

Article

Sphalerite and Pyrite Geochemistry from the Pusangguo Co-Rich Cu–Zn–Pb Skarn Deposit, Tibet: Implications for Element Occurrence and Mineralization

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Abstract: The Pusangguo deposit (1.42 Mt @ 1.42% Cu, 0.14 Mt @ 1.82% Zn, 0.08 Mt @ 1.01% Pb, and 285.8 t Co @ 140 g/t Co) is the first Co-rich Cu–Zn–Pb skarn deposit discovered in the Gangdese metallogenic belt. However, the trace and minor element geochemistry of the sulfides in this deposit has not been studied, limiting further understanding of elements' occurrence and mineralization. Here, we identified four ore stages, and two types of sphalerites (SpI and SpII) and pyrites (PyI and PyII), in this deposit. In this study, LA-ICP-MS in-situ trace element analyses were conducted on sphalerite and pyrite, to obtain their chemical compositions, elemental substitution mechanisms, and mineralization physicochemical conditions. The results indicate that two types of sphalerites are generally more enriched with Co than pyrite. SpI has higher concentrations of Co, Cr, Cu, Ag, and As compared to SpII. Both types of sphalerite have very low contents of Sn, Ge, and Ga. PyII has higher contents of most trace elements, such as Co, Ni, Mn, Zn, Cu, As, Sn, Se, Pb, Ag, and Bi, compared to PyI. Both types of pyrite are poor in Mn, Ga, Ge, and Cd, but enriched in As, Co, and Ni. The Mn, Fe, Co, and Cd in sphalerite, and Co, Ni, and Mn in pyrite are generally lattice-bound, while Cu, As, Ag, and Sb are usually present in both micro-inclusions and coupled substitution. Significant elemental correlations in sphalerite indicate the possible substitution mechanisms $2\text{Fe}^{2+} + \text{Ga}^{2+} \leftrightarrow 3\text{Zn}^{2+}$, $2\text{Fe}^{2+} + \text{Ge}^{4+} \leftrightarrow 4\text{Zn}^{2+}$, and $(\text{Sb}^{3+}, \text{Sn}^{3+}) + (\text{Cu}^{+}, \text{Ag}^{+}) \leftrightarrow 2\text{Zn}^{2+}$. The correlation trends between trace elements in pyrite suggest the coupled substitution mechanisms of $(\text{Ti}^{+} + \text{Cu}^{+} + \text{Ag}^{+}) + (\text{As}^{3+} + \text{Sb}^{3+}) \leftrightarrow 2\text{Zn}^{2+}$ and $\text{As}^{3+} + \text{Cu}^{+} \leftrightarrow 2\text{Zn}^{2+}$. The mineralization temperature at Pusangguo, as determined by the GGIMFis sphalerite geothermometer, is 237–345 °C (avg. 307 °C), consistent with the high Zn/Cd ratio (avg. 203), low Ga/In (avg. 0.06), and high In/Ge (avg. 15.9) in sphalerite, and high Co/Ni ratio (avg. 24) in pyrite. These results indicate that the ore-forming fluid was high-temperature, with a low sulfur fugacity (f_{S_2}) ($10^{-13.4}$ to $10^{-8.3}$) and low oxygen fugacity (f_{O_2}). The high temperature, and low sulfur fugacity and oxygen fugacity of the ore-forming fluid, and the fluid-mixing process, jointly controlled the sulfide precipitation, which caused the formation of the Pusangguo deposit.

Keywords: LA-ICP-MS; sulfides; geochemistry; trace element occurrence; substitution; Pusangguo; Tibet



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1. Introduction

Located in the central Tibetan Plateau (Figure 1a), the Gangdese metallogenic belt (GMB) is one of the most important non-ferrous metal resource bases in China [1]. Through decades of research and exploration, numerous large porphyry and skarn polymetallic deposits have been successively discovered and evaluated in the GMB [2,3]. However, cobalt-bearing deposits are rarely reported, except for the Pusangguo deposit in the GMB. The Pusangguo deposit is the first cobalt-rich Cu–Pb–Zn skarn deposit discovered in the GMB, and has metal resources of 1.42 Mt Cu at 1.42%, 0.08 Mt Pb at 1.01%, 0.14 Mt

Zn at 1.82%, and 285.8 t Co at 140 g/t Co [4]. Previous studies have mainly focused on the geological characteristics [5,6], diagenetic and metallogenic geochronology [7–9], isotopic geochemistry [10], mineralogy and cobalt occurrence [11,12], and ore-forming fluids [13,14]. However, the trace and minor element geochemistry of sphalerite and pyrite in the Pusangguo has not been studied, which may give better insights into the physicochemical conditions of ore mineralization, and improve our understanding of ore formation.

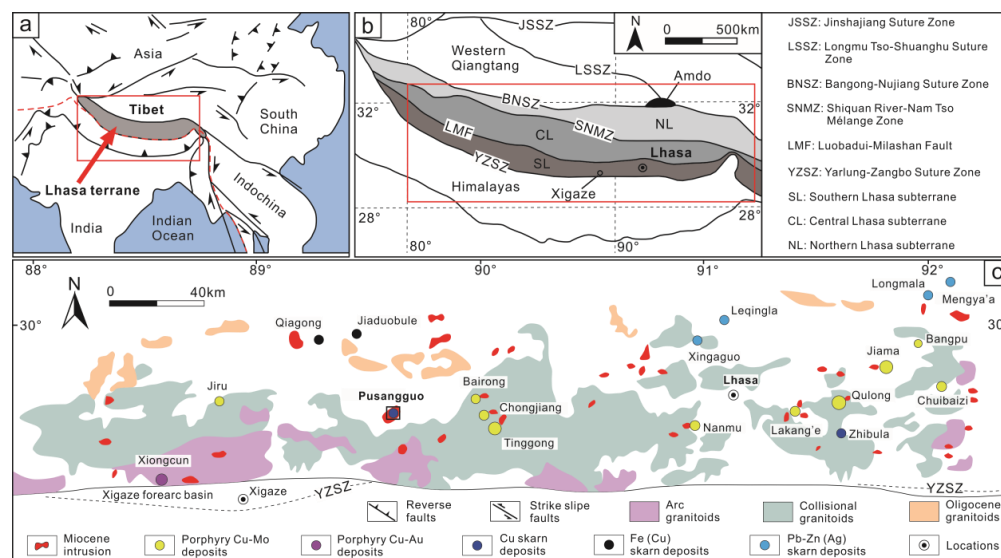


Figure 1. (a) Simplified map showing the location of the Himalayan–Tibetan orogeny; (b) simplified regional geological map of the Himalayan–Tibetan orogeny, showing the location of GMB, modified from [14]; (c) geological map of GMB, modified from [14].

In recent years, laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely applied to obtain the trace element distributions in sulfides and oxides [15–19], which can provide new insights into ore geochemistry at the micro-scale. The trace element concentrations in sphalerite and pyrite can be used to determine the physicochemical conditions of the ore formation [20–24], the source of the ore-forming materials [25–27], the type of ore deposit [28–30], and the precipitation processes [24,31–33]. At Pusangguo, two types of sphalerite and pyrite are recognized, which provides an excellent opportunity to study the geochemical evolution of the sulfides. The primary purpose of this paper is to present an in-situ LA-ICP-MS analysis of sphalerite and pyrite, to reveal the trace element distribution and substitution mechanisms, and to provide new insights into the physicochemical environment of the Pusangguo deposit.

2. Regional Geology

The Tibetan Plateau, from north to south, can be divided into the Qiangtang terrane, Lhasa terrane, and Himalayas, which are separated by the Jinsha (JSSZ), Longmu Tso–Shuanghu (LSSZ), Bangong–Nujiang (BNSZ), and Yarlung Zangbo (YZSZ) suture zones, respectively (Figure 1b) [34]. The Lhasa terrane can be further subdivided by the Shiquan River–Nam Tso Mélange Zone (SNMZ) and the Luobadui–Milashan Fault (LMF) into the northern, central, and southern subterrane, according to the differences in the basement rocks and sedimentary cover (Figure 1b) [35]. The central Lhasa subterrane is mainly covered by Mesozoic and Cenozoic sedimentary units, as well as a large amount of dispersed Mesozoic–Cenozoic volcanic sedimentary rocks [35–37]. The Mesozoic–Cenozoic sedimentary units mainly contain Paleocene–Eocene collision-related granitoids, with minor Late Triassic to Cretaceous subduction-related arc granitoids [38,39]. The Mesozoic and Cenozoic volcanic–sedimentary rocks are predominantly composed of the lower Cretaceous Zenong and Duoni Formations [40,41], and the Paleocene–Eocene Linzizong

volcanic successions [42,43]. Granitoids are widespread in the GMB [44] and, in particular, in the huge plutonic belt, i.e., the Gangdese batholith. Previous studies revealed that the Gangdese batholith was active from the Late Triassic to the Miocene, with three magmatic peaks, i.e., Late Jurassic (ca. 170–150 Ma) [45], Early Cretaceous (ca. 125–100 Ma) [46], and Paleocene–Eocene [36,47]. Several pulses of magmatic activities occurred during the Oligocene–Miocene, Paleocene–Eocene, and Cretaceous periods [48]. There are mainly three identified mineralization phases: (1) The Neo-Tethys subduction-related mineralization event between 180–160 Ma, the Xiongcu porphyry Cu–Au deposit [49,50], (2) the India–Asia collision-related Mo–Cu–Pb–Zn mineralization event between 65–40 Ma, the Tangbula and Sharang porphyry Mo deposits [51], and the Mengya’a skarn Pb–Zn deposits [52], and (3) the India–Asia post-collision-related porphyry–skarn mineralization event between 20–10 Ma, including the Jiama, Qulong, Bangpu, Chongjiang, Tinggong, Zhunuo, and Jiru Cu–Mo deposits [53–55]. The mineralization was formed in different environments, from the Jurassic setting to the Cenozoic continent–continent collision environment [56]. Moreover, the Miocene Cu mineralization was mainly formed at 18–12 Ma, in a post-collision environment associated with the uplift and exhumation of the Gangdese batholith (21–18 Ma), E–W crustal extension (18 Ma), and N–S-striking normal faults (23–14 Ma) [57].

The regional strata exposed in the Pusangguo deposit mainly include the Upper Cretaceous Shexing Formation dominated by siltstone and sandstone, the Lower Cretaceous Takena Formation dominated by limestone and sandstone, the Paleocene Dianzhong Formation dominated by volcanism, the Oligocene Rigongla Formation dominated by sandstone, the Eocene Nianbo Formation dominated by andesite and dacite, the Pliocene Nianbo Formation dominated by volcanism, the Oligocene Rigongla Formation dominated by sandstone, the Eocene Nianbo Formation dominated by andesite and dacite, the Pliocene Gazhacun Formation dominated by volcanic breccia, the Pliocene Zongdangcun Formation by conglomerate, and Quaternary. The Takena Formation is the most widespread formation. Early Cretaceous granite, Paleocene quartz monzonite and Miocene granodiorite are the most prominent regional igneous rocks. The regional structures are mostly faults (i.e., F1, F2, F3) and strike-slip faults (Figure 2a).

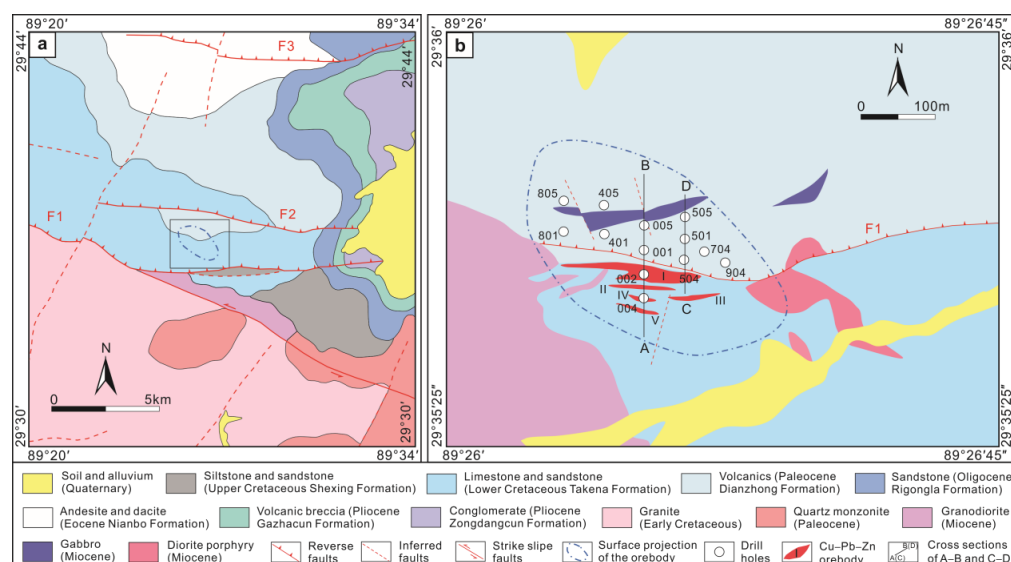


Figure 2. Regional geological map of the Pusangguo district (a), and simplified geological map of the Pusangguo deposit (b), modified from [14].

3. Deposit Geology

The Pusangguo Co-rich Cu–Zn–Pb skarn deposit (latitude 29°35′ N, longitude 89°26′ E) is located in the southern Lhasa subterranean. The Lower Cretaceous Takena Formation and the Paleocene Dianzhong Formation are the main lithostratigraphic units of the Pusang-

guo ore field (Figure 2b). The Takena Formation dominates the deposit area, comprising limestone and sandstone, and trending east–northeast, with a thickness of over 300 m. The Paleocene Dianzhong Formation, outcropping in the northern part of the Pusangguo deposit, consists of volcanic rocks. The Pusangguo deposit mainly consists of EW and NS striking faults, and the EW striking fault (F1), controlling the distribution of the orebody. The NNW–NW trending faults are probably the main post-mineralization structures (Figure 2b). Three types of magmatic intrusions are identified in the Pusangguo orefield, including granodiorite, diorite porphyry, and gabbro. The granodiorite and diorite porphyry stocks in the middle position mainly intrude into the Takena Formation, and the gabbro intrudes into the Dianzhong Formation. There is no evident intrusion relationship among the granodiorite, diorite porphyry, and gabbro. The zircon U–Pb geochronology indicates that the granodiorite and diorite porphyry were formed in the Miocene [8], which is consistent with the timing of the mineralization (13.2 ± 0.7 Ma, [7]).

The mineralization primarily occurs at the contact zone between the granodiorite, diorite porphyry, and marble of the Lower Cretaceous Takena Formation, which formed the predominant Cu–Zn–Pb mineral resources. Five major Cu–Zn–Pb orebodies (I, II, III, IV, and V) from north to south have been identified. The largest orebody (No. I) (Figure 3) is located along the EW trending F1 Fault, and is 350 m long and 10 to 109 m thick, and accounts for 50% of the total Cu + Zn + Pb reserves of the Pusangguo deposit. The second largest No. II orebody is also controlled by the EW trend fault (F1), and is at least 80 m long, with an average thickness of 12 m. The No. III and other smaller orebodies generally strike at 40–50 degrees. The mineralization is dominated by Cu, Zn, Pb, and Co, accompanied by various useful metals, such as Cd, Bi, and Ni. Disseminated, massive, and banded ores of chalcopyrite, sphalerite, and pyrite are the main ore types. The mineral assemblages vary from prograde garnet–clinopyroxene to retrograde epidote–actinolite (Figure 4). Retrograde epidote, quartz, or quartz sulfide veins generally cut the prograde garnet aggregates (Figure 4a–e). The main sulfides are chalcopyrite, sphalerite, pyrite, and galena, with minor amounts of bornite and aikinite ($2\text{PbS} \cdot \text{Cu}_2\text{S} \cdot \text{Bi}_2\text{S}_3$). The Co-bearing minerals are mostly composed of three independent cobalt minerals, including cobaltite (CoAsS), carrollite ($\text{Cu}(\text{Co},\text{Ni})_2\text{S}_4$), and linnaeite (Co_3S_4) [12]. The gangue minerals are mainly garnet, diopside, epidote, actinolite, and quartz, with minor amounts of hornblende, chlorite, and calcite (Figure 5).

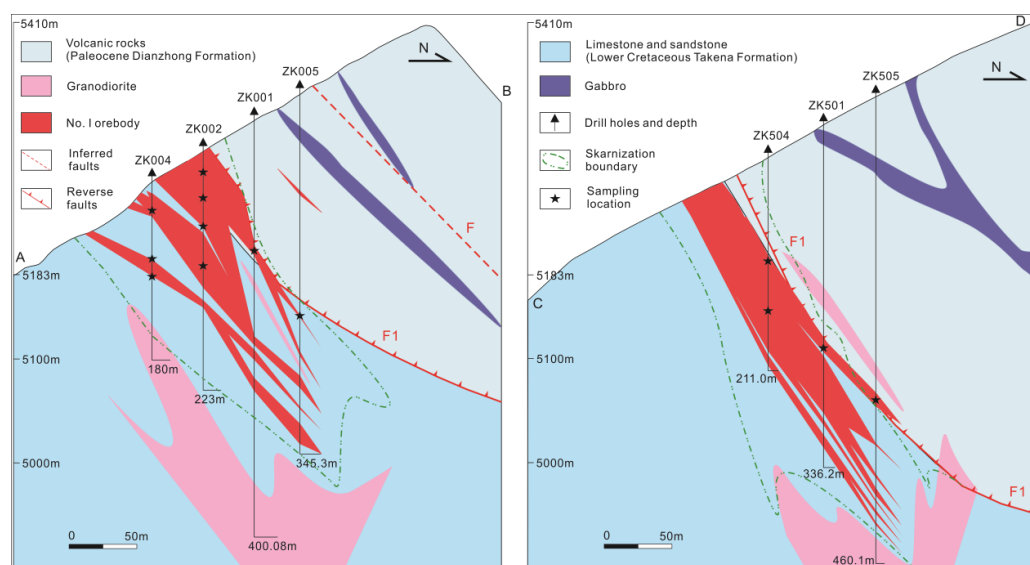


Figure 3. North–south geologic cross-section (A–B and C–D are shown in Figure 2b) of the Cu–Zn–Pb orebody in the Pusangguo deposit.

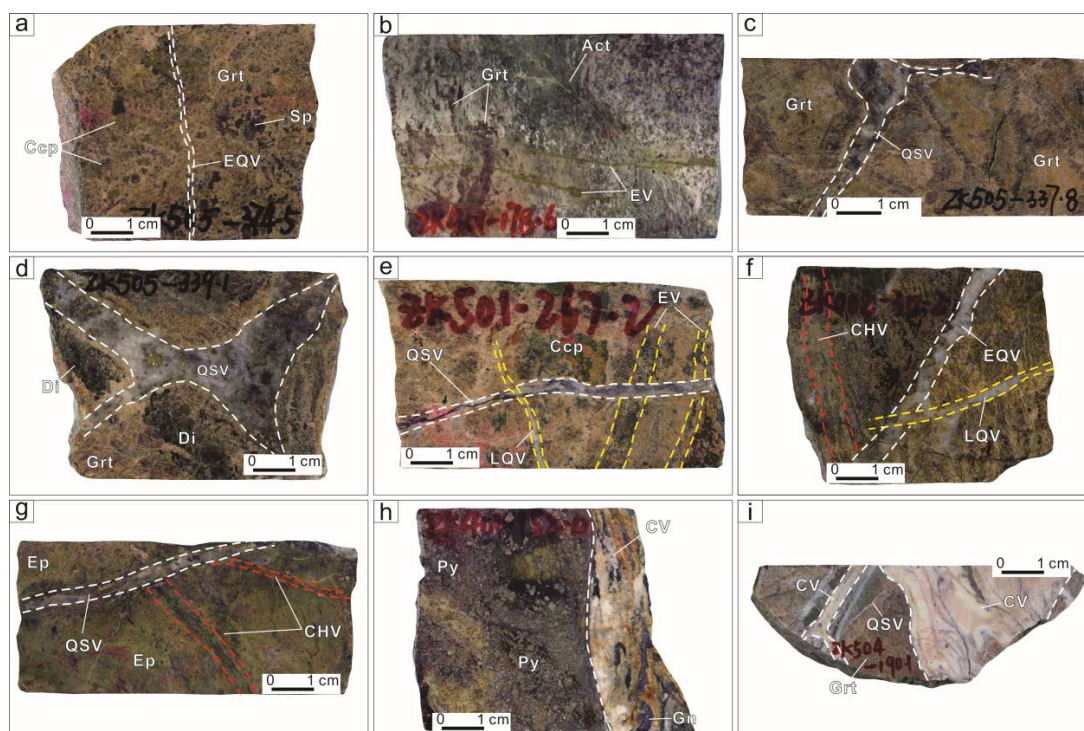


Figure 4. Representative hand specimen photographs and different mutual crosscutting veins in the Pusanguo deposit. (a) Chalcopyrite–sphalerite-bearing garnet skarn in the pre-ore stage cut by the EQV from the oxide-ore stage; (b) garnet skarn in the pre-ore stage cut by the epidote vein in the oxide-ore stage; (c) garnet skarn ore in the pre-ore stage cut by the quartz–sulfide vein from the quartz–sulfide-ore stage; (d) garnet–diopside skarn ore cut by the quartz–sulfide vein in the quartz–sulfide-ore stage; (e) chalcopyrite-bearing garnet skarn in the pre-ore stage cut by the epidote vein from the oxide-ore stage, quartz–sulfide vein in the quartz–sulfide-ore stage, and late quartz vein from the post-ore stage; (f) early quartz vein in the oxide-ore stage cut by the late quartz vein from the post-ore stage; (g) epidote skarn and chlorite vein from the oxide-ore stage cut by the quartz–sulfide vein in the quartz–sulfide-ore stage; (h) pyrite-bearing skarn ore from the quartz–sulfide-ore stage cut by the calcite vein in the post-ore stage; (i) quartz–sulfide vein from the quartz–sulfide-ore stage cut by calcite vein in the post-ore stage. Abbreviations: Grt, garnet; Ep, epidote; Act, actinolite; Di, diopside; Ccp, chalcopyrite; Sp, sphalerite; Gn, galena; Py, pyrite; EQV, early quartz vein; CHV, chlorite vein; EV, epidote vein; QSV, quartz–sulfide vein; LQV, late quartz vein; CV, calcite vein.

Four mineralization stages have been recognized, based on the hand specimen, the mineral assemblage, and the crosscutting relations (Figure 4). These four stages mainly include the pre-ore stage, oxide-ore stage, quartz–sulfide-ore stage, and post-ore stage (Figure 6). Moreover, the quartz–sulfide-ore stage can be further subdivided into the Fe–Cu–Zn sulfide and Pb–Zn sulfide substages. The pre-ore stage features island and chain anhydrous silicates, such as garnet and diopside. Garnet, essentially of the andradite–grossularite series ($\text{And}_{47.39-98.17}\text{Gro}_{0.59-50.22}$) [11], is the dominant prograde mineral in the pre-ore stage, and usually occurs as independent massive aggregates (Figures 4a and 5a). Clinopyroxene, with the composition of hedenbergite–johannsenite–diopside ($\text{Hd}_{37.91-74.16}\text{Jo}_{0.91-61.66}\text{Di}_{0.43-46.07}$) [11], occurs mainly as discrete massive aggregates, with euhedral to subhedral crystals (Figure 5b). Subsequent hydrothermal fluids have altered clinopyroxene into actinolite (Figure 5c). The oxide-ore stage is dominated by hematite (Figure 5d), with other retrograde minerals including epidote (Figure 5e), actinolite, chlorite, hornblende, quartz, and pyrite (PyI). The PyI grains mainly occur in euhedral aggregates coexisting with chalcopyrite (Figure 5f). The sulfide-ore stage has abundant sulfides, including chalcopyrite, pyrite, carrollite, sphalerite, galena, cobaltite, and linnaeite with

quartz. The Fe-Cu-Zn sulfide substage is dominated by chalcopyrite, sphalerite (SpI), pyrite (PyII), and quartz, with minor amounts of carrollite. The carrollite occurs before, or is coeval with, the chalcopyrite [12]. The PyII grains are usually subhedral aggregates, and are replaced by chalcopyrite (Figure 5g). The SpI grains are mainly dark brown, with the internal reflection color of red–brown, forming the exsolution structure with chalcopyrite (Figure 5h,i). The Pb-Zn sulfide substage is characterized by sphalerite (SpII) and galena, with minor amounts of cobaltite and linnaeite. The cobaltite and linnaeite mostly occur with sphalerite, or surrounded by sulfide [12]. The SpII grains are yellow–brown, with the internal reflection color of yellow, which is primarily associated with galena (Figure 5j–l). Low-temperature calcite and quartz veins intersect the prograde and retrograde minerals at the post-ore stage (Figure 4i).

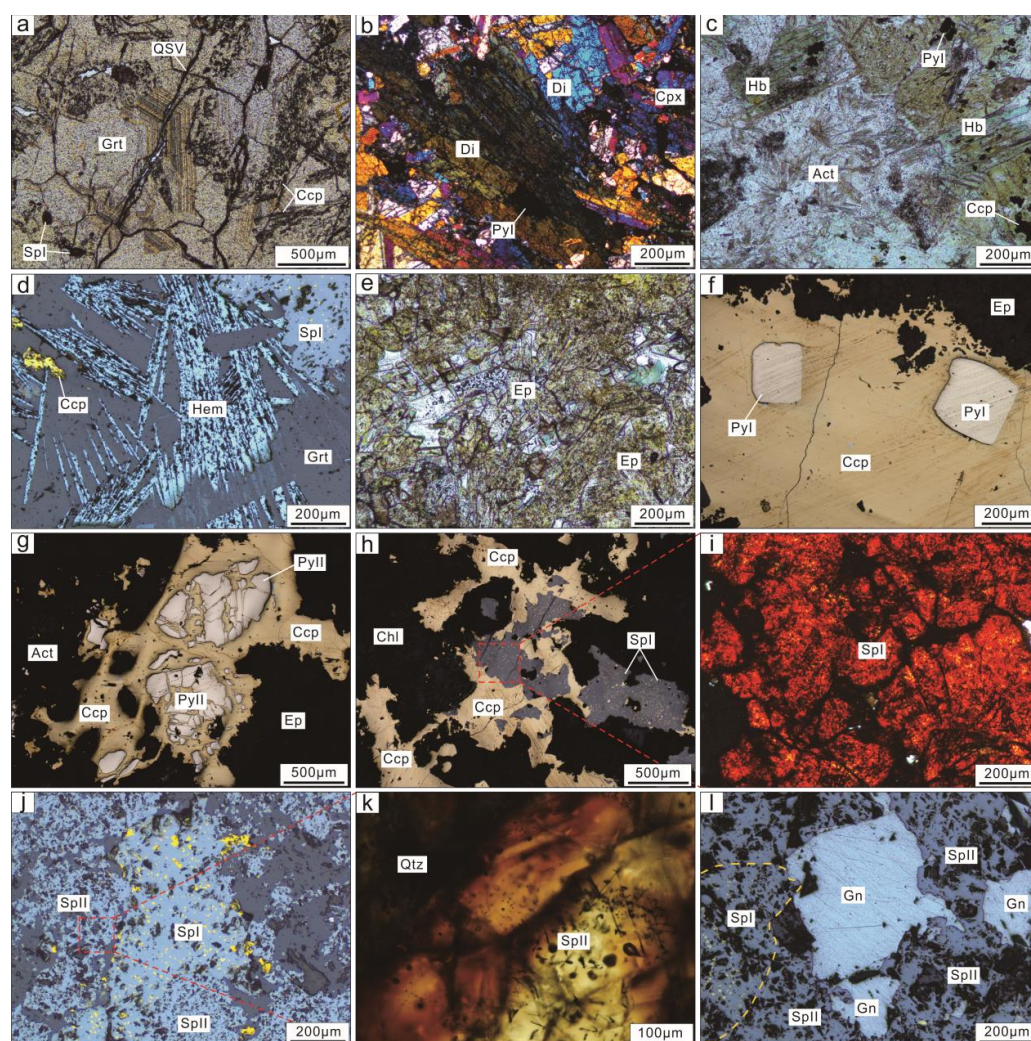


Figure 5. Microphotographic ore mineral assemblages from the Pusangguo deposit. (a) HedraI garnets cut by the chalcopyrite and quartz sulfide vein (+); (b) subhedral diopside with multiple interference colors (+); (c) actinolite and hornblende with pyrite mineralization (+); (d) radiated hematite (−); (e) subhedral epidote grains (+); (f) hedraI PyI within the chalcopyrite (−); (g) subhedral-to-anhedral PyII replaced by the anhedral chalcopyrite (−); (h) SpI coexisting with the chalcopyrite (−); (i) the SpI with red internal reflections (+); (j) SpII coexisting with SpI (−); (k) SpII with yellow internal reflections (+); (l) SpI and SpII coexisting with galena (−). Abbreviations: QSV, quartz–sulfide vein; Grt, garnet; Di, diopside; Cpx, clinopyroxene; Ep, epidote; Chl, chlorite; Act, actinolite; Ccp, chalcopyrite; Hem, hematite; Gn, galena; SpI, type I sphalerite; SpII, type II sphalerite; PyI, type I pyrite; PyII, type II pyrite; (+), orthogonal polarization light; (−), single polarization light.

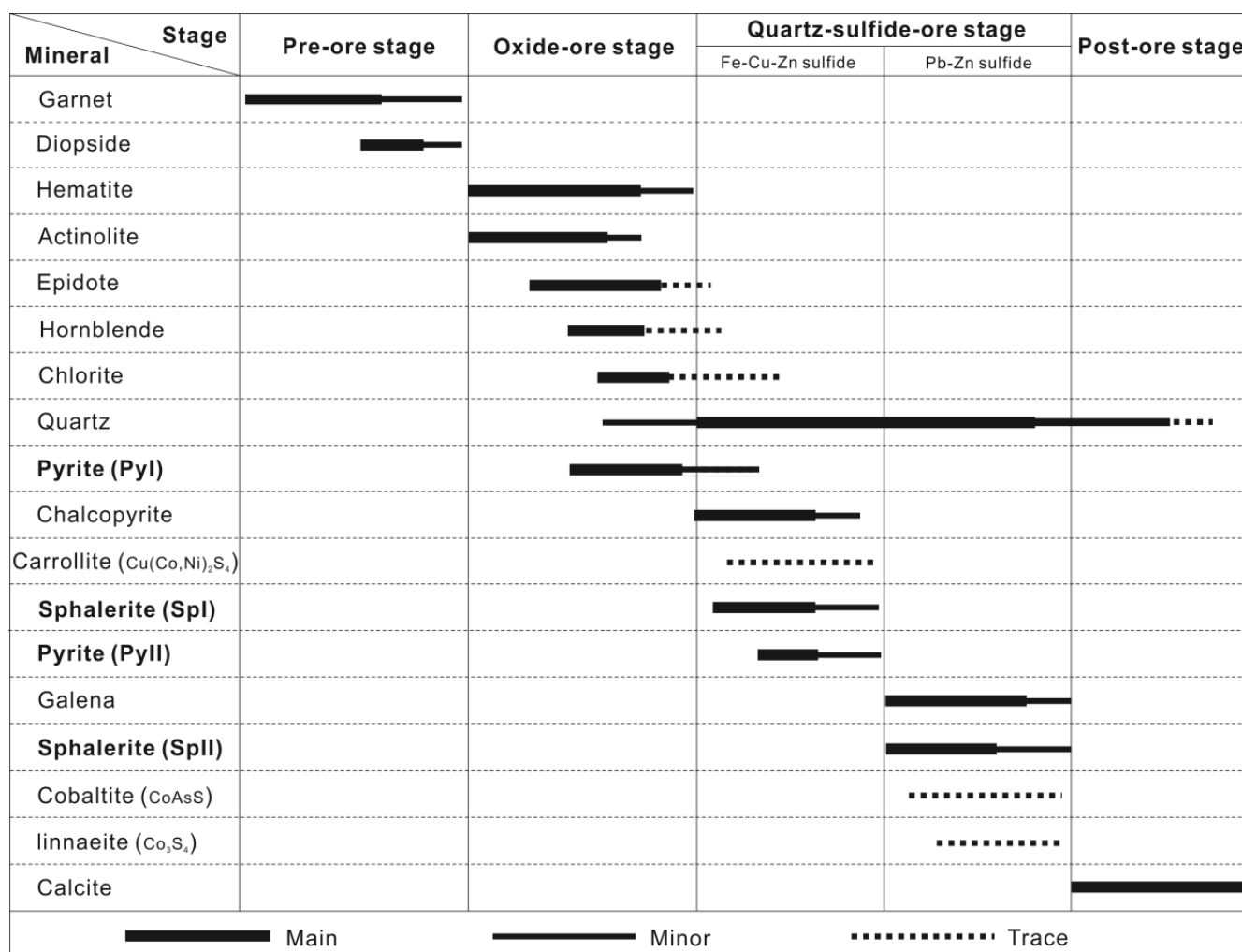


Figure 6. The mineral paragenesis for the Pusangguo Cu–Zn–Pb deposit.

4. Sampling and Analytical Methods

4.1. Sampling

A total of 13 representative mineralized samples were collected from the Pusangguo deposit in this study. The samples were collected from underground No. I orebody, in seven boreholes at different drilling depths (ZK004-23.4, ZK004-79.9, ZK004-90.5, ZK002-24.5, ZK002-66.2, ZK002-86.2, ZK002-109.5, ZK504-108.6, ZK504-132.7, ZK505-374.5, ZK001-131.7, ZK005-202.3, and ZK501-258.2) (Figure 3). For each sample, standard polished thin sections (30 μm) were prepared before the analysis. They were examined via reflected and transmitted light microscopy for mineralogical and paragenetic associations, particularly sphalerite and pyrite types. The detailed sampling locations and descriptions of the samples are given in Table S1.

4.2. EPMA Major Element Analysis

The major elemental contents of sphalerite and pyrite were measured using a JEOL-JXA 8230 electron microprobe equipped with 4-channel spectrometers at the Electron Probe Microanalysis Laboratory (Zijin School of Geology and Mining, Fuzhou University). The samples were coated with a uniform carbon layer before the analysis. The analytical conditions comprised a 20 nA beam current, 20 kV accelerating voltage, and 5 μm spot size, with count times of 20 s [58]. The correction of the matrix was carried out using the ZAF correction program, resulting in an accuracy of better than 1 wt%. The elements measured include Zn, Fe, S, Pb, Cu, Ni, Co, Bi, As, Se, and Ag. The detection limits for As, Se, S,

Pb, Bi, Ag, Fe, Co, Ni, Cu, and Zn are 469 ppm, 256 ppm, 135 ppm, 520 ppm, 734 ppm, 372 ppm, 180 ppm, 193 ppm, 191 ppm, 262 ppm, and 273 ppm. The following synthetic sulfides and natural minerals were used for calibration: sphalerite (for Zn), chalcopyrite (for Fe, Cu and S), cobaltous oxide (for Co), nickel (for Ni), arsenic (for As), lead (for Pb), selenium (for Se), hessite (for Ag), and bismuth (for Bi).

4.3. LA-ICP-MS Trace Element Analysis

The trace element compositions of the sphalerite and pyrite were determined via LA-ICP-MS on polished thick sections at the State Key Laboratory of Continental Dynamics, Northwest University, using an Agilent 7700x Quadrupole ICPMS instrument to acquire the ion signal, coupled with a high-performance Resolution Coherent GeoLas-Pro 193 nm ArF excimer laser ablation system equipped with Geostar software (version 4.0). Helium (0.35 L/min) was used as the carrier gas, and argon was applied as the make-up gas. The analytical conditions included a 40 μm laser spot diameter, 10 Hz laser frequency, and 2 J/cm² energy density. The masses of the following elements were measured: ⁶⁶Zn, ⁵⁷Fe, ⁵⁵Mn, ⁶⁵Cu, ⁶⁰Ni, ⁵⁹Co, ⁶⁹Ga, ⁷³Ge, ⁷⁵As, ⁷⁸Se, ¹⁰⁷Ag, ¹¹⁴Cd, ⁵³Cr, ¹¹⁵In, ¹¹⁸Sn, ⁴⁹Ti, ⁵¹V, ¹²¹Sb, ¹⁹⁷Au, ²⁰⁸Pb, ²⁰⁵Tl, and ²⁰⁹Bi. Each spot analysis took 80 s, with ca. 20 s of background acquisition (laser off), and ca. 60 s of sample data collection (laser on). The NIST610, BCR-2G, and GSE-1G standard reference materials were used as external standards to calibrate the element concentrations [59]. The detection limits for Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, and Bi were 28.8 ppm, 0.016 ppm, 1.078 ppm, 0.10 ppm, 0.139 ppm, 0.166 ppm, 0.223 ppm, 0.573 ppm, 0.043 ppm, 0.70 ppm, 0.161 ppm, 4.52 ppm, 0.039 ppm, 0.148 ppm, 0.007 ppm, 0.153 ppm, 0.042 ppm, 0.008 ppm, 0.005 ppm, 0.014 ppm, and 0.005 ppm. Data reduction was performed using the software Iolite (version 3.73), an add-in in Igor Pro (version 6.37, WaveMetrics, Lake Oswego, OR, USA). Sphalerite and pyrite were processed using 60.2% Zn and 45.9% Fe, measured using EPMA as the internal standards for data reduction, respectively (Tables S2 and S3). The analytical uncertainties were calculated for each element in each spot analysis through running the above three standard reference materials after every 8 unknowns. The accuracy for most elements was expected to be better than 20% [59]. The contents of Cr, Ti, V, Te, Au, Se, and Tl were very low, and are not discussed below.

5. Results

The complete major element data from EPMA, and trace element data from LA-ICP-MS analysis, for sphalerite and pyrite are presented in Tables S2–S5, respectively. The representative time-resolved profiles of laser ablation signals for sphalerite and pyrite are shown in Figure 7. The LA-ICP-MS dataset includes 83 sphalerite and 48 pyrite spot analyses. The absolute concentration ranges of the selected elements are shown as box-and-whisker plots in Figures 8 and 9.

5.1. Major and Trace Elements in Sphalerite

In total, 45 EPMA spot analyses were carried out on 13 ores (28 spots on SpI, and 17 spots on SpII), with the results presented in Table S2. The two sphalerite types have similar average S and Zn contents (SpI: 33.13 wt% and 60.22 wt%; SpII: 33.25 wt% and 60.16 wt%, respectively). However, SpI has a higher average Co content (avg. 0.27 wt%) than SpII (avg. 0.12 wt%), and has a slightly lower average Fe content (avg. 5.68 wt%) than SpII (avg. 6.09 wt%).

The LA-ICP-MS spot analysis was performed on 44 spots for SpI, and 39 spots for SpII, and the results are shown in Table S4, and are illustrated in Figure 8. Generally, the two sphalerite types differ slightly in the content of most trace elements. Fe is the most abundant trace element (31,656–88,891 ppm, median 53,191 ppm) (Figure 8). The Mn contents in sphalerite are generally high (1317–6443 ppm, median 2531 ppm) (Figure 8). The Mn contents of SpI and SpII ranged from 1436 to 5315 ppm (median 2648 ppm), and

1317 to 6443 ppm (median 2351 ppm), respectively. The Cu content in sphalerite is relatively high, ranging from 7.35 to 33,121 ppm, with a median of 1296 ppm.

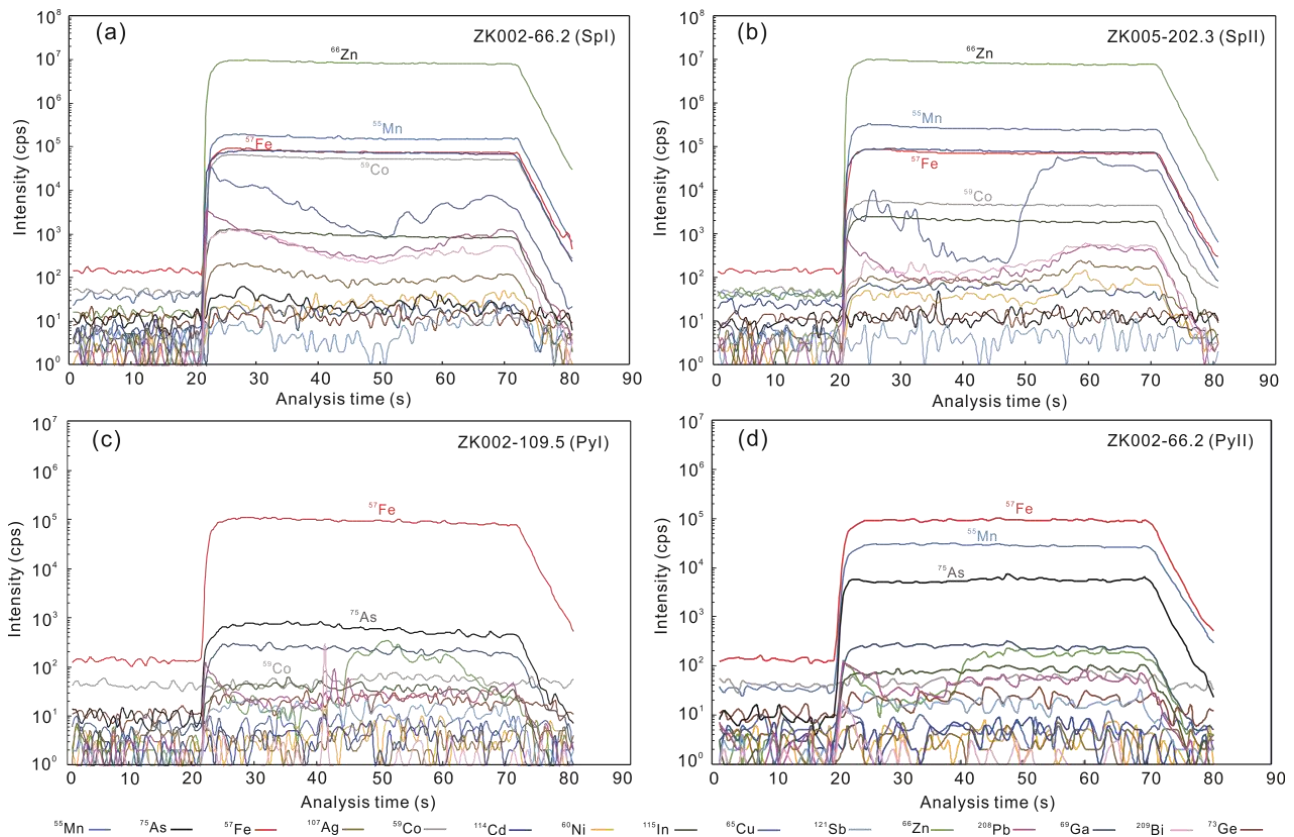


Figure 7. The representative LA-ICP-MS time-resolved depth profiles for sphalerite (a,b) and pyrite (c,d) from the Pusangguo deposit.

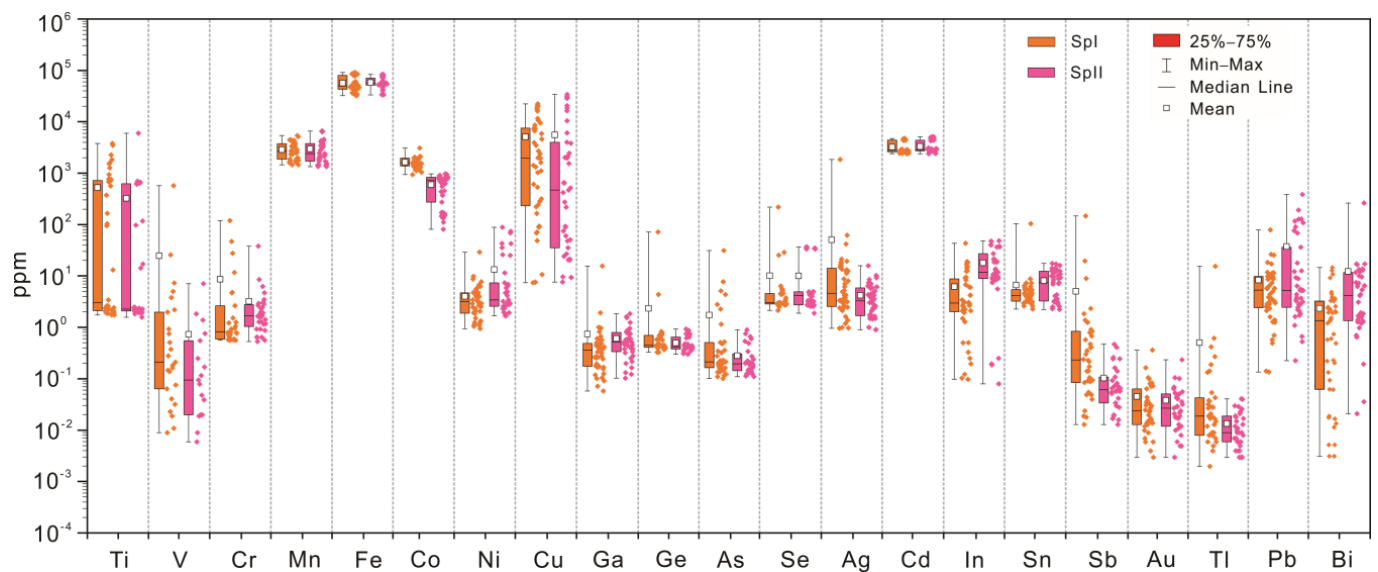


Figure 8. Statistical box-and-whisker plots for the sphalerite trace elements, analyzed via LA-ICP-MS, from the Pusangguo deposit.

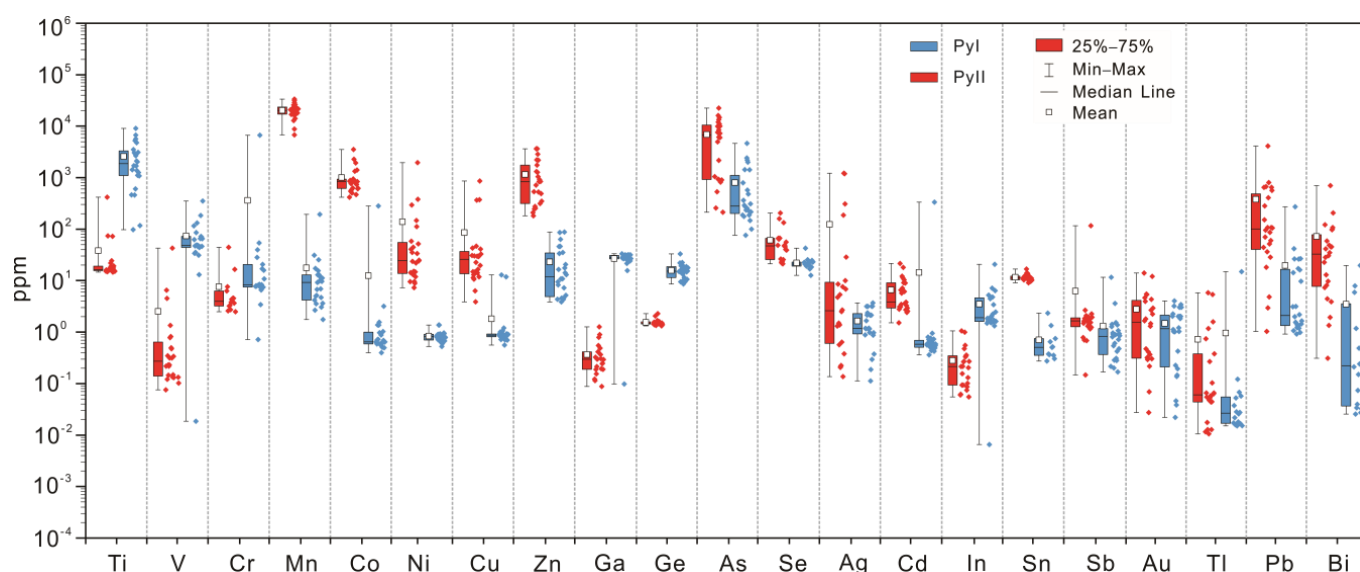


Figure 9. Statistical box-and-whisker plots for the pyrite trace elements, analyzed via LA-ICP-MS, from the Pusanguo deposit.

The two types of sphalerite have high Co contents (80.1–3038 ppm, median 1102 ppm), with a decreasing trend from SpI to SpII. The Co contents of SpI and SpII range from 928 to 3038 ppm (median 1567 ppm), and from 80.1 to 949 ppm (median 721 ppm), respectively. The Cd in sphalerite is high (2334–5020 ppm, median 2776 ppm) and the Cd contents in SpI and SpII range from 2349 to 4651 ppm (median 2742 ppm), and from 2334 to 5020 ppm (median 2812 ppm), respectively.

The Ga and Ge concentrations in sphalerite are low (Ga: 0.126–15.6 ppm, median 0.44 ppm; Ge: 0.3–71.2 ppm, median 0.44), with some analytical results below detection limits (b.d.l.). The In content of sphalerite is low (0.08–47.8 ppm, median 8.64 ppm). The Sn and Pb contents range from 2.22 to 103 ppm (median 4.3 ppm), and from 0.14 to 379 ppm (median 5.2 ppm), respectively. The other trace elements found in sphalerite, such as Au, Sb, and Tl, are present at extremely low levels. In summary, SpI is enriched with Co, Cr, Cu, Ag, and As, compared to SpII.

5.2. Major and Trace Elements in Pyrite

A total of 26 EPMA spot analyses were carried out on eight ore samples (14 spots for PyI, and 12 spots for PyII), and the results are presented in Table S3. The two types of pyrite have similar average concentrations of Fe and S (PyI: 45.99 wt% and 53.58 wt%; PyII: 45.89 wt% and 53.79 wt%, respectively). However, PyII has a higher average Co content (avg. 0.23 wt%) than PyI (avg. 0.05 wt%), and a higher average As content (avg. 0.11 wt%) than PyI (avg. 0.04 wt%).

LA-ICP-MS analysis was performed on 24 spots for PyI, and 24 spots for PyII, and the analytical results are presented in Table S5 and Figure 9. The pyrite has lower contents of trace elements relative to the sphalerite. The contents of some of the elements, such as Ti, As, Co, and Mn, can be tens to thousands of ppm, but some are below 10 ppm or the detection limits (Table S5). In general, the Co contents in PyII (403–3397 ppm, median 811 ppm) are higher than those in PyI (0.4–278 ppm, median 0.65 ppm). The distributions of Ni in PyII (7.08–1874 ppm, median 23.68 ppm) are higher than those in PyI (0.53–1.38 ppm, median 0.83 ppm).

The As content in the pyrite (75.7–21,386 ppm, median 883 ppm) is significantly higher than that in the sphalerite, and the As contents of PyI and PyII are 75.7–4565 ppm (median 280 ppm) and 206–21,386 ppm (median 6406 ppm), respectively, with an increasing trend from PyI to PyII (Figure 9).

The concentrations of Mn have the largest range (1.46–32,797 ppm), with a median of 188 ppm. The Mn contents in PyI (1.72–188 ppm, median 9.03 ppm) are lower than those in PyII (6608–32,797 ppm, median 19,185 ppm). The Cu content in the pyrite is low (0.56–828 ppm, median 8.30 ppm), while the Cu contents in PyI and PyII range from 0.56 to 12.8 ppm (median 0.88 ppm), and from 3.78 to 828 ppm (median 25.2 ppm), respectively, with an increasing trend from PyI to PyII.

The Zn content in the pyrite has a wide range of variation (3.85–3509 ppm), with a median of 86.8 ppm. The Zn concentrations of PyI and PyII are 3.85–86.8 ppm (median 11.9 ppm), and 176–3509 ppm (median 806 ppm), respectively, with an increasing trend from PyI to PyII (Figure 9).

The Ti content in the pyrite (21.3–8874 ppm, median 107 ppm) is higher than that in the sphalerite. The Ti contents in PyI and PyII range from 97.4 to 8874 ppm (median 1843 ppm), and from 21.3 to 4.3 ppm (median 16.0 ppm), respectively, with a decreasing trend from PyI to PyII. The Cd content in the pyrite (0.37–332 ppm, median 1.48 ppm) is much lower than that in the sphalerite, and the Cd contents of PyI and PyII are 0.37–332 ppm (median 0.59 ppm) and 1.48–20.8 ppm (median 3.71 ppm), respectively. The Pb content in the pyrite ranges from 2.89 to 3945 ppm, with a median of 26.2 ppm. The Pb concentrations of PyI and PyII are 0.92–268 ppm (median 2.10 ppm), and 2.89–3945 ppm (median 96.9 ppm), respectively. The other elements (e.g., Cr, Tl, Bi, Ag, Au, In) are much lower, or are below the detection limits.

6. Discussion

6.1. Trace Element Distributions and Substitutions in Sphalerite

Extensive studies have been carried out on the trace element distributions and substitution mechanisms in sphalerite [25,60–64]. The substitution of Zn^{2+} with trace elements in the sphalerite crystal lattice mainly occurs via simple/direct and coupled substitution mechanisms [65–67]. In a simple substitution mechanism, the divalent cations with an ionic radius and charge similar to Zn^{2+} directly replace Zn^{2+} in sphalerite, such as $\text{Fe}^{2+} \leftrightarrow \text{Zn}^{2+}$, $\text{Cd}^{2+} \leftrightarrow \text{Zn}^{2+}$, $\text{Mn}^{2+} \leftrightarrow \text{Zn}^{2+}$, $\text{Co}^{2+} \leftrightarrow \text{Zn}^{2+}$, and $\text{Ge}^{2+} \leftrightarrow \text{Zn}^{2+}$ (e.g., [16,60]). In a coupled substitution mechanism, the monovalent (Cu^+ , Ag^+), trivalent (As^{3+} , Ga^{3+} , Sb^{3+} , In^{3+}), and tetravalent (Sn^{4+} , Ge^{4+}) cations with a larger ionic radius and charge replace Zn^{2+} in the sphalerite lattice, such as $2(\text{Ag}, \text{Cu})^+ + \text{Sn}^{4+} \leftrightarrow 3\text{Zn}^{2+}$ and $2\text{Cu}^+ + \text{Ge}^{4+} \leftrightarrow 3\text{Zn}^{2+}$ [68,69]. Furthermore, some trace elements may be present as micro-inclusions or nanoparticles [70].

The occurrence and distribution of trace elements in minerals can be inferred from the shape of elemental signals in the time-resolved depth profiles [71–73]. Disregarding the possibility of a uniform distribution of mineral micro-inclusions at the level of ablation, smooth signal profiles tend to indicate that the element is present as a lattice-bound solution, while more jagged or fluctuant signal profiles suggest that the element is present as micro-inclusions or nanoparticles in the sphalerite crystal.

Previous studies have documented that Zn^{2+} in a sphalerite lattice was generally replaced by Fe^{2+} , Mn^{2+} , Co^{2+} , and Cd^{2+} through simple substitution mechanisms [19,74–77]. The smooth Fe, Mn, Cd, and Co signal curves in the LA-ICP-MS profiles of the sphalerite (Figure 7a,b) indicate that these elements directly substitute Zn^{2+} (Fe^{2+} , Mn^{2+} , Cd^{2+} , $\text{Co}^{2+} \leftrightarrow \text{Zn}^{2+}$). In binary plots (Figure 10a), Fe and Mn in sphalerite from the Pusangguo deposit show a significant positive correlation ($R^2 = 0.40$), indicating that the incorporation of Mn into sphalerite inhibits the replacement of Fe, and the coupled substitution mechanism ($2\text{Zn}^{2+} \leftrightarrow \text{Mn}^{2+} + \text{Fe}^{2+}$, [64]). Elements such as Ga and Ge are usually incorporated into the sphalerite lattice through coupled mechanisms, and have different valences (Ga^{4+} , Ga^{3+} , Ge^{2+} , Ge^{4+}) [20]. The positive correlations between Fe, Ga, and Ge possibly indicate coupled substitutions: $3\text{Zn}^{2+} \leftrightarrow 2\text{Fe}^{2+} + \text{Ga}^{2+}$ and $4\text{Zn}^{2+} \leftrightarrow 2\text{Fe}^{2+} + \text{Ge}^{4+}$ (Figure 10b,c).

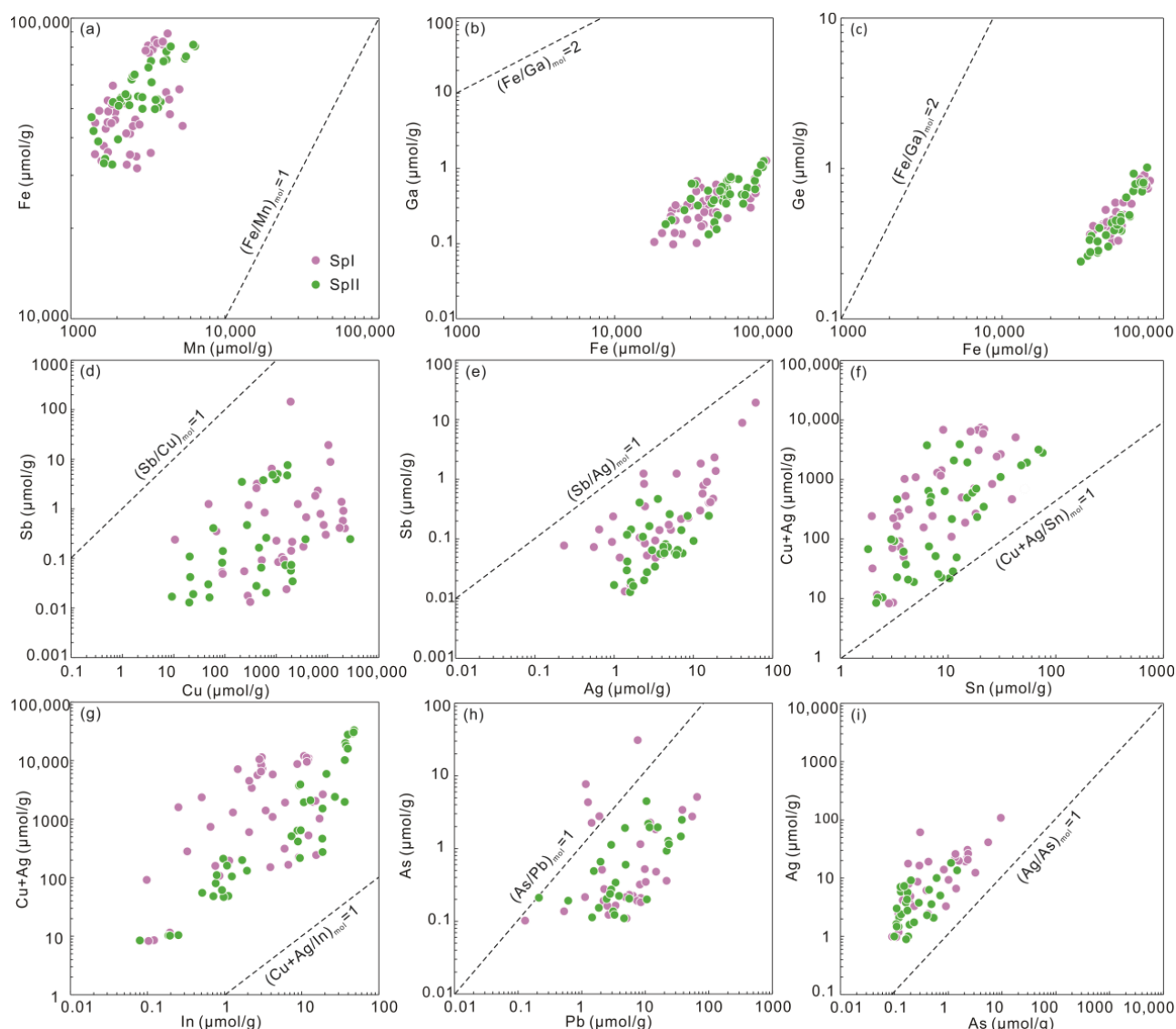


Figure 10. Binary plots of Mn and Fe (a), Ga and Fe (b), Ge and Fe (c), Sb and Cu (d), Ag and Sb (e), Sn and Cu + Ag (f), In and Cu + Ag (g), As and Pb (h), Ag and As (i) in sphalerite from the Pusanguo deposit, derived from the total dataset.

Trivalent (As^{3+} , Sb^{3+} , Sn^{3+} , In^{3+} , Ga^{3+}) or tetravalent cations (Sn^{4+} , Ge^{4+}) generally combine with monovalent cations (Cu^+ , Ag^+) to replace Zn^{2+} in a sphalerite lattice, via coupled substitutions [78,79]. The positive Cu vs. Sb (Figure 10d) and Ag vs. Sb (Figure 10e) correlations suggest the substitution mechanism of $\text{Sb}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Zn}^{2+}$ and $\text{Ag}^+ + \text{Sb}^{3+} \leftrightarrow 2\text{Zn}^{2+}$, respectively. Almost all the data points are on the side of the molar ratio $(\text{Sb}/\text{Cu})_{\text{mol}} < 1$ and $(\text{Sb}/\text{Ag})_{\text{mol}} < 1$, indicating that the equation is not adequate for the intake of Cu and Ag, respectively. The positive correlations between Sn, In, Cu, and Ag strongly support the coupled substitution mechanisms $\text{Sn}^{3+} + (\text{Cu}^+, \text{Ag}^+) \leftrightarrow 2\text{Zn}^{2+}$ and $\text{In}^{3+} + (\text{Cu}^+, \text{Ag}^+) \leftrightarrow 2\text{Zn}^{2+}$, but the Sn and In contribute less to Cu and Ag substitution, because all the points are mainly above the line with a slope of 1 (Figure 10f,g).

Although Pb generally occurs as micro-inclusions in sphalerite, its substitution mechanism remains unclear [16,20]. In the sulfide crystal lattice, As may occur as As^{3+} [79]. The possibility of a coupled substitution mechanism, $4\text{Zn}^{2+} \leftrightarrow \text{Pb}^{2+} + 2\text{As}^{3+} + \square$ (vacancy), is suggested by the positive correlation between Pb and As in sphalerite (Figure 10h) [25,69]. In addition, there is a good correlation between As and Ag in sphalerite (Figure 10i), suggesting the possibility of the coupled substitution mechanism $\text{As}^{3+} + \text{Ag}^+ \leftrightarrow 2\text{Zn}^{2+}$.

6.2. Trace Element Distributions and Substitutions in Pyrite

As is the case with sphalerite, the trace elements in pyrite are usually present as substitutes for the Fe and S in the crystal lattice, or as micro-inclusions in the mineral [80,81]. The mineral inclusions generally show some peaks in time-resolved depth profiles, whereas pure pyrite would show flat time-resolved depth profiles. Mineral inclusions would, in most cases, significantly alter the content of some elements, resulting in a small number of anomalies.

Mn can directly substitute Fe in the pyrite lattice ($\text{Mn}^{2+} \leftrightarrow \text{Fe}^{2+}$), consistent with the flat signal of Mn in the LA-ICP-MS profiles of pyrite, due to the similar properties of Fe^{2+} and Mn^{2+} (Figure 7c,d). In the binary plots (Figure 11a), Co and Ni in pyrite from Pusangguo have a subtle correlation, suggesting that Co^{2+} and Ni^{2+} directly substitute Fe^{2+} , which is consistent with previous studies ($\text{Co}^{2+} \leftrightarrow \text{Fe}^{2+}$, $\text{Ni}^{2+} \leftrightarrow \text{Fe}^{2+}$) [82,83]. However, the replacements of Co and Ni in the pyrite lattice are sensitive to the temperature and $f\text{S}_2$ (sulfur fugacity), and a decrease in temperature or increase in $f\text{S}_2$ firstly favors $\text{Co}^{2+} \leftrightarrow \text{Fe}^{2+}$, followed by $\text{Ni}^{2+} \leftrightarrow \text{Fe}^{2+}$ [84].

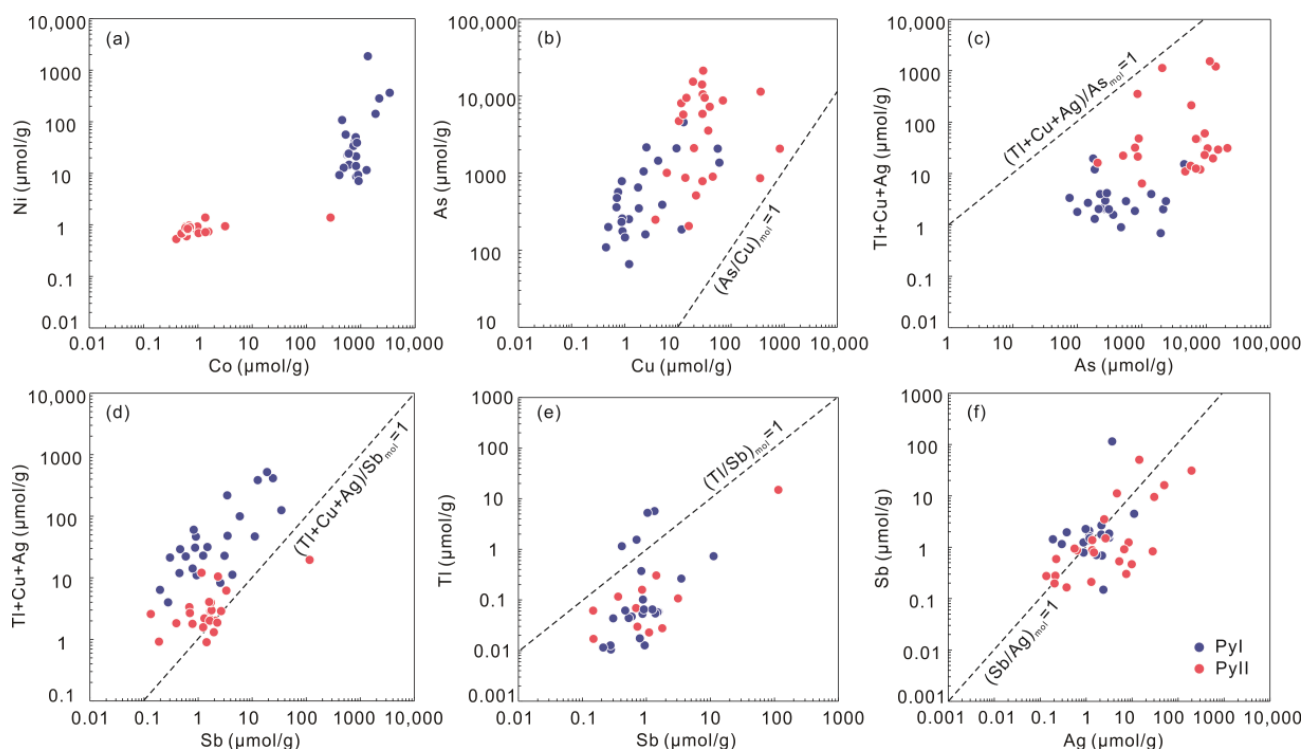


Figure 11. Binary plots of Co and Ni (a), As and Cu (b), As and Ti + Cu + Ag (c), Sb and Ti + Cu + Ag (d), Ti and Sb (e), Ag and Sb (f) in pyrite from the Pusangguo deposit, derived from the total dataset.

Previous studies have shown that monovalent, divalent, and trivalent cations can replace Fe^{2+} through coupled substitutions in the pyrite lattice [64]. The smooth and ragged time-resolved depth profile (Figure 7) indicates that As and Cu may enter into the pyrite both lattice-bound, and as micro-inclusions. Moreover, As and Cu display a positive correlation (Figure 11b), indicating the possible coupled substitution mechanism $\text{As}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$. Based on the flat signal profile of As (Figure 7c,d), and previous studies, it is also possible that As directly replaces S during pyritization [85]. However, some As and Sb may enter the pyrite by a coupled substitution mechanism: $(\text{Ti}^+ + \text{Cu}^+ + \text{Ag}^+) + (\text{As}^{3+}, \text{Sb}^{3+}) \leftrightarrow 2\text{Fe}^{2+}$ [64], as indicated by the good correlation between As, Sb, and Ti + Cu + Ag (Figure 11c,d). Furthermore, the Sb and Ti in the pyrite show a positive correlation in the binary plots (Figure 11e). This suggests that, in some

cases, the incorporation of Sb into pyrite may promote the substitution of Tl in pyrite, through the coupled substitution mechanism $\text{Sb}^{3+} + \text{Tl}^+ \leftrightarrow 2\text{Fe}^{2+}$.

The time-resolved LA-ICP-MS depth profiles (Figure 7c,d) show the presence of Ag- and Sb-bearing micro-inclusions in the pyrite. Simultaneously, there is a positive correlation between Ag and Sb (Figure 11f), indicating that some Ag and Sb entered the pyrite lattice via the coupled substitution $\text{Sb}^{3+} + \text{Ag}^+ \leftrightarrow 2\text{Fe}^{2+}$. Pb generally struggles to replace Fe, because it has a much larger ionic radius than Fe [71]. The ragged Pb signal curves (Figure 7c) indicate that Pb may be incorporated into the pyrite lattices as micro-inclusions, which, in turn, may indicate that Pb is present as galena micro-inclusions within the pyrite.

6.3. Physicochemical Condition of Mineralization

Sphalerite and pyrite formations are influenced by physicochemical conditions, including the temperature, sulfur fugacity ($f\text{S}_2$), and oxygen fugacity ($f\text{O}_2$), which can cause trace element variations [61,84,86,87]. Therefore, some physicochemical characteristics of the mineralization may be reflected through the variations in trace elements in sphalerite and pyrite.

6.3.1. Temperature

Previous studies have shown that the contents of some trace elements in sphalerite, such as Fe, Mn, Co, In, Cd, Ga, Ge, Sn, and Te, can be an effective indicator of the temperature of mineralization [16,28,88,89]. High-temperature (200–355 °C) sphalerite is generally enriched with Fe (3.58–11.42 wt%), Mn (0.2–0.4 wt%), Co, In, Sn, and Te, and has high In/Ge and low Ga/In ratios, forming the dark iron sphalerite (e.g., the Dulong, Laochang, and Hetaoping deposits, [90]); whereas low-temperature-associated sphalerite (110–180 °C) is commonly enriched in Ga, Cd, and Ge (>50 ppm), and poor in Fe (0.23–2.0 wt%) and Mn (30–50 ppm), and has low In/Ge and high Ga/In ratios [91,92]. Sphalerite in the Pusangguo deposit is characterized by a high median level of Fe (53,191 ppm), Mn (2531 ppm), Co (1102 ppm), In (8.64 ppm), Sn (4.3 ppm) and In/Ge (15.9), but low Ga (0.44 ppm), Ge (0.44 ppm), and Ga/In (0.06), implying a high crystallization temperature. Moreover, SpI is relatively more enriched in Co than SpII (Figure 8), suggesting a decreasing trend in temperature from SpI to SpII. The Cd content in the Pusangguo sphalerite (median 2776 ppm) is similar to that in high-temperature sphalerite; this is also supported by its high Zn/Cd ratio (average 203) ($100 < \text{Zn}/\text{Cd} < 500$, [93]).

The Pusangguo deposit contains a large number of iron-bearing minerals, such as chalcopyrite and pyrite (Figure 5), indicating that Fe is the primary component of the ore-forming fluid. Previous studies have shown that the temperature obtained from the garnet fluid inclusions in the prograde stage varies from 413 to 532 °C [14], implying high-temperature conditions. The temperatures (267–340 °C, average 298 °C) obtained according to empiric thermometry ($\text{Fe}/\text{Zn}_{\text{sphalerite}} = 0.0013 \times t - 0.2953$, [94]) are similar to those obtained from the quartz fluid inclusions (256–378 °C) [14], suggesting that the sphalerite formed at high temperatures. Furthermore, Frenzel et al. [28] proposed that the Fe, Mn, Ga, In, and Ge in sphalerite are mainly associated with the mineralization temperature, and suggested the sphalerite geothermometer (GGIMFis). The GGIMFis was used to attain the mineralization temperatures at the Pusangguo deposit, and yielded the sphalerite crystallization temperatures (237–345 °C, average 307 °C), all of which indicated high-temperature conditions. Therefore, the mineralization in the Pusangguo deposit was formed in a relatively high-temperature environment.

Temperature changes during mineralization may also be reflected in some trace elements in pyrite. Pyrite formed in high-temperature conditions is usually poor in some thermally sensitive elements (e.g., As, Sb, Zn, Pb) [84]. The pyrite in the Pusangguo deposit has low levels of Zn (median 86.8 ppm), As (median 883 ppm), Sb (median 1.24 ppm) and Pb (median 26.2 ppm) (Table S5), indicating that the pyrite was formed under high-temperature conditions. In addition, the Co/Ni ratio of the pyrite can also be used as a temperature indicator: when $\text{Co}/\text{Ni} > 1$, the pyrite was formed at a high temperature,

and if $\text{Co/Ni} < 1$, the pyrite was formed at a low temperature [84,95,96]. The Co/Ni ratios (0.6–201.2, average 24.0) of the pyrite from the Pusangguo deposit are much higher than 1, further implying that the pyrite in the Pusangguo deposit was formed under high-temperature conditions.

6.3.2. Sulfur Fugacity (f_{S_2})

The incorporation of iron into the sphalerite lattice is influenced by both the temperature and the sulfur fugacity (f_{S_2}) [69,97]. The f_{S_2} can be estimated based on the temperature at which the sphalerite was formed (determined via GGIMFis), and the FeS mol% contained in the sphalerite [98,99]. The FeS mol% of the sphalerite in the Pusangguo deposit ranges from 4.99 to 14 (Table S4), and the f_{S_2} is estimated to range from $10^{-13.4}$ to $10^{-8.3}$ (Figure 12), suggesting a low f_{S_2} condition.

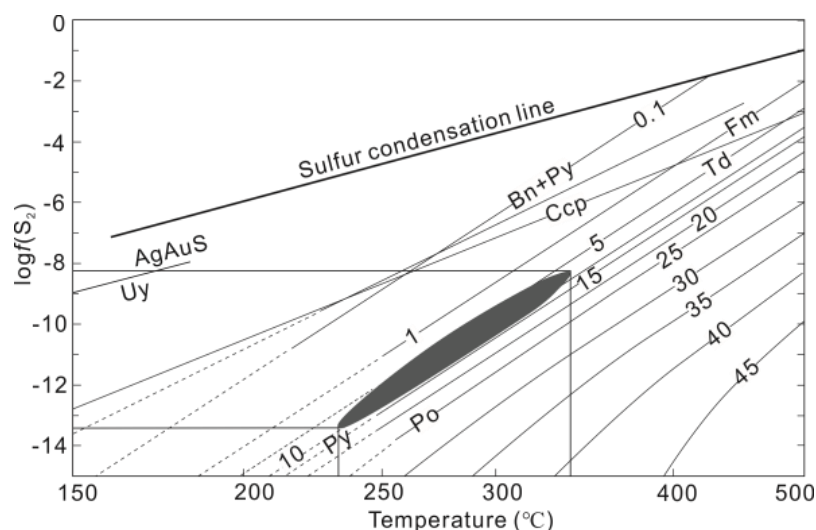


Figure 12. Sulfur fugacity diagram for the sphalerite from the Pusangguo deposit (modified from [99]). Abbreviations: Td, tetrahedrite; Uy, uytenbogaardtite; Fm, famatinite; Py, pyrite; Ccp, chalcopyrite; Bn, bornite; Po, pyrrhotite.

6.3.3. Oxygen Fugacity (f_{O_2})

The Mn content of sphalerite is strongly influenced by the ore-forming redox conditions, and Mn is mainly incorporated into the sphalerite lattice as MnS [69,100]. The high Mn contents in sphalerite generally reflect the mineralization having been formed under a reduced environment [25,88,100]. The Mn concentrations in sphalerite from the Pusangguo deposit are high (1317–6443 ppm, average 2868 ppm), indicating that the quartz–sulfide-ore stage of mineralization occurred under relatively reduced conditions. The increasing Mn contents from SpI (avg. 2830 ppm) to SpII (avg. 2910 ppm) suggest that the ore-forming fluids from the Fe–Cu–Zn sulfide substage to the Pb–Zn sulfide substage evolved to a more reduced environment.

6.4. Pyrite Chemistry as an Indicator of Fluid Evolution

Pyrites in hydrothermal ore deposits usually contain trace amounts of Zn, Cu, As, Pb, Au, Ag, Ni, Co, Se, Sb, Bi, and Tl, which directly record the information of the ore-forming fluid [82,101]. Consequently, the chemistry of pyrites is widely studied, and is considered to be an indicator of the composition of mineralized fluids in hydrothermal systems [83,102].

Pyrite is widely distributed in the Pusangguo deposit, mainly including PyI in the oxide-ore stage, and PyII in the quartz–sulfide-ore stage, with different geochemical compositions. It is generally believed that the mixing of the ore-forming fluid is responsible for the geochemical variation in pyrite at different stages [103–105]. Previous fluid inclusion studies showed that the fluid-mixing process took place in the Pusangguo deposit [14].

In comparison with PyII, Ti, V, Cr, Ga, Ge, and In are slightly enriched in PyI, in the same order of magnitude as in PyII (Figure 9). However, most of the elements (such as Cu, Pb, Zn, Co, Ni, As, Sn, Sb, Ag, and Bi) show a higher concentration in PyII than in PyI, indicating that the contents of these elements in the ore-forming fluid increased from the oxide-ore stage to the quartz–sulfide-ore stage. The ore-forming-fluid-mixing process is crucial to the subsequent mineralization of Pb, Zn, Cu, and Co sulfides. The absence of oxides (hematite) in the quartz–sulfide-ore stage indicates that the oxygen fugacity of the ore-forming fluid was lower than that of the oxide-ore stage, probably favoring the occurrence of Zn, Pb, and Cu in the fluids. Additionally, Mn was enriched in PyII, as opposed to in PyI (Figure 9), implying that the Mn content increased from the oxide-ore stage to the Fe–Cu–Zn–sulfide substage (Figure 6). It is generally assumed that Mn is remobilized from carbonate wall rocks via fluid–rock reactions in the skarn system [106]. This reaction raised the pH value of the ore-forming fluid, and consumed large quantities of ore-forming fluid, reducing the concentration of most elements (e.g., Cu, Pb, Zn, and Co) and promoting the precipitation of chalcopyrite, sphalerite, galena, carrollite, cobaltite, and linnaeite.

7. Conclusions

(1) Two types of sphalerites (SpI and SpII) and pyrites (PyI and PyII) have developed in the Pusangguo deposit. The sphalerite is generally more enriched with Co than the pyrite. SpI has a higher Co content than SpII, and PyII has higher contents of most trace elements (e.g., Mn, Co, and Ni) than PyI.

(2) Trace elements such as Co and Mn mainly directly replaced Zn in sphalerite, and Fe in pyrite, through simple substitution mechanisms ($\text{Co}^{2+} \leftrightarrow \text{Zn}^{2+}$, $\text{Mn}^{2+} \leftrightarrow \text{Fe}^{2+}$), while trace elements (e.g., Sb, Sn, Cu, Ag, As) mainly replaced Zn in sphalerite, and Fe in pyrite through coupled substitution mechanisms (e.g., $(\text{Sb}^{3+}, \text{Sn}^{3+}) + (\text{Cu}^+, \text{Ag}^+) \leftrightarrow 2\text{Zn}^{2+}$, $\text{Sb}^{3+} + \text{Ag}^+ \leftrightarrow 2\text{Fe}^{2+}$).

(3) The trace element compositions of the sphalerite and pyrite indicate that the mineralization in the Pusangguo deposit is mainly formed under the conditions of high temperature, low sulfur fugacity, and low oxygen fugacity.

(4) The fluid-mixing process is mainly responsible for the Pb, Zn, Cu, and Co mineralization in the Pusangguo deposit.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13091165/s1>, Table S1. Summary of the samples collected from the Pusangguo deposit in this study; Table S2. EPMA major element compositions for sphalerite from the Pusangguo deposit (wt%); Table S3. EPMA major element compositions for pyrite from the Pusangguo deposit (wt%); Table S4. Summary of the LA-ICP-MS trace elemental data (in ppm) obtained for sphalerite from the Pusangguo deposit; Table S5. Summary of the LA-ICP-MS trace elemental data (in ppm) obtained for pyrite from the Pusangguo deposit.

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References

1. Tang, J.X.; Wang, Q.; Yang, H.H.; Gao, X.; Zhang, Z.B.; Zou, B. Mineralization, Exploration and Resource Potential of Porphyry-skarn-epithermal Copper Polymetallic Deposits in Tibet. *Acta Geosci. Sin.* **2017**, *38*, 5–47, (In Chinese with English Abstract).
2. Tang, J.X. Mineral resources base investigation and research status of the Tibet Plateau and its adjacent major metallogenic belts. *Acta Petrol. Sinica* **2019**, *35*, 617–624, (In Chinese with English Abstract).
3. Tang, J.X.; Yang, H.H.; Song, Y.; Wang, L.Q.; Liu, Z.B.; Li, B.L.; Lin, B.; Peng, B.; Wang, G.H.; Zhong, Q.G.; et al. The copper polymetallic deposits and resource potential in the Tibet Plateau. *China Geol.* **2021**, *4*, 1–16. [\[CrossRef\]](#)
4. Liu, Z.J.; Chen, J.; Yin, G.F.; Zhang, J.Y.; Dai, S.J. *The Geological Survey Report on the Pusangguo Cu Polymetallic Deposit in Tibet*; Tibet Bureau Publishing House: Tibet, China, 2012; pp. 1–152, (In Chinese with English Abstract).
5. Cui, X.L. Research on Metallization of Pusangguo Polymetallic Copper Deposit in Tibet, China. Ph.D. Thesis, Chengdu University of Technology, Chengdu, China, 2013. (In Chinese with English Abstract).
6. Yang, H.R. The Mineralogical Characteristics and Its Genetic Significance of Pusangguo Copper Poly-Metal Ore Deposit in Tibet. Master's Thesis, Chengdu University of Technology, Chengdu, China, 2013. (In Chinese with English Abstract).
7. Li, Z.; Lang, X.H.; Rickleman, D.; Duan, J.L.; Zhang, Q.Z. Age and genesis of the Pusangguo skarn Cu-dominated polymetallic deposit, Gangdese metallogenic belt, Tibet. *J. Asian Earth Sci.* **2019**, *169*, 210–227. [\[CrossRef\]](#)
8. Li, Z.; Lang, X.H.; Zhang, Q.Z.; Liu, X.K.; Yang, X. Petrogenesis and geodynamic implications of the intrusions related to the Pusangguo skarn Cu-dominated polymetallic deposit in Tibet: Constraints from geochronology, geochemistry, and Sr-Nd-Pb-Hf isotopes. *Geol. J.* **2020**, *55*, 7659–7686. [\[CrossRef\]](#)
9. Cao, M.J.; Qin, K.Z.; Evans, N.J.; Li, G.M.; Ling, X.X.; McInnes, B.I.A.; Zhao, J.X. Titanite in situ SIMS U-Pb geochronology, elemental and Nd isotopic signatures record mineralization and fluid characteristics at the Pusangguo skarn deposit, Tibet. *Miner. Depos.* **2021**, *56*, 907–916. [\[CrossRef\]](#)
10. Li, Z.; Wang, L.Q.; Li, H.F.; Danzhen, W.X.; Shi, S. Sulfur and Lead isotopic compositions of the Pusangguo Cu-Pb-Zn polymetallic deposit in Tibet: Implications for the source of ore-forming material. *Geoscience* **2018**, *32*, 56–65, (In Chinese with English Abstract).
11. Li, Z.; Tang, J.X.; Wang, L.Q.; Li, H.F.; Liu, W.Y. Mineralogical characteristics of skarn in the Pusangguo Pb-Zn polymetallic deposit of Tibet and their geological significance. *Acta Petrol. Mineral.* **2018**, *37*, 241–258, (In Chinese with English Abstract).
12. Wang, S.; Cao, M.J.; Li, G.M.; Silang, W.D.; Shan, P.F.; Qin, K.Z. The occurrence of cobalt and implications for genesis of the Pusangguo cobalt-rich skarn deposit in Gangdese, Tibet. *Ore Geol. Rev.* **2022**, *150*, 105193. [\[CrossRef\]](#)
13. Li, M.; Zheng, Y.Y.; Feng, Q.L.; Xu, J.; Wu, S.; Sun, G.P. Ore genesis of skarn mineralization in continental collision orogens: A case study from the Pusangguo Co-bearing Cu-Pb-Zn deposit in Tibet. *Ore Geol. Rev.* **2020**, *122*, 103523. [\[CrossRef\]](#)
14. Li, Z.; Zhang, P.; Zhu, J.R.; Xu, J.Q.; Niu, X.D. Fluid origin and evolution of the Pusangguo Cu-Pb-Zn skarn deposit in Tibet: Constraints from fluid inclusions and isotope compositions. *Ore Geol. Rev.* **2022**, *150*, 105197. [\[CrossRef\]](#)
15. Zhao, H.X.; Frimmel, H.E.; Jiang, S.Y.; Dai, B.Z. LA-ICP-MS trace element analysis of pyrite from the Xiaoqinling gold district, China: Implications for ore genesis. *Ore Geol. Rev.* **2011**, *43*, 142–153. [\[CrossRef\]](#)
16. Lockington, J.A.; Cook, N.J.; Ciobanu, C.L. Trace and minor elements in sphalerite from metamorphosed sulphide deposits. *Miner. Petrol.* **2014**, *108*, 873–890. [\[CrossRef\]](#)
17. Sykora, S.; Cook, D.R.; Meffre, S.; Stephanov, A.S.; Gardner, K.; Scott, R.; Selley, D.; Harris, A.C. Evolution of pyrite trace element compositions from porphyry-style and epithermal conditions at the Lihir Gold deposit: Implications for ore genesis and mineral processing. *Econ. Geol.* **2018**, *113*, 193–208. [\[CrossRef\]](#)
18. Chen, F.C.; Deng, J.; Wang, Q.F.; Huizengga, J.M.; Li, G.J.; Gu, Y.W. LA-ICP-MS trace element analysis of magnetite and pyrite from the Hetaoping Fe-Zn-Pb skarn deposit in Baoshan block, SW China: Implications for ore-forming processes. *Ore Geol. Rev.* **2020**, *117*, 103309. [\[CrossRef\]](#)
19. Wei, C.; Ye, L.; Huang, Z.; Hu, Y.; Wang, H. In situ trace elements and S isotope systematics for growth zoning in sphalerite from MVT deposits: A case study of Nayongzhi, South China. *Mineral. Mag.* **2021**, *85*, 364–378. [\[CrossRef\]](#)
20. George, L.L.; Cook, N.J.; Ciobanu, C.L. Partitioning of trace elements in cocrystallized sphalerite-galena-chalcopyrite hydrothermal ores. *Ore Geol. Rev.* **2016**, *77*, 97–116. [\[CrossRef\]](#)
21. Bauer, M.E.; Burisch, M.; Ostendorf, J.; Krause, J.; Frenzel, M.; Seifert, T.; Gutzmer, J. Trace element geochemistry of sphalerite in contrasting hydrothermal fluid systems of the Freiberg district, Germany: Insights from LA-ICP-MS analysis, near-infrared light microthermometry of sphalerite-hosted fluid inclusions, and sulfur isotope geochemistry. *Miner. Depos.* **2019**, *54*, 237–262.
22. Bao, T.; Ni, P.; Dai, B.Z.; Wang, G.G.; Chen, H.; Li, S.N.; Chi, Z.; Li, W.S.; Ding, J.Y.; Chen, L.L. Pyrite Rb-Sr geochronology, LA-ICP-MS trace element and telluride mineralogy constraints on the genesis of the Shuangqishan gold deposit, Fujian, China. *Ore Geol. Rev.* **2021**, *138*, 104158. [\[CrossRef\]](#)
23. Xu, J.; Cook, N.J.; Ciobanu, C.L.; Li, X.; Kontonikas-Charos, A.; Gilbert, S.; Lv, Y. Indium distribution in sphalerite from sulfide-oxide-silicate skarn assemblages: A case study of the Dulong Zn-Sn-In deposit, Southwest China. *Miner. Depos.* **2021**, *56*, 307–324. [\[CrossRef\]](#)
24. Frenzel, M.; Cook, N.J.; Ciobanu, C.L.; Slattery, A.D.; Wade, B.P.; Gilbert, S.; Ehrig, K.; Burisch, M.; Verdugo-Ihl, M.R.; Voudouris, P. Halogens in hydrothermal sphalerite record origin of ore-forming fluids. *Geology* **2020**, *48*, 766–770. [\[CrossRef\]](#)
25. Zhuang, L.L.; Song, Y.; Liu, Y.; Fard, M.; Hou, Z. Major and trace elements and sulfur isotopes in two stages of sphalerite from the world-class Angouran Zn-Pb deposit, Iran: Implications for mineralization conditions and type. *Ore Geol. Rev.* **2019**, *109*, 184–200. [\[CrossRef\]](#)

26. Xing, B.; Mao, J.W.; Xiao, X.N.; Liu, H.; Zhang, C.; Guo, S.; Li, H.Y.; Huang, W.Y.; Lai, C. Metallogenic discrimination by sphalerite trace element geochemistry: An example from the Fengyan Zn-Pb deposit in central Fujian, SE China. *Ore Geol. Rev.* **2022**, *141*, 104651. [\[CrossRef\]](#)
27. Zhang, J.K.; Shao, Y.J.; Liu, Z.F.; Chen, K. Sphalerite as a record of metallogenic information using multivariate statistical analysis: Constraints from trace element geochemistry. *J. Geochem. Explor.* **2022**, *232*, 106883. [\[CrossRef\]](#)
28. Frenzel, M.; Hirsch, T.; Gutzmer, J. Gallium, germanium, indium, and other trace and minor elements in sphalerite as a function of deposit type—A meta-analysis. *Ore Geol. Rev.* **2016**, *76*, 52–78. [\[CrossRef\]](#)
29. Wang, J.L.; Deng, A.P.; Zhang, Y.; Shao, Y.J.; Li, H.B. Cu–Pb–Zn and W–Mo–Pb–Zn systematic mineralization environment of Huangshaping deposit in Hunan: Indicator of sphalerite geochemistry. *Miner. Res. Geol.* **2020**, *34*, 56–63, (In Chinese with English Abstract).
30. Xing, B.; Mao, J.W.; Xiao, X.N.; Liu, H.; Jia, F.D.; Wang, S.H.; Huang, W.Y.; Li, H.Y. Genetic discrimination of the Dingjiashan Pb–Zn deposit, SE China, based on sphalerite chemistry. *Ore Geol. Rev.* **2021**, *135*, 104212. [\[CrossRef\]](#)
31. Gottesmann, W.; Kampe, A. Zn/Cd ratios in calcsilicate-hosted sphalerite ores at Tumurtijn-ovoo, Mongolia. *Chem. Erde-Geochem.* **2007**, *67*, 323–328. [\[CrossRef\]](#)
32. Belissont, R.; Muñoz, M.; Boiron, M.; Luais, B.; Mathon, O. Distribution and oxidation state of Ge, Cu and Fe in sphalerite by μ -XRF and K-edge μ -XANES: Insights into Ge incorporation, partitioning and isotopic fractionation. *Geochim. Cosmochim. Acta* **2016**, *177*, 298–314. [\[CrossRef\]](#)
33. Cugerone, A.; Cenik-Tok, B.; Oliot, E.; Muñoz, M.; Barou, F.; Motto-Ros, V.; Le Goff, E. Redistribution of germanium during dynamic recrystallization of sphalerite. *Geology* **2019**, *48*, 236–241. [\[CrossRef\]](#)
34. Zhu, D.C.; Zhao, Z.D.; Niu, Y.; Mo, X.X.; Chung, S.L.; Hou, Z.Q.; Wang, L.Q.; Wu, F.Y. The Lhasa Terrane: Record of a microcontinent and its histories of drift and growth. *Earth Planet. Sci. Lett.* **2011**, *301*, 241–255. [\[CrossRef\]](#)
35. Zhu, D.C.; Zhao, Z.D.; Niu, Y.L.; Dilek, Y.; Hou, Z.Q.; Mo, X.X. The origin and pre-Cenozoic evolution of the Tibetan Plateau. *Gondwana Res.* **2013**, *23*, 1429–1454. [\[CrossRef\]](#)
36. Zhang, Z.M.; Zhao, G.C.; Santosh, M.; Wang, J.L.; Dong, X.; Shen, K. Late Cretaceous charnockite with adakitic affinities from the Gangdese batholith, southeastern Tibet: Evidence for Neo-Tethyan mid-ocean ridge subduction? *Gondwana Res.* **2010**, *17*, 615–631. [\[CrossRef\]](#)
37. Dong, X.; Zhang, Z.M.; Santosh, M.; Wang, W.; Yu, F.; Liu, F. Late Neoproterozoic thermal events in the northern Lhasa terrane, south Tibet: Zircon chronology and tectonic implications. *J. Geodyn.* **2011**, *52*, 389–405. [\[CrossRef\]](#)
38. Lang, X.H.; Deng, Y.L.; Wang, X.H.; Tang, J.X.; Yin, Q.; Xie, F.W.; Yang, Z.Y.; Li, Z.; He, Q.; Li, L.; et al. Geochronology and geochemistry of volcanic rocks of the Bima Formation, southern Lhasa subterranean, Tibet: Implications for early Neo-Tethyan subduction. *Gondwana Res.* **2020**, *80*, 335–349. [\[CrossRef\]](#)
39. Wang, X.H.; Lang, X.H.; Klemm, R.; Deng, Y.L.; Tang, J.X. Subduction initiation of the Neo-Tethys oceanic lithosphere by collision-induced subduction transference. *Gondwana Res.* **2022**, *104*, 54–69. [\[CrossRef\]](#)
40. Kang, Z.Q.; Xu, J.F.; Wilde, S.A.; Feng, Z.H.; Chen, J.L.; Wang, B.D.; Wen, C.F.; Pan, H.B. Geochronology and geochemistry of the Sangri Group Volcanic Rocks, Southern Lhasa Terrane: Implications for the early subduction history of the Neo-Tethys and Gangdese Magmatic Arc. *Lithos* **2014**, *200–201*, 157–168. [\[CrossRef\]](#)
41. Wei, Y.Q.; Zhao, Z.D.; Niu, Y.L.; Zhu, D.C.; Liu, D.; Wang, Q.; Hou, Z.Q.; Mo, X.X.; Wei, J.C. Geochronology and geochemistry of the Early Jurassic Yeba Formation volcanic rocks in southern Tibet: Initiation of back-arc rifting and crustal accretion in the southern Lhasa Terrane. *Lithos* **2017**, *278–281*, 477–490. [\[CrossRef\]](#)
42. Mo, X.X.; Hou, Z.Q.; Niu, Y.L.; Dong, G.C.; Qu, X.M.; Zhao, Z.D.; Yang, Z.M. Mantle contributions to crustal thickening in south Tibet in response to the India–Asia collision. *Lithos* **2007**, *96*, 225–242. [\[CrossRef\]](#)
43. Lee, H.Y.; Chung, S.L.; Lo, C.H.; Ji, J.Q.; Lee, T.Y.; Qian, Q.; Zhang, Q. Eocene Neotethyan slab breakoff in southern Tibet inferred from the Linzizong volcanic record. *Tectonophysics* **2009**, *477*, 20–35. [\[CrossRef\]](#)
44. Mo, X.X.; Hou, Z.Q.; Niu, Y.L.; Dong, G.C.; Qu, X.M.; Zhao, Z.D.; Hou, Z.Q.; Zhou, S.; Ke, S. Contribution of syncollisional felsic magmatism to continental crust growth: A case study of the Paleogene Linzizong volcanic Succession in southern Tibet. *Chem. Geol.* **2008**, *250*, 49–67. [\[CrossRef\]](#)
45. Chen, X.L.; Liang, H.Y.; Zhang, J.; Sotiriou, P.; Huang, W.T.; Ren, L.; Zhang, L.; Zou, Y.Q. Geochemical characteristics and magma fertility for the Jurassic arc rocks in the Gangdese belt, Tibet. *Ore Geol. Rev.* **2019**, *115*, 103169. [\[CrossRef\]](#)
46. Wu, F.Y.; Ji, W.Q.; Liu, C.Z.; Chung, S.L. Detrital zircon U–Pb and Hf isotopic data from the Xigaze fore-arc basin: Constraints on Transhimalayan magmatic evolution in southern Tibet. *Chem. Geol.* **2010**, *271*, 13–25. [\[CrossRef\]](#)
47. Ji, W.Q.; Wu, F.Y.; Liu, C.Z.; Chung, S.L. Early Eocene crustal thickening in southern Tibet: New age and geochemical constraints from the Gangdese batholith. *J. Asian Earth Sci.* **2012**, *53*, 82–95. [\[CrossRef\]](#)
48. Chu, M.F.; Chung, S.L.; O'Reilly, S.Y.; Pearson, N.J.; Wu, F.Y.; Li, X.H.; Lee, H.Y. India's hidden inputs to Tibetan orogeny revealed by Hf isotopes of Trans Himalayan zircons and host rocks. *Earth Planet. Sci. Lett.* **2011**, *307*, 479–486. [\[CrossRef\]](#)
49. Tang, J.X.; Lang, X.H.; Xie, F.W.; Gao, Y.M.; Li, Z.J.; Yang, H.H.; Zhang, L.; Wang, Q.; Zhou, Y. Geological characteristics and genesis of the Jurassic No. 1 porphyry Cu–Au deposit in the Xiongcu district, Gangdese porphyry copper belt, Tibet. *Ore Geol. Rev.* **2015**, *70*, 438–456. [\[CrossRef\]](#)

50. Lang, X.H.; Wang, X.H.; Deng, Y.L.; Tang, J.X.; Xie, F.W.; Yang, Z.Y.; Jiang, K. Hydrothermal evolution and ore precipitation of the No. 2 porphyry Cu–Au deposit in the Xiongcu district, Tibet: Evidence from cathodoluminescence, fluid inclusions, and isotopes. *Ore Geol. Rev.* **2019**, *114*, 103141. [\[CrossRef\]](#)
51. Zhao, J.X.; Qin, K.Z.; Li, G.M.; Li, J.X.; Xiao, B.; Chen, L.; Yang, Y.; Li, C.; Liu, Y.S. Collision-related genesis of the Sharang porphyry molybdenum deposit, Tibet: Evidence from zircon U–Pb ages, Re–Os ages and Lu–Hf isotopes. *Ore Geol. Rev.* **2014**, *56*, 312–326. [\[CrossRef\]](#)
52. Fu, Q.; Xu, B.; Zheng, Y.C.; Yang, Z.S.; Hou, Z.Q.; Huang, K.X.; Liu, Y.; Zhang, C.; Zhao, L. Two episodes of mineralization in the Mengya’a deposit and implications for the evolution and intensity of Pb–Zn–(Ag) mineralization in the Lhasa terrane, Tibet. *Ore Geol. Rev.* **2017**, *90*, 877–896. [\[CrossRef\]](#)
53. Zhou, A.R.G.L.; Dai, J.G.; Li, Y.L.; Li, H.A.; Tang, J.X.; Wang, C.S. Differential exhumation histories between Qulong and Xiongcu porphyry copper deposits in the Gangdese copper metallogenic Belt: Insights from low temperature thermochronology. *Ore Geol. Rev.* **2019**, *107*, 801–819. [\[CrossRef\]](#)
54. Sun, X.; Hollings, P.; Lu, Y.J. Geology and origin of the Zhunuo porphyry copper deposit, Gangdese belt, southern Tibet. *Miner. Depos.* **2021**, *56*, 457–480. [\[CrossRef\]](#)
55. Zheng, W.B.; Liu, B.L.; Tang, J.X.; McKinley, J.M.; Cooper, M.R.; Tang, P.; Lin, B.; Li, C.; Wang, L.; Zhang, D. Exploration indicators of the Jiamia porphyry-skarn deposit, southern Tibet, China. *J. Geochem. Explor.* **2022**, *236*, 106982. [\[CrossRef\]](#)
56. Hou, Z.Q.; Yang, Z.M.; Qu, X.M.; Meng, X.J.; Li, Z.Q.; Beaudoin, G.; Rui, Z.Y.; Gao, Y.F.; Zaw, K. The Miocene Gangdese porphyry copper belt generated during postcollisional extension in the Tibetan Orogen. *Ore Geol. Rev.* **2009**, *36*, 25–51. [\[CrossRef\]](#)
57. Zhao, X.Y.; Zheng, Y.C.; Yang, Z.S.; Hu, Y. Formation and evolution of multistage ore-forming fluids in the Miocene Bangpu porphyry-skarn deposit, Southern Tibet: Insights from LA–ICP–MS trace elements of quartz and fluid inclusions. *J. Asian Earth Sci.* **2020**, *203*, 104–124. [\[CrossRef\]](#)
58. Liu, W.Y.; Nigel, J.C.; Cristiana, L.C.; Liu, Y.; Qiu, X.P.; Chen, Y.C. Mineralogy of tin-sulfides in the Zijinshan porphyry-epithermal system, Fujian Province, China. *Ore Geol. Rev.* **2016**, *72*, 682–698.
59. Danyushevsky, L.; Robinson, P.; Gilbert, S.; Norman, M.; Large, R.; McGoldrick, P.; Shelley, M. Routine quantitative multi-element analysis of sulphide minerals by laser ablation ICP-MS: Standard development and consideration of matrix effects. *Geochem. Explor. Environ. Anal.* **2011**, *11*, 51–60. [\[CrossRef\]](#)
60. Belissont, R.; Boiron, M.; Luais, B.; Cathelineau, M. LA-ICP-MS analyses of minor and trace elements and bulk Ge isotopes in zoned Ge-rich sphalerites from the Noailhac-Saint-Salvy deposit (France): Insights into incorporation mechanisms and ore deposition processes. *Geochim. Cosmochim. Acta* **2014**, *126*, 518–540. [\[CrossRef\]](#)
61. Gagnevin, D.; Menuge, J.F.; Kronz, A.; Barrie, C.; Boyce, A.J. Minor elements in layered sphalerite as a record of fluid origin, mixing, and crystallization in the Navan Zn–Pb ore deposit, Ireland. *Econ. Geol.* **2014**, *109*, 1513–1528. [\[CrossRef\]](#)
62. Bonnet, J.; Mosser-Ruck, R.; Caumon, M.C. Trace element distribution (Cu, Ga, Ge, Cd, and Fe) IN sphalerite from the tennessee MVT Deposits, USA, By combined EMPA, LA-ICP-MS, raman spectroscopy, and crystallography. *Can. Mineral.* **2016**, *54*, 1261–1284. [\[CrossRef\]](#)
63. Zhou, C.; Yang, Z.; Sun, H.S.; Koua, K.A.D.; Lyu, C.L. LA-ICP-MS trace element analysis of sphalerite and pyrite from the Beishan Pb–Zn ore district, south China: Implications for ore genesis. *Ore Geol. Rev.* **2022**, *150*, 105128. [\[CrossRef\]](#)
64. Yang, Q.; Zhang, X.J.; Ulrich, T.; Zhang, J.; Wang, J. Trace element compositions of sulfides from Pb–Zn deposits in the Northeast Yunnan and northwest Guizhou Provinces, SW China: Insights from LA-ICP-MS analyses of sphalerite and pyrite. *Ore Geol. Rev.* **2022**, *141*, 104639. [\[CrossRef\]](#)
65. Tauson, V.L.; Chernyshev, L.V.; Makeev, A.B. Phase relations and structural peculiarities of mixed-crystals in ZnS–MnS system. *Geokhimiya* **1977**, *5*, 679–692.
66. Patrick, R.A.D.; Mosselmans, J.F.W.; Charnock, J.M. An X-ray absorption study of doped sphalerites. *Eur. J. Mineral.* **1998**, *10*, 239–249. [\[CrossRef\]](#)
67. Cook, N.J.; Ciobanu, C.L.; Pring, A.; Skinner, W.; Shimizu, M.; Danyushevsky, L.; Saini-Eidukat, B.; Melcher, F. Trace and minor elements in sphalerite: A LA-ICPMS study. *Geochim. Cosmochim. Acta* **2009**, *73*, 4761–4791. [\[CrossRef\]](#)
68. Li, Z.L.; Ye, L.; Hu, S.Y.; Wei, C.; Huang, Z.L.; Yang, Y.L.; Danyushevsky, L. Trace elements in sulfides from the Maozu Pb–Zn deposit, Yunnan Province, China: Implications for trace-element incorporation mechanisms and ore genesis. *Am. Mineral.* **2020**, *105*, 1734–1751. [\[CrossRef\]](#)
69. Liu, S.; Zhang, Y.; Ai, G.L.; Xue, X.L.; Li, H.B.; Shah, S.A.; Wang, N.H.; Chen, X. LA-ICP-MS trace element geochemistry of sphalerite: Metallogenic constraints on the Qingshuitang Pb–Zn deposit in the Qinghang Ore Belt, South China. *Ore Geol. Rev.* **2022**, *141*, 104659. [\[CrossRef\]](#)
70. Wang, K.X.; Zhai, D.G.; Liu, J.J.; Wu, H. LA-ICP-MS trace element analysis of pyrite from the Dafang gold deposit, South China: Implications for ore genesis. *Ore Geol. Rev.* **2021**, *139*, 104507. [\[CrossRef\]](#)
71. Ye, L.; Cook, N.J.; Ciobanu, C.L.; Liu, Y.P.; Zhang, Q.; Liu, T.G.; Gao, W.; Yang, Y.L.; Danyushevskiy, L. Trace and minor elements in sphalerite from base metal deposits in South China: A LA-ICPMS study. *Ore Geol. Rev.* **2011**, *39*, 188–217. [\[CrossRef\]](#)
72. Hu, Y.S.; Ye, L.; Huang, Z.L.; Danyushevsky, L.; Wang, H.Y. LA-ICP-MS sphalerite and galena trace element chemistry and mineralization-style fingerprinting for carbonate-hosted Pb–Zn deposits: Perspective from early Devonian Huodehong deposit in Yunnan, South China. *Ore Geol. Rev.* **2021**, *136*, 104253. [\[CrossRef\]](#)

73. Zhao, Z.X.; Wei, J.H.; Liang, S.N.; Gao, T. Sulfide remobilization and trace element redistribution during metamorphism and deformation at the Xitianshan Pb-Zn deposit, NW China. *Ore Geol. Rev.* **2021**, *136*, 104170. [\[CrossRef\]](#)
74. Wright, K. The incorporation of cadmium, manganese and ferrous iron in sphalerite: Insights from computer simulation. *Can. Miner.* **2009**, *47*, 615–623. [\[CrossRef\]](#)
75. Murakami, H.; Ishihara, S. Trace elements of Indium-bearing sphalerite from tinpolymetallic deposits in Bolivia, China and Japan: A femto-second LA-ICPMS study. *Ore Geol. Rev.* **2013**, *53*, 223–243. [\[CrossRef\]](#)
76. Yuan, B.; Zhang, C.Q.; Yu, H.J.; Yang, Y.M.; Zhao, Y.X.; Zhu, C.C.; Ding, Q.F.; Zhou, Y.B.; Yang, J.C.; Xu, Y. Element enrichment characteristics: Insights from element geochemistry of sphalerite in Daliangzi Pb–Zn deposit, Sichuan, Southwest China. *J. Geochem. Explor.* **2018**, *186*, 187–201. [\[CrossRef\]](#)
77. Torro, L.; Benites, D.; Vallance, J.; Laurent, O.; Ortiz-Benavente, B.A.; Chelle-Michou, C.; Proenza, J.A.; Fontboté, L. Trace element geochemistry of sphalerite and chalcopryrite in arc hosted VMS deposits. *J. Geochem. Explor.* **2022**, *232*, 106882. [\[CrossRef\]](#)
78. Cook, N.J.; Ciobanu, C.L.; Brugger, J.; Etschmann, B.; Howard, D.L.; de Jonge, M.D.; Ryan, C.; Paterson, D. Determination of the oxidation state of Cu in substituted Cu–In–Fe-bearing sphalerite via–XANES spectroscopy. *Am. Mineral.* **2012**, *97*, 476–479. [\[CrossRef\]](#)
79. Makovicky, E.; Topa, D. Crystal chemical formula for sartorite homologues. *Mineral. Mag.* **2018**, *79*, 25–31. [\[CrossRef\]](#)
80. Thomas, H.V.; Large, R.R.; Bull, S.W.; Maslennikov, V.; Berry, R.F.; Fraser, R.; Froud, S.; Moye, R. Pyrite and pyrrhotite textures and composition in sediments, laminated quartz veins, and reefs at Bendigo gold mine, Australia: Insights for ore genesis. *Econ. Geol.* **2011**, *106*, 1–31. [\[CrossRef\]](#)
81. Ciobanu, C.L.; Cook, N.J.; Utsunomiya, S.; Kogagwa, M.; Green, L.; Gilbert, S.; Wade, B. Gold-telluride nanoparticles revealed in arsenic-free pyrite. *Am. Mineral.* **2012**, *97*, 1515–1518. [\[CrossRef\]](#)
82. Reich, M.; Deditius, A.; Chrysosoulis, S.; Li, J.W.; Ma, C.Q.; Parada, M.A.; Barra, F.; Mittermayr, F. Pyrite as a record of hydrothermal fluid evolution in a porphyry copper system: A SIMS/EMPA trace element study. *Geochim. Cosmochim. Acta* **2013**, *104*, 42–62. [\[CrossRef\]](#)
83. Grant, H.L.J.; Hannington, M.D.; Petersen, S.; Frische, M.; Fuchs, S.H. Constraints on the behavior of trace elements in the actively-forming TAG deposit, Mid-Atlantic Ridge, based on LA-ICP-MS analyses of pyrite. *Chem. Geol.* **2018**, *498*, 45–71. [\[CrossRef\]](#)
84. Maslennikov, V.V.; Maslennikova, S.P.; Large, R.R.; Danyushevsky, L.V. Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanichosted massive sulfide deposit (Southern Urals, Russia) using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). *Econ. Geol.* **2009**, *104*, 1111–1141. [\[CrossRef\]](#)
85. Deditius, A.P.; Utsunomiya, S.; Reich, M.; Kesler, S.E.; Ewing, R.C.; Hough, R.; Walshe, J. Trace metal nanoparticles in pyrite. *Ore Geol. Rev.* **2011**, *42*, 32–46. [\[CrossRef\]](#)
86. Deditius, A.P.; Reich, M.; Kesler, S.; Utsunomiya, S.; Chrysosoulis, S.L.; Walshe, J.; Ewing, R.C. The coupled geochemistry of Au and As in pyrite from hydrothermal ore deposits. *Geochim. Cosmochim. Acta* **2014**, *140*, 644–670. [\[CrossRef\]](#)
87. Rottier, B.; Kouzmanov, K.; Walle, M.; Bendezu, R.; Fontbote, L. Sulfide replacement processes revealed by textural and LA-ICP-MS trace element analyses: Example from the early mineralization stages at Cerro de Pasco, Peru. *Econ. Geol.* **2016**, *111*, 1347–1367. [\[CrossRef\]](#)
88. Kelley, K.; Leach, D.; Johnson, C.; Clark, J.; Fayek, M.; Slack, J.; Anderson, V.; Ayuso, R.; Ridley, W. Textural, Compositional, and Sulfur Isotope Variations of Sulfide Minerals in the Red Dog Zn-Pb-Ag Deposits, Brooks Range, Alaska: Implications for Ore Formation. *Econ. Geol.* **2004**, *99*, 1509–1532. [\[CrossRef\]](#)
89. Bauer, M.E.; Seifert, T.; Burisch, M.; Krause, J.; Richter, N.; Gutzmer, J. Indium bearing sulfides from the Hammerlein skarn deposit, Erzgebirge, Germany: Evidence for late-stage diffusion of indium into sphalerite. *Miner. Depos.* **2019**, *54*, 175–192. [\[CrossRef\]](#)
90. Guo, F.; Wang, Z.L.; Xu, D.R.; Yu, D.S.; Dong, G.J.; Ning, J.T.; Kang, B.; Peng, E.K. Trace element characteristics of sphalerite in the Lishan Pb-Zn polymetallic deposit in Hunan Province and the metallogenic implications. *Earth Sci. Front.* **2020**, *27*, 66–81.
91. Ye, L.; Li, Z.L.; Hu, Y.S.; Huang, Z.L.; Zhou, J.X.; Fan, H.F.; Danyushevskiy, L. Trace elements in sulfide from the Tianbaoshan Pb-Zn deposit, Sichuan Province, China: A LA-ICPMS study. *Acta Petrol. Sin.* **2016**, *32*, 3377–3393, (In Chinese with English Abstract).
92. Wu, Y.; Sun, Z.G.; Chen, M.H.; Zhang, C.Q.; Cao, L.; Tang, Y.J.; Yuan, X.; Zhang, P. Trace elements in sphalerites from the Mississippi Valley-type lead-zinc deposits around the margins of Yangtze Block and its geological implications: A LA-ICP-MS study. *Acta Petrol. Sin.* **2019**, *35*, 3443–3460.
93. Wen, H.J.; Zhu, C.W.; Zhang, Y.X.; Cloquet, C.; Fan, H.F.; Fu, S.H. Zn/Cd ratios and cadmium isotope evidence for the classification of lead–zinc deposits. *Sci. Rep.* **2016**, *6*, 25273. [\[CrossRef\]](#)
94. Keith, M.; Haase, K.M.; Schwarz-Schampera, U.; Klemm, R.; Petersen, S.; Bach, W. Effects of temperature, sulfur, and oxygen fugacity on the composition of sphalerite from submarine hydrothermal vents. *Geology* **2014**, *42*, 699–702. [\[CrossRef\]](#)
95. Cook, N.J. Mineralogy of the sulphide deposits at Sulitjelma, Northern Norway. *Ore Geol. Rev.* **1996**, *11*, 303–338. [\[CrossRef\]](#)
96. Maghfouri, S.; Rastad, E.; Lentz, D.R.; Mousivand, F.; Choulet, F. Mineralogy, microchemistry and fluid inclusion studies of the Besshi-type Nuddeh Cu-Zn VMS deposit, Iran. *Geochemistry* **2018**, *78*, 40–57. [\[CrossRef\]](#)
97. Li, H.B.; Ishiyama, D.Z.; Zhang, Y.; Shao, Y.J. Geology and geochemical characteristics of the Xiajinbao gold deposit in the Hebei Province, China. *J. Mineral. Petrol. Sci.* **2018**, *113*, 24–40. [\[CrossRef\]](#)
98. Scott, S.D.; Barnes, H.L. Sphalerite geothermometry and geobarometry. *Econ. Geol.* **1971**, *66*, 653–669. [\[CrossRef\]](#)

99. Warmada, I.W.; Lehmann, B. Polymetallic sulfides and sulfosalts of the Pongkor epithermal gold-silver deposit, west java, Indonesia. *Can. Mineral.* **2003**, *41*, 185–2003. [[CrossRef](#)]
100. Bernardini, G.P.; Borgheresi, M.; Cipriani, C.; Di Benedetto, F.; Romanelli, M. Mn distribution in sphalerite: An EPR study. *Phys. Chem. Miner.* **2004**, *31*, 80–84. [[CrossRef](#)]
101. Large, R.R.; Danyushevsky, L.; Hollit, C.; Maslennikov, V.; Meffffre, S.; Gilbert, S.; Bull, S.; Scott, R.; Emsbo, P.; Thomas, H.; et al. Gold and trace element zonation in pyrite using a laser imaging technique: Implications for the timing of gold in orogenic and Carlin-style sediment-hosted deposits. *Econ. Geol.* **2009**, *104*, 635–668. [[CrossRef](#)]
102. Houghton, J.L.; Shanks, W.C., III; Seyfried, W.E., Jr. Massive sulfide deposition and trace element remobilization in the Middle Valley sediment-hosted hydrothermal system, northern Juan de Fuca Rdge. *Geochim. Cosmochim. Acta* **2004**, *68*, 2863–2873. [[CrossRef](#)]
103. Kampmann, T.C.; Jansson, N.F.; Stephens, M.B.; Olin, P.H.; Gilbert, S.; Wanhainen, C. Syn-tectonic sulphide remobilization and trace element redistribution at the Falun pyritic Zn-Pb-Cu-(Au-Ag) sulphide deposit, Bergslagen, Sweden. *Ore Geol. Rev.* **2018**, *96*, 48–71. [[CrossRef](#)]
104. Shu, Q.H.; Chang, Z.S.; Mavrogenes, J. Fluid compositions reveal fluid nature, metal deposition mechanisms, and mineralization potential: An example at the Haobugao Zn-Pb skarn, China. *Geology* **2021**, *49*, 473–477. [[CrossRef](#)]
105. Shu, Q.H.; Chang, Z.S.; Hammerli, J.; Lai, Y.; Huizenga, J.M. Composition and evolution of fluids forming the Baiyinnuo'er skarn Zn-Pb deposit, northeastern China: Insights from laser ablation ICP-MS study of fluid inclusions. *Econ. Geol.* **2017**, *112*, 1441–1460. [[CrossRef](#)]
106. Meinert, L.D.; Dipple, G.M.; Nicolescu, S. World Skarn Deposits. In *Economic Geology 100th Anniversary Volume*; Society of Economic Geologists: Littleton, CO, USA, 2005; pp. 299–336.

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