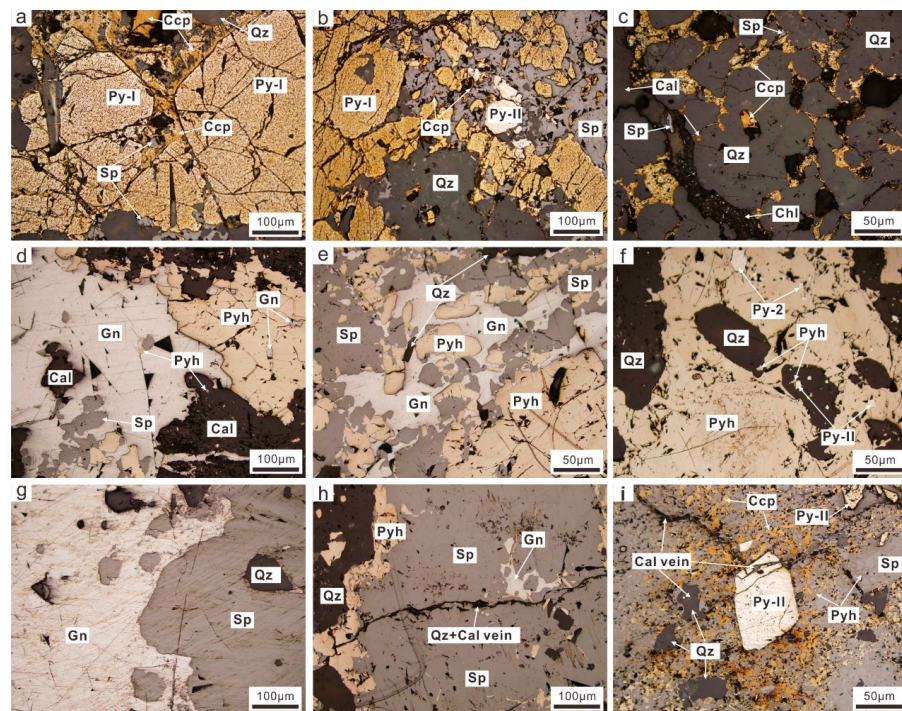


Figure 5. Representative photographs of the Caoziwa Pb–Zn deposit. (a) Euhedral Py-I overprinted by chalcopyrite, sphalerite, and quartz. (b) Py-I and coexisting quartz crosscut by chalcopyrite, sphalerite, and subhedral Py-II. (c) Chalcopyrite and sphalerite coexisting with quartz, calcite, and chlorite. (d) Calcite coexisting with sphalerite, galena, and pyrrhotite. (e) Sphalerite coexisting with galena, pyrrhotite, and quartz. (f) Subhedral to euhedral Py-II coexisting with pyrrhotite and quartz. (g) Coexistence of sphalerite, galena, and quartz. (h) Hydrothermal stage sphalerite–galena–pyrrhotite–quartz aggregates crosscut by supergene stage quartz–calcite vein. (i) Hydrothermal stage sphalerite–chalcopyrite–pyrrhotite–pyrite (Py-II)–quartz–calcite aggregates crosscut by supergene stage calcite. Cal = calcite, Ccp = chalcopyrite, Chl = chlorite, Gn = galena, Pyh = pyrrhotite, Py = pyrite, Qz = quartz, Sp = sphalerite [26].

3. Sampling and Analytical Methods

In order to trace the sources of ore-forming materials and reveal the ore-forming processes, 11 primary sulfide samples were selected for sulfur isotopic analysis, and eight primary sulfide samples were selected for LA-ICP-MS in situ trace elemental analysis in this study.

For sulfur isotopic analysis, the sulfide-bearing samples were crushed into sizes of 0.2–0.5 mm, and then sulfide grains (including pyrite, sphalerite, and galena) were carefully handpicked under a binocular microscope. The purity of these separated sulfides was greater than 99%. Sulfur isotopic analysis was performed in the Stable Isotope Laboratory, China University of Geosciences (Beijing) with the humidity at 20% and room temperature at 23 °C. Standard samples of GBW04414 and GBW04415 were used to calibrate the analysis. The analytical precision for the sulfur isotopic results of the Caoziwa deposit is better than 0.2%.

The in situ trace elemental analyses were completed at the CODES LA-ICP-MS facility at the University of Tasmania, Hobart, Australia [27,28]. Single-spot analysis was performed with a New Wave UP-213 nm laser ablation coupled with an Agilent 7700 s Quadrupole ICP-MS (Agilent Technologies, Inc., New York, NY, USA), with laser-ablating spot diameters of 30 µm and a repetition rate of 5 Hz. The detailed experimental parameters are provided in [27,28]. Data correction was completed according to analytical minerals, with Fe, Zn, and Pb as the internal standards for pyrite, sphalerite, and galena, respectively. Before the trace elemental analysis via LA-ICP-MS was carried out, the major elements (including Fe, Zn, and Pb) of pyrite, sphalerite, and galena were determined via EPMA. The calibrated standard was STDGL2b-2 [29], which consisted of powdered sulfides doped with certified element solutions that were fused to a lithium borate glass disk. The standard was analyzed twice per 90 min, with a 100 µm beam size at 10 Hz to correct for instrument drift. The analysis accuracy is expected to be better than 20% for most elements [30].

4. Analytical Results

4.1. Sulfur Isotope

The sulfur isotopic compositions of sulfides in the Caoziwa deposit are listed in Table 1. The $\delta^{34}\text{S}$ values obtained from syn-sedimentary stage pyrite (Py-I) range from 11.5‰ to 15.3‰ (mean 13.9‰, $n = 4$), while the $\delta^{34}\text{S}$ values obtained from hydrothermal stage pyrite (Py-II), sphalerite, and galena range from 4.5‰ to 6.7‰ (mean 5.6‰, $n = 3$), 2.8‰ to 6.1‰ (mean 4.7‰, $n = 6$), and 3.1‰ to 5.9‰ (mean 4.4‰, $n = 6$), respectively. The $\delta^{34}\text{S}$ values of hydrothermal stage sulfides (including Py-II, sphalerite, and galena) are obviously lower than that of Py-I.

Table 1. Sulfur isotopic compositions from the Caoziwa Pb–Zn deposit.

Stage	Sample No.	Description	Sulfide	$\delta^{34}\text{S}$ (‰)
Syn-sedimentary stage	CZW-01	Euhedral Py-I in dolomite	Py-I	15.3
	CZW-02	Euhedral Py-I in marble	Py-I	14.2
	CZW-03	Subhedral to euhedral Py-I in marble	Py-I	14.7
	CZW-05	Euhedral Py-I in marble	Py-I	11.5
Hydrothermal stage	CZW-06	Massive sulfide ores	Py-II	6.7
			Sphalerite	6.1
			Galena	5.9
	CZW-09	Massive sulfide ores	Py-II	4.5
			Galena	4.2
	CZW-10	Massive sulfide ores	Sphalerite	3.7
			Galena	3.1
	CZW-12	Massive sulfide ores	Sphalerite	4.9
			Galena	4.1
	CZW-13	Massive sphalerite ores	Sphalerite	2.8
			Sphalerite	5.4
	CZW-14	Massive sulfide ores	Galena	4.7
			Py-II	5.5
			Sphalerite	5.2
	CZW-15	Massive sulfide ores	Galena	4.6

4.2. Trace Elements of Sulfides

As listed in Table 2, Co, Ni, As, Se, and Pb are abundant in both Py-I and Py-II. The concentrations of Co, Ni, As, Se, and Pb in Py-I are 5.93–23.95 ppm (average of 13.14 ppm), 12.38–35.06 ppm (average of 22.66 ppm), 508.26–1123.08 ppm (average of 866.05 ppm), 1.45–7.06 ppm (average of 4.49 ppm), and 1.38–10.56 ppm (average of 4.53 ppm), respectively. Those in Py-II are 70.34–300.85 ppm (average of 159.17 ppm), 4.98–119.67 ppm (average of 33.88 ppm), 5.05–799.66 ppm (average of 185.11), 4.37–11.53 ppm (average of 7.54 ppm), and 0.12–1925.98 ppm (average of 154.79 ppm), respectively. Meanwhile, Cu, Ag, Sn, Sb, Te, and Bi are lower in both Py-I and Py-II, with concentrations of 0.05–0.13 ppm (average of 0.08 ppm) for Cu, 0.01–0.28 ppm (average of 0.10 ppm) for Ag, 0.26–0.52 ppm (average of 0.38 ppm) for Sn, 0.36–1.28 ppm (average of 0.70 ppm) for Sb, 0.05–0.13 ppm (average of 0.10 ppm) for Te, and 0.01–0.05 ppm (average of 0.03 ppm) for Bi in Py-I, and 0.01–2.11 ppm (average of 0.31 ppm) for Cu, 0.01–14.32 ppm (average of 1.26 ppm) for Ag, 0.12–5.66 ppm (average of 0.57 ppm) for Sn, 0.01–5.46 ppm (average of 0.73 ppm) for Sb, 0.03–0.92 ppm (average of 0.17 ppm) for Te, and 0.01–25.42 ppm (average of 2.50 ppm) in Py-II. It is noteworthy that the concentration of Mn in Py-I is significantly higher than that in Py-II, and the concentrations of Zn and Pb in Py-II range widely, from 0.46 ppm to 893.03 ppm and 0.12 ppm to 1925.98 ppm, respectively.

Sphalerite in the Caoziwa deposit contains a lot of Mn, Fe, Cu, and Cd, with an average concentration greater than 100 ppm (Table 3). The concentrations of Mn, Fe, Cu, and Cd in sphalerite are 1181.83–2409.85 ppm (average of 1861.11 ppm), 17,067.29–52,692.60 ppm (average of 34,125.69 ppm), 83.38–172.36 ppm (average of 121.81 ppm), and 2942.11–3839.88 ppm (average of 3367.60 ppm), respectively. The contents of Co, Se, Ag, Sn, Sb, Te, and Tl are obviously lower, with average concentrations of 6.42 ppm, 1.42 ppm, 36.65 ppm, 15.02 ppm, 24.95 ppm, 0.19 ppm, and 0.09 ppm, respectively. Furthermore, the average concentration of Pb in sphalerite is 4327.85 ppm, but the concentration of Pb varies widely (0.73–46,978.23 ppm) and is significantly affected by two outliers.

Ag, Sn, and Sb are widely distributed in galena from the Caoziwa deposit, with an average concentration greater than 1000 ppm (Table 4). The concentration variations of Ag, Sn, and Sb between different galena grains are also relatively narrow. Element Ag ranges from 1831.32 ppm to 2943.08 ppm, Sn ranges from 273.76 ppm to 1589.97 ppm, and Sb ranges from 1815.03 ppm to 2918.12 ppm. Moreover, the galena also contains a lot of Cd (21.44–162.54 ppm, averaging 49.13 ppm), Te (14.93–73.98 ppm, averaging 32.11 ppm), and Bi (70.44–260.70 ppm, averaging 146.88 ppm), and smaller amounts of Mn (0.89–121.71 ppm, averaging 15.93 ppm), Co (0.01–0.77 ppm, averaging 0.11 ppm), Ni (0.08–0.55 ppm, averaging 0.23 ppm), As (0.02–0.44 ppm, averaging 0.17 ppm), Se (0.89–23.76 ppm, averaging 6.89 ppm), and Tl (5.80–6.86 ppm, averaging 6.58 ppm). Furthermore, there is an interesting fact that the Fe, Cu, and Zn contents vary widely in galena from the Caoziwa deposit, with concentration ranges of 1.03–3847.24 ppm, 0.01–1742.96 ppm, and 0.19–26,108.08 ppm, respectively, indicating that these elements are highly unevenly distributed in galena.

Table 2. Trace elemental compositions of pyrite from the Caoziwa Pb–Zn deposit.

Stage	Sample No.	Analysis Spot	Mn	Co	Ni	Cu	Zn	As	Se	Ag	Sn	Sb	Te	Pb	Bi	Co/Ni
Syn-sedimentary stage	CZW-01	1	24.31	5.93	12.38	0.06	0.51	1123.08	1.45	0.13	0.35	1.28	0.10	1.38	0.05	0.48
		2	102.53	23.95	35.06	0.05	0.23	853.17	3.62	0.02	0.26	0.36	0.05	3.42	0.02	0.68
		3	56.28	15.38	26.19	0.08	0.47	508.26	7.06	0.07	0.52	0.55	0.13	10.56	0.01	0.59
	CZW-03	1	17.96	8.06	21.02	0.13	0.38	1038.49	5.03	0.01	0.31	0.63	0.08	4.13	-	0.38
		2	46.72	12.37	18.65	0.06	0.15	807.25	5.28	0.28	0.45	0.68	0.12	3.15	0.03	0.66
	average		49.56	13.14	22.66	0.08	0.35	866.05	4.49	0.10	0.38	0.70	0.10	4.53	0.03	0.56
Hydrothermal stage	CZW-06	1	0.15	93.39	23.16	0.03	0.80	578.32	5.25	0.05	0.13	0.02	0.04	0.41	0.02	4.03
		2	-	70.67	9.74	0.04	0.71	5.05	8.63	0.01	0.16	0.28	0.03	0.22	0.01	7.26
		3	0.67	123.59	10.47	2.11	75.13	258.82	4.49	1.76	0.41	0.51	0.16	233.36	2.71	11.80
		4	0.03	70.34	11.55	0.12	1.88	7.86	9.03	0.25	0.17	0.21	0.08	1.03	0.18	6.09
	CZW-07	1	2.02	80.37	4.98	0.88	893.03	155.58	6.26	14.32	5.66	5.46	0.92	1925.98	25.42	16.14
		2	-	127.51	14.81	0.06	1.09	799.66	4.57	0.03	0.12	0.02	0.07	0.51	0.05	8.61
		3	0.25	300.85	7.81	0.06	2.93	455.28	4.37	0.01	0.14	0.13	0.10	0.44	0.02	38.52
	CZW-09	1	0.08	233.10	119.67	0.01	2.71	26.76	10.93	0.11	0.16	0.11	0.13	0.94	0.09	1.95
		2	0.31	235.05	60.19	0.09	1.17	11.95	8.70	0.05	0.17	0.01	0.11	0.36	0.02	3.91
		3	0.52	169.63	30.63	0.49	0.63	30.92	7.86	0.19	0.22	2.51	0.34	2.97	1.48	5.54
		4	-	74.81	9.20	-	0.46	7.69	8.44	0.22	0.15	0.01	0.09	0.12	0.01	8.13
	CZW-15	1	0.06	219.63	37.41	0.05	0.75	170.17	6.26	0.01	0.17	-	0.11	0.16	-	5.87
		2	0.18	148.36	69.16	0.06	1.01	36.24	11.53	0.35	0.15	0.25	0.08	0.41	0.03	2.15
		3	0.03	281.02	65.54	0.02	0.91	47.29	9.21	0.21	0.15	0.01	0.09	0.20	-	4.29
	average		0.39	159.17	33.88	0.31	70.23	185.11	7.54	1.26	0.57	0.73	0.17	154.79	2.50	8.88

Table 3. Trace elemental compositions of sphalerite from Caoziwa Pb–Zn deposit.

Sample No.	Analysis Spot	Mn	Fe	Co	Cu	Se	Ag	Cd	Sn	Sb	Te	Tl	Pb
CZW-06	1	1406.59	24,882.29	2.1	98.31	2.08	16.62	3661.64	6.55	11.25	0.15	0.04	549.2
	2	1516.71	23,740.63	2.11	104.63	1.52	34.33	3686.11	8.99	18.93	0.18	0.04	103.69
	3	1429.94	23,440.69	2.07	92.99	1.46	49.27	3569.55	8.55	4.99	-	0.01	36.38
	4	1569.93	23,899.2	2.02	91.72	1.32	24.59	3529.78	2.91	2.92	0.1	0.01	16.94

Table 3. Cont.

Sample No.	Analysis Spot	Mn	Fe	Co	Cu	Se	Ag	Cd	Sn	Sb	Te	Tl	Pb
CZW-09	1	1181.83	30,266.42	5.76	83.38	1.42	133.28	3774.55	60.58	142.57	0.89	0.39	46,978.23
	2	1282.31	31,925.25	4.79	87.55	1.04	11.83	3839.88	2.48	4.52	0.01	0.01	5.84
CZW-10	1	2192.58	17,375.21	0.74	105.14	1.23	126.79	3261.22	36.14	98.97	0.35	0.32	8539.14
	2	1997.65	17,067.29	0.76	106.45	1.28	43.3	3287.32	7.71	18.98	0.2	0.02	20.87
CZW-12	1	2305.61	49,215.74	12.36	162.67	1.38	9.26	3143.3	3.14	5.57	0.09	0.01	2.92
	2	2409.85	52,692.6	12.41	158.47	0.84	4.35	2942.11	5.2	0.61	0.05	-	1.9
	3	2340.28	51,972.76	12.12	158.73	1.64	5.16	2965.04	2.08	2.2	0.05	-	2.06
	4	2319.28	49,137.61	13.25	161.18	1.7	4.91	3122.01	19.18	0.41	0.08	-	0.73
	5	2241.9	48,018.31	12.97	172.36	1.52	12.74	2996.27	31.7	12.37	0.07	0.03	4.18
Average		1861.11	34,125.69	6.42	121.81	1.42	36.65	3367.60	15.02	24.95	0.19	0.09	4327.85

Table 4. Trace elemental compositions of galena from the Caoziwa Pb–Zn deposit.

Sample No.	Analysis Spot	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Te	Tl	Bi
CZW-06	1	1.48	7.71	0.02	0.17	1.16	56.62	0.07	1.07	2247.21	38.28	1074.87	2430.48	16.50	6.53	78.86
	2	21.93	42.75	0.02	0.10	27.67	610.69	0.06	1.37	2330.95	40.82	1151.27	2533.65	17.62	6.86	70.44
	3	1.86	2.14	0.02	0.12	0.07	0.37	0.11	1.15	2306.04	44.03	1117.27	2484.49	17.22	6.78	75.81
CZW-10	1	1.73	1.17	0.02	0.23	0.01	0.27	0.02	1.15	2449.45	46.90	1391.01	2525.53	14.93	6.84	116.73
	2	2.34	1.52	0.02	0.19	0.08	0.31	-	1.04	2425.76	52.65	1395.26	2537.40	15.29	6.68	113.64
CZW-12	1	0.89	1.50	0.02	0.10	0.03	0.19	0.13	1.57	2300.33	38.94	1115.49	2377.96	16.63	6.81	98.90
	2	1.18	1.03	0.03	0.12	0.11	0.49	0.35	0.89	2172.98	43.30	1118.99	2347.34	17.52	6.61	97.04
	3	1.60	7.88	0.03	0.17	0.10	1.10	0.44	1.60	2359.82	47.44	1179.92	2422.43	15.69	6.74	95.14
CZW-15	1	8.00	2289.04	0.23	0.44	26.54	1491.33	0.11	13.19	1831.32	23.67	273.76	1815.03	57.24	6.39	249.51
	2	121.71	3847.24	0.77	0.50	1742.96	26,108.08	0.13	13.41	2054.06	162.54	1589.97	2090.94	56.38	6.35	251.66
	3	13.13	1068.74	0.01	0.55	5.33	7.10	0.12	23.76	2943.08	21.44	402.38	2918.12	73.98	6.59	254.12
	4	15.36	371.90	0.09	0.08	280.64	2960.02	0.28	22.42	1959.96	29.50	390.19	1946.39	66.26	5.80	260.70
Average		15.93	636.89	0.11	0.23	173.73	2603.05	0.17	6.89	2281.75	49.13	1016.70	2369.15	32.11	6.58	146.88

5. Discussion

5.1. Trace Element Speciation in Sulfides

Before using trace elements in sulfides to discuss scientific issues related to mineralization, it is necessary to identify the occurrences of trace elements in sulfides. Some outliers caused by fluid or mineral inclusions must be excluded to avoid their effects on the accuracy of conclusions.

Trace elements usually appear in the lattice of pyrite by directly substituting Fe and S, or as mineral inclusions [31–33]. Pure pyrite is characterized by flat time-resolved depth profiles (Figure 6a), while the mineral inclusions are generally characterized by elemental peaks (Figure 6b). The existence of mineral inclusions obviously changes the concentrations of some trace elements, resulting in some outliers. As listed in Table 2, two pyrite grains are characterized by abnormally high concentrations of Zn, Ag, Sn, Sb, Pb, and Bi, and display elemental peaks in the time-resolved depth profiles (Figure 6b); this suggests that small proportions of Zn, Ag, Sn, Sb, Pb, and Bi can enter the pyrite grains as sub-micro-scale mineral inclusions (e.g., sphalerite and galena). Excluding these two outliers, the other LA-ICP-MS analysis results show that abundant Co, Ni, As, and Se are hosted in pyrite, and display flat time-resolved depth profiles, indicating Co, Ni, As, and Se as compatible trace elements for pyrite that could extensively enter the pyrite crystal lattice by isomorphic substitution. Furthermore, small amounts of Cu, Zn, Ag, Cd, Sn, Sb, Te, Pb, and Bi are hosted in pyrite, and also display flat time-resolved depth profiles in most pyrite grains, implying that these elements could enter the pyrite crystal lattice in certain amounts by isomorphic substitution.

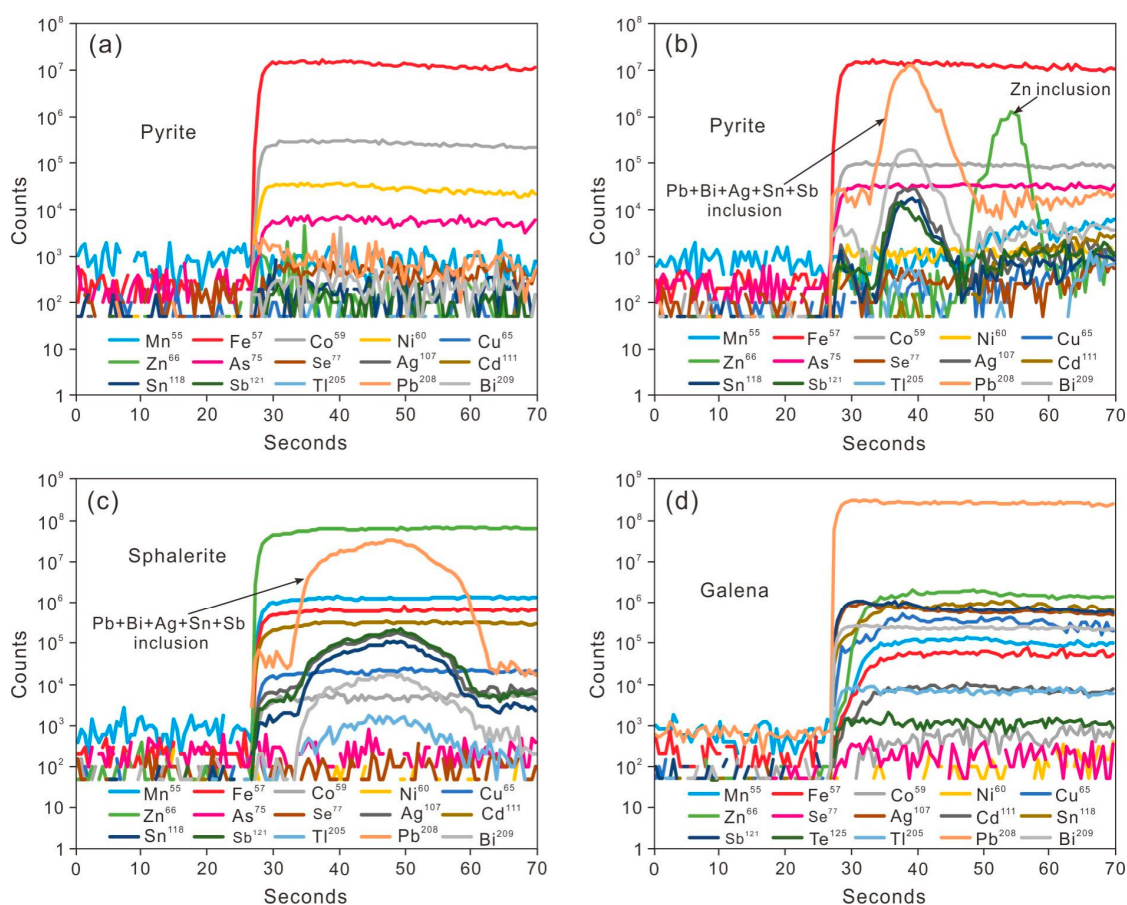


Figure 6. Representative time-resolved analytical signals of LA-ICP-MS. (a) Pyrite with isomorphic trace elemental substitutions; (b) pyrite with a Pb–Bi–Ag–Sn–Sb-rich inclusion and a Zn-rich inclusion; (c) sphalerite with a Pb–Bi–Ag–Sn–Sb-rich inclusion; (d) galena with isomorphic trace elemental substitutions.

Similarly to pyrite, trace elements enter the sphalerite mainly by isomorphic substitution and sub-micro-scale mineral inclusions [34–37]. As shown in Table 3, abundant Mn, Fe, Cu, and Cd elements and less Co, Ni, Cu, As, Se, Ag, Sb, and Te elements are distributed in the sphalerite from the Caoziwa deposit. Numerous studies have investigated the substitution mechanisms of trace elements in the sphalerite lattice, suggesting that divalent cations such as Mn^{2+} , Fe^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} could directly replace Zn^{2+} in the crystal lattice of sphalerite because their ionic radii and valence states are similar to Zn^{2+} [34–36,38,39]. Monovalent (Ag^+ , Cu^+), trivalent (Sb^{3+} , Sn^{3+}), and tetravalent (Sn^{4+}) cations with larger ionic radii and different valence states are usually substituted for Zn^{2+} in the sphalerite lattice by forming cation groups, such as $(\text{Ag}, \text{Cu})^+ + (\text{Sb}, \text{Sn})^{3+} \leftrightarrow 2\text{Zn}^{2+}$ and $2(\text{Ag}, \text{Cu})^+ + \text{Sn}^{4+} \leftrightarrow 3\text{Zn}^{2+}$ [34,40–47]. However, in sphalerite from the Caoziwa deposit, the concentration of Pb varies in several orders of magnitude, implying that it is significantly affected by Pb-rich inclusions (e.g., galena). Meanwhile, Ag, Sn, and Sb show positive correlations with Pb (Figure 7a–c), indicating that they are mainly controlled by the Pb-rich inclusions in sphalerite, which are identified in the analytical signals as well (Figure 6c).

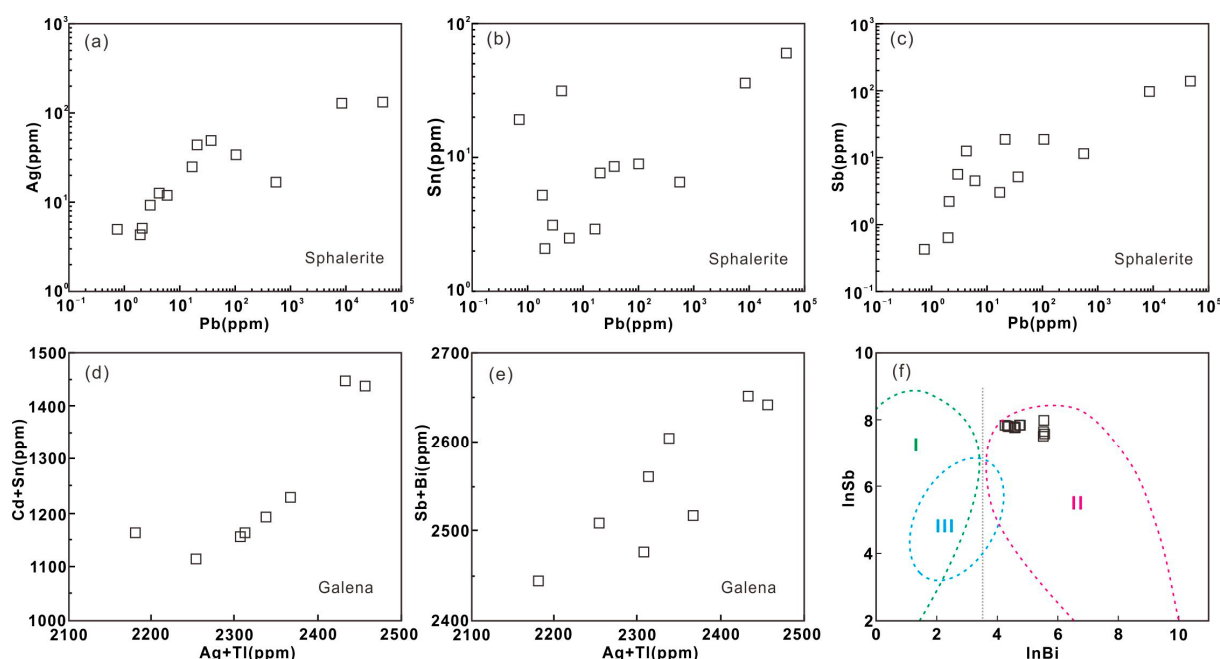


Figure 7. Binary plots of (a) Ag vs. Pb, (b) Sn vs. Pb, (c) Sb vs. Pb in sphalerite, and (d) Cd + Sn vs. Ag + Tl, (e) Sb + Bi vs. Ag + Tl, (f) $\ln\text{Sb}$ vs. $\ln\text{Bi}$ in galena from the Caoziwa Pb–Zn deposit. The trace elemental concentrations are listed in Tables 3 and 4, respectively. Field I = sedimentary transformation Pb–Zn deposits; Field II = magmatic hydrothermal Pb–Zn deposit; Field III = volcanic-type Pb–Zn deposit.

The trace elemental composition of galena is significantly different from that of sphalerite in the Caoziwa Pb–Zn deposit. Except for sample CZW-15, which is affected by Fe–Cu–Zn-rich inclusions, in most samples, the galena is enriched with Ag, Sn, Sb, Cd, Te, and Bi, with less Mn, Fe, Co, Ni, Cu, Zn, As, Se, and Tl (Table 4). George et al. (2015) proposed that there is an isomorphic substitution of $\text{Bi}^{3+} + (\text{Ag}, \text{Tl})^+ \leftrightarrow 2\text{Pb}^{2+}$ in galena [39]. Meanwhile, Guo et al. (2023) suggested that Ag, Sn, Cd, Tl, and Bi could enter the galena by the isomorphic substitution of $\text{Bi}^{3+} + (\text{Cd}, \text{Sn})^{2+} + (\text{Ag}, \text{Tl})^+ \leftrightarrow 3\text{Pb}^{2+}$ [47]. In the Caoziwa deposit, the time-resolved analytical signals of galena are relatively flat (Figure 6d), indicating that the detected elements mainly enter the galena grains by isomorphic substitution. Furthermore, the concentrations of Ag + Tl show obvious positive correlations with Cd + Sn and Sb + Bi, probably indicating an isomorphic substitution mechanism of $(\text{Bi}, \text{Sb})^{3+} + (\text{Cd}, \text{Sn})^{2+} + (\text{Ag}, \text{Tl})^+ \leftrightarrow 2\text{Pb}^{2+}$.

5.2. Sources of Ore-Forming Materials

Sulfur is one of the most important mineralization materials in Pb–Zn deposits. The sulfides in the Caoziwa Pb–Zn deposit mainly include pyrite, sphalerite, galena, pyrrhotite, and chalcopyrite without any sulfate. The absence of sulfate implies that the $\delta^{34}\text{S}$ values of sulfide minerals approximate the $\delta^{34}\text{S}$ values of ore-forming fluid [48–50]. In the Caoziwa deposit, the pyrite, sphalerite, and galena from the hydrothermal ore stage yielded $\delta^{34}\text{S}$ values of 4.5–6.7‰, 2.8–6.1‰, and 3.1–5.9‰ (Table 1), respectively, indicating the $\delta^{34}\text{S}$ values of ore-forming fluid in this stage are 2.8–6.7‰. These values coincide well with magmatic sulfur (−3‰ to 7‰) [51], and are obviously lower than the $\delta^{34}\text{S}$ values of the pyrite (Py-I) hosted in the surrounding dolomite and limestone ranging from 11.5‰ to 15.3‰ (Table 1, Figure 8); this probably indicates that the sulfur forming the Caoziwa Pb–Zn deposit predominantly originated from magmatic hydrothermal fluids. Moreover, the sulfur isotopic compositions of the Caoziwa Pb–Zn deposit are similar to those of skarn polymetallic deposits and greisen Sn deposits with magmatic origins (Figure 8), implying that the Caoziwa Pb–Zn deposit mainly contributed by magmatic hydrothermal fluids as well.

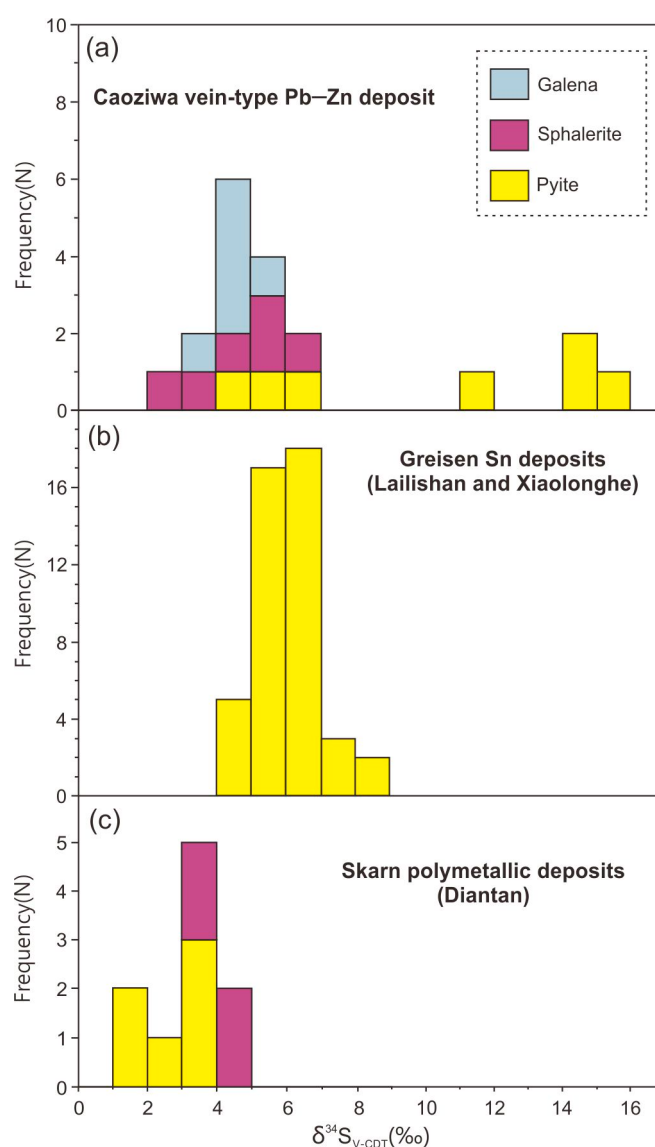


Figure 8. Histograms of $\delta^{34}\text{S}$ values for sulfide minerals from the Caoziwa Pb–Zn deposit (a). Also shown are values from greisen Sn deposit (e.g., Laishan and Xiaolonghe) (b) and skarn Fe deposits (e.g., Diantan) in the Tengchong block (c) [8,28].

The Co/Ni ratios of pyrite have also been used to trace the origins and ore-forming conditions of pyrite [28]. Reducing conditions in organic matter-rich sedimentary rocks may enhance the uptake of Ni into pyrite [52,53], resulting in low Co/Ni ratios. Previous studies have found that pyrite characterized by low Co/Ni ratios ($\text{Co/Ni} < 1$) is attributed to sedimentary origins, while pyrite characterized by high Co/Ni ratios ($\text{Co/Ni} > 1$) is considered to be dominated by magmatic hydrothermal fluid [34,54,55]. The Co/Ni ratios of Py-I vary from 0.38–0.68, with an average of 0.56 ($n = 5$), consistent with a sedimentary origin. Py-II yields relatively wide Co/Ni ratios of 1.95–38.52. These higher values are similar to those of magmatic hydrothermal pyrite.

Both the sulfur isotopic compositions of sulfides and the Co/Ni ratios of pyrite altogether are consistent with a magmatic–hydrothermal origin for the Caoziwa Pb–Zn deposit.

5.3. Genetic Type of Caoziwa Deposit

The trace elemental compositions of sulfides have been proposed to be controlled by ore sources, the nature of ore-forming fluid (e.g., elemental composition, temperature, and oxygen fugacity), host rocks, and mineralization processes [27,35,37,56–58]. Meanwhile, different types of deposits are generally characterized by distinct ore sources, ore-forming fluid, host rocks, and mineralization processes. Hence, it seems that the trace elemental compositions of sulfides could be used to indicate the genetic types of ores.

Recently studies have demonstrated that sphalerite formed in deposits associated with high-temperature magmatic hydrothermal fluids (e.g., skarn and epithermal deposits) is characterized by high Fe, Mn, Sn, and Co contents, and low Cd, Ge, and Ga contents; moreover, deposits associated with low-temperature hydrothermal fluids (e.g., MVT deposit) are characterized by low Fe, Mn, Sn, and Co contents, and high Cd, Ge, and Ga contents [34,37,59,60]. In the Caoziwa Pb–Zn deposit, the Mn, Fe, Sn, Co, and Cd contents in sphalerite are similar to the deposits related to high-temperature hydrothermal fluids (VMS, skarn and epithermal deposits), which are obviously distinct from that of the sphalerite from MVT deposit (Figure 9a–d). Among them, Mn, Fe, Sn, and Co in sphalerite from the Caoziwa deposit are relatively higher than that of the sphalerite from MVT deposit, while the Cd content in sphalerite from the Caoziwa deposit is relatively lower than that of the sphalerite from MVT deposit (Figure 9e). As illustrated by Figure 10, the sphalerite samples in the Caoziwa deposit are also plotted in the areas of VMS, skarn, and epithermal deposits, which are related to high-temperature hydrothermal fluids, consistent with the magmatic hydrothermal proven by sulfur isotopes of sulfides and Co/Ni ratios of pyrite. Furthermore, Figure 11 summarizes the trace elemental compositions of galena from different genetic types of deposits (skarn, SEDEX, epithermal, and MVT). Elemental Bi is generally associated with high-temperature ore-forming fluids, whereas elemental Sb is more mobile in low-temperature ore-forming fluids [61,62]. The galena from skarn deposits, which are characterized by high-temperature fluids, is distinctly enriched in Bi while depleted in Sb. Except for three analytical spots significantly affected by mineral inclusions, the galena from the Caoziwa deposit is characterized by high Bi content (Figure 11a–d), relatively high Sn/Cu ratios (Figure 11c), and low Cu/Ag ratios (Figure 11d), similar to the galena from skarn-type deposits. Although no obvious skarnization was found in the orebodies, some skarnization occurred in the northern part of the ore field, near the Paleocene granite (Figure 2a). This indicates that the Caoziwa Pb–Zn deposit is a magmatic hydrothermal vein-type Pb–Zn deposit that probably belongs to a skarn mineralization system. The Paleocene granitic magmatism provided metal-rich magmatic hydrothermal fluids and developed some skarn in the contact zones between the granite and carbonate wall rock, and the NS-trending faults provided pathways for the migration of ore-forming fluids and space for ore precipitation, jointly forming the Caoziwa Pb–Zn deposit.

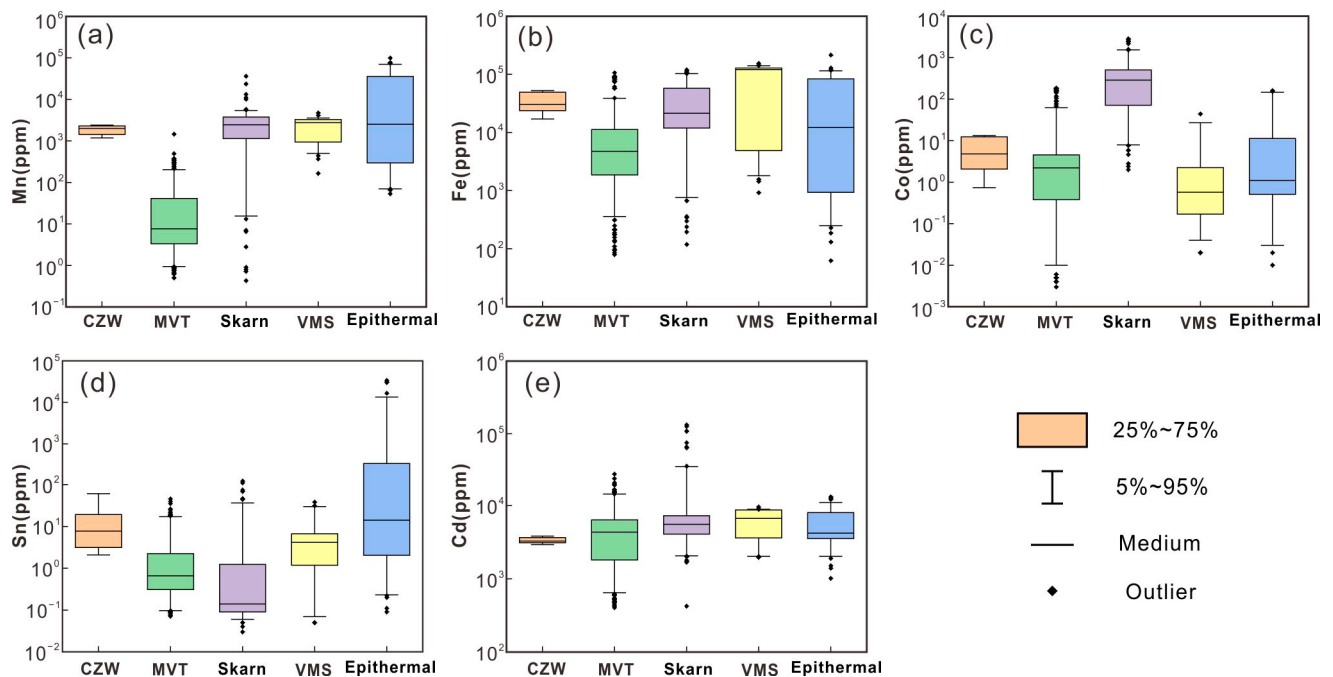


Figure 9. Comparative box plots of trace elemental concentrations in sphalerite from the Caoziwa Pb–Zn deposit and other genetic types of deposits [34,35,42,46,63,64]. (a) Mn concentrations in sphalerite from Caoziwa and other genetic types of deposits, (b) Fe concentrations in sphalerite from Caoziwa and other genetic types of deposits, (c) Co concentrations in sphalerite from Caoziwa and other genetic types of deposits, (d) Sn concentrations in sphalerite from Caoziwa and other genetic types of deposits, (e) Cd concentrations in sphalerite from Caoziwa and other genetic types of deposits.

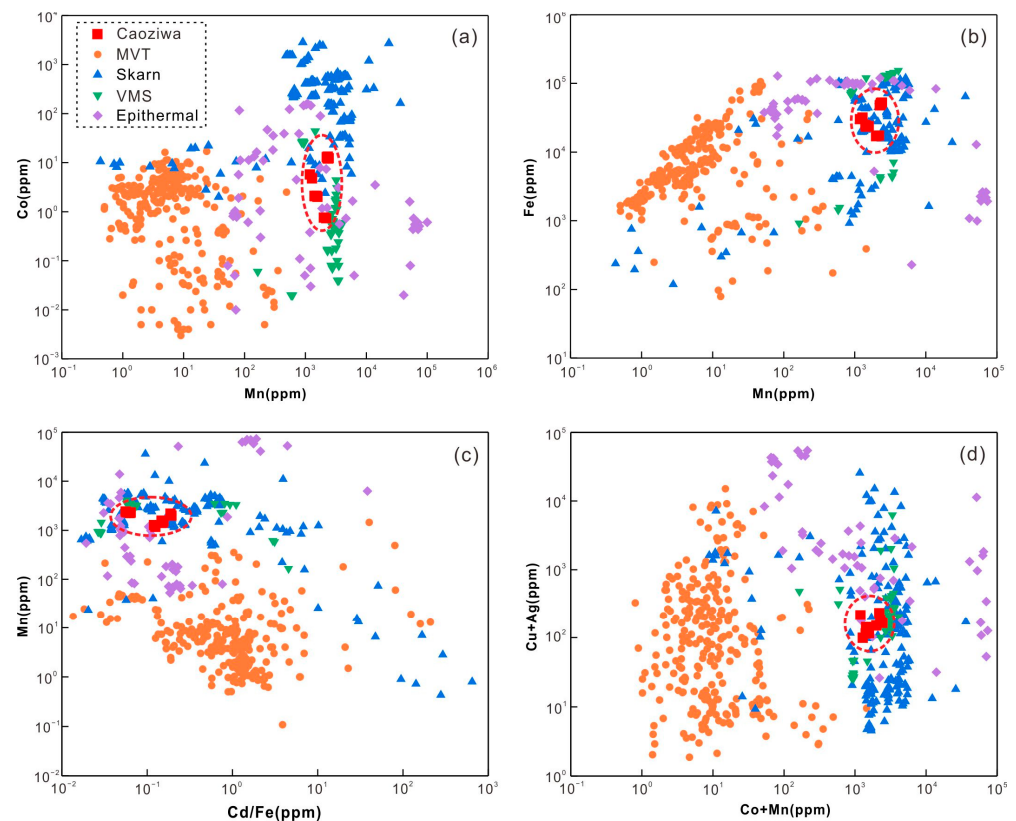


Figure 10. Binary plots of (a) Co vs. Mn, (b) Fe vs. Mn, (c) Mn vs. Cd/Fe, and (d) Cu + Ag vs. Co + Mn in sphalerite from the Caoziwa Pb–Zn deposit and other genetic types of deposits [34,35,42,46,63,64].

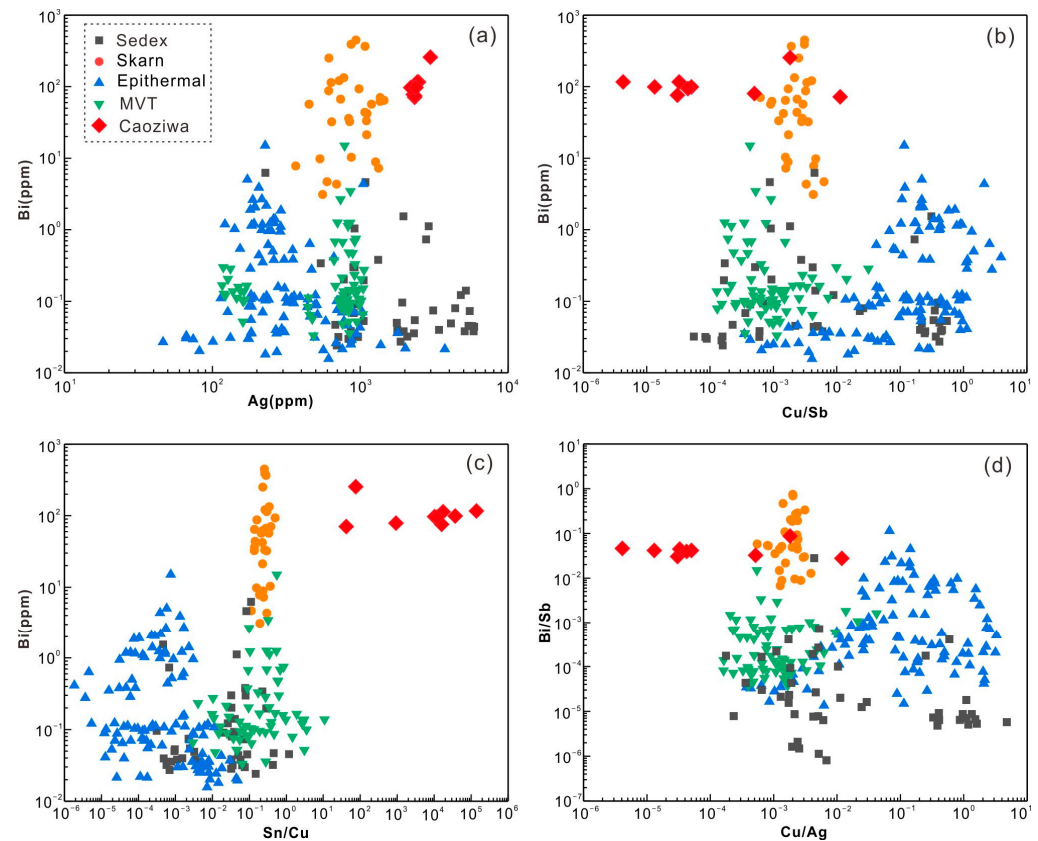


Figure 11. Binary plots of (a) Bi vs. Ag, (b) Bi vs. Cu/Sb, (c) Bi vs. Sn/Cu, and (d) Bi/Sb vs. Cu/Ag in galena from the Caoziwa Pb–Zn deposit and other genetic types of deposits [65–67].

In summary, the magmatic hydrothermal vein-type Caoziwa Pb–Zn deposit probably belongs to a distal part of a skarn mineralization system developed by the intrusion of Paleocene granitic magmatism in the western part of the Tengchong block. This means that skarn-type orebodies probably developed in the deeper part of the Caoziwa ore field.

6. Conclusions

- (1). In the Caoziwa Pb–Zn deposit, abundant Co, Ni, As, and Se, and less Cu, Zn, Ag, Cd, Sn, Sb, Te, Pb, and Bi could enter the pyrite crystal lattice by isomorphous substitution. Elemental Mn, Fe, Cd, Co, and Ni could enter the crystal lattice of sphalerite by isomorphous substitution, while the Ag, Sn, and Sb contents are mainly controlled by the Pb-rich inclusions in sphalerite. Elemental Bi, Sb, Cd, Sn, Ag, and Tl mainly enter the galena grains by the isomorphous substitution mechanism of $(\text{Bi, Sb})^{3+} + (\text{Cd, Sn})^{2+} + (\text{Ag, Tl})^{+} \leftrightarrow 2\text{Pb}^{2+}$.
- (2). The ore-forming materials and fluids of the Caoziwa Pb–Zn deposit mainly originate from magmatic hydrothermal fluid.
- (3). The Caoziwa deposit is a magmatic hydrothermal vein-type Pb–Zn deposit that probably belongs to a distal part of a skarn mineralization system developed by the intrusion of Paleocene granitic magmatism in the western part of the Tengchong block.

Author Contributions: Methodology, Y.C. and F.C.; investigation F.B. and C.Y.; data curation, Y.C. and F.B.; writing—original draft preparation, Y.C. and F.C.; writing—review and editing, M.D. and F.C.; funding, M.D. and F.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was jointly supported by the special selection program for high-level technology talents and innovation teams “formation mechanism and resource potentiality assessment of W, Be, and other strategic minerals in the Geza–Mahuaping area of Shangri-la” (grant no. 202305AT350004), and the National Natural Science Foundation of China (42272078 and 42262011).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: Chunhai Yang and Fuchuan Chen are employees of Yunnan Gold and Mineral Group Co., Ltd. The paper reflects the views of the scientists and not the company.

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