



# Article Mineralized Zones of the Shizhuyuan Ore Field and Their Genetic Relationship with the Qianlishan Granite Complex, NE China: Evidence from Pyrite In Situ Geochemistry

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**Abstract:** The Shizhuyuan ore field has three mineralized zones around the Qianlishan granite complex with a radius of ~6 km: W-Sn-Mo-Bi (inner zone), Pb-Zn (middle zone), and Hg-Sb (outer zone). However, whether Pb-Zn and Hg-Sb mineralization is genetically related to the Qianlishan granites is still debated. Here, we conducted in situ pyrite trace element analysis to study the combinations and distributions. The Bi concentration gradually decreases from the inner zone to the outer zone, while the Mn and Sb contents show the opposite trend. Pyrites from each zone are distributed in distinct zones in the binary plot of Co/Ni-Bi, which is an effective discrimination diagram indicating the degree of hydrothermal alteration. Collectively, the gradual changes in pyrite trace element characteristics among the three ore-forming zones provide evidence to indicate that these zones probably compose a whole magmatic-hydrothermal system associated with the Qianlishan granite complex.

**Keywords:** mineralized zones; Shizhuyuan ore field; pyrite trace elements; ore-forming hydrothermal system

# 1. Introduction

The Nanling Range in SE China is renowned worldwide for its voluminous Mesozoic granites, which are associated with W, Sn, Pb, Zn, and rare earth element (REE) deposits [1–11]. Among these deposits is the Shizhuyuan tungsten polymetallic deposit, which contains 80 Mt of W, 40 Mt of Sn, 20 Mt of Bi, and 10 Mt of Mo [12–14]. The skarngreisen type of mineralization in Shizhuyuan has been suggested to be genetically related to the QGC (Qianlishan granite complex) [10,11,13,15,16].

Around the QGC, a series of mineralization zones are continuously distributed, such as W-Sn-Mo-Bi in Chaishan; Pb-Zn-(Ag) in Chaishan, Shexingping and Zongshupo; and Hg-Sb in Wutongping. Pb-Zn mineralized veins in Chaishan and Shexingping are located hundreds to thousands of meters to the southwest of the QGC [14]. Hg-Sb veins in Wutongping are approximately 6 km south of the QGC. Although the QGC is closely related spatially to the surrounding mineralized veins, their genetic relationship is still debated. Wu et al. [17] suggested that these veins are genetically related to the QGC on the basis of fluid inclusion and S-O isotope studies. Mao et al. [14] argued that Pb-Zn mineralization in Jinshiling represents a sedimentary deposit due to the absence of contacts with the granites. Few investigations have been carried out on the Hg-Sb mineralization in Wutongping. Therefore, the genetic relationship between the QGC and the Pb-Zn and Hg-Sb deposits is still debated.



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Pyrite trace elements are an effective tool to reflect the type of metal mineralization [18], discriminate distinct mineralization stages [19], and investigate depositional environments (e.g., distinguish between magmatic-hydrothermal and sedimentary environments) [20]. Pyrite is ubiquitous in the Shizhuyuan ore field and occurs in all of the mineralized veins (W-Sn-Mo-Bi, Pb-Zn and Hg-Sb) around the QGC. Here, we conducted in situ pyrite trace element analysis to reveal the distinct element combination and distribution characteristics in each mineralized zone, in order to investigate the genetic association between the QGC and the surrounding mineralization.

## 2. Geological Setting

# 2.1. Tectonic Setting

As shown in Figure 1, the Nanling Range, which is located in the southern part of the South China Block (SCB), comprises the Yangtze Block and the Cathaysia Block; these blocks amalgamated during the early Neoproterozoic along the Qin-Hang deep fault zone [6,21,22]. This collision zone was reactivated in the middle and late Mesozoic, leading to the formation of numerous nonferrous and rare metal mineralizations, including tungsten, tin, lead, zinc, uranium, copper, gold, silver, and REEs [23]. The Shizhuyuan ore field is located approximately 16 km southeast of Chenzhou city, Hunan Province (Figure 1).

#### 2.2. Stratigraphy

The Shizhuyuan ore field comprises Sinian metasedimentary rocks, Carboniferous rocks, Devonian clastic sedimentary and carbonate rocks, and Quaternary sediments (Figure 2) [24]. The Sinian metasedimentary rocks are present only on the eastern edge of the ore field and represent weakly metamorphosed clastic sediments that comprise mainly gray-green to gray-black, moderately thick, fine-grained quartz-rich sandstones, feldspathic sandstones, siltstones, phyllites, and slate [25]. Lower Carboniferous rocks ( $C_1$ , >538 m) are located in the southern regions of this ore field, containing consist of silty shale and limestone. Middle and Upper Devonian clastic sedimentary and carbonate rocks, which have been intensely altered by magmatic activity and fracturing, are the main host rocks. From bottom to top, the Middle Devonian rocks have been subdivided into the Tiaomajian and Qiziqiao formations, and the Upper Devonian rocks have been subdivided into the Shetianqiao and Xikuangshan formations [26]. The Tiaomajian Formation ( $D_2t$ , >358 m thick), which is distributed in both the eastern and western regions of the ore field, is dominated by pebble-bearing and quartz-rich sandstones with subordinate rocks, such as conglomerates, slates, and silicic sandstones. The Qiziqiao Formation (D<sub>2</sub>q, >520 m thick), which is located in the middle and southern sections of the ore field, contains mainly gray-white dolomites, limestones, and dolomitic limestones that are interlayered with thin slates and siltstones. The Shetiangiao Formation ( $D_{3s}$ , >296 m thick), which is located in the Shizhuyuan, Dongpo and Chaishan areas, consists mainly of banded micrite limestones. The Xikuangshan Formation ( $D_3x$ , >363 m thick) comprises thick-bedded limestones and dolomitic limestones containing flint concretions [24]. Quaternary sediments (~10 m thick), which represent slope wash, are rare; they occur only on the sides of the river in the northern part of the Shizhuyuan ore field.



**Figure 1.** Geological map of the Nanling Range, South China (modified after [2,27]). Faults: (1) Jiangshan–Shaoxing–Pingxiang Fault; (2) Zhenghe–Dapu Fault; (3) Changle–Nan'ao Fault; (4) Chenzhou–Linwu Fault; (5) Changlin–Guangchang buried Fault; (6) Wuzhou–Sihui buried Fault.



**Figure 2.** Schematic geological map of the Qianlishan district showing the Qianlishan granite complex (modified after [10,14]).

# 2.3. Geology and Mineralization of the Three Zones

A series of deposits transect the Shizhuyuan ore field southward from the Qianlishan granites: the supergiant Shizhuyuan W-Sn-Mo-Bi deposit, Jinchuantang Sn-Bi deposit, Jinshiling Pb-Zn deposit, and Hengshanling Pb-Zn deposit and the small Hg-Sb deposit (Figure 3). In general, three mineralized zones are distinguished based on the distribution of these deposits: (1) W-Sn-Mo-Bi; (2) Pb-Zn; and (3) Hg-Sb (Figure 3).

The temperature of mineralization gradually increases from the inner zone to the outermost zone. The inner zone (W-Sn-Mo-Bi) includes two types of mineralization: (1) complex skarn, which is skarn overprinted by greisenization, and (2) simple skarn, which formed during the retrograde metamorphism process [14]. Based on the homogeneous temperatures of fluorite fluid inclusions, the simple skarn formed in the temperature range of 202–288 °C, while complex skarn was generated in the higher temperature range of 270–400 °C [14,24]. Wu et al. [17] carried out a fluid inclusion study on sphalerite, fluorite, carbonate and quartz in the Hengshanling, Baibulong, and Shexingping deposits. Their results suggested that fluorite inclusions in the Chaishan district (S3-2, S8-2) reached homogeneity at 299–344 °C and the those in the Shexingping district (QX-1) reached homo-



geneity at temperatures of 187–362 °C. Half of Sb<sup>3+</sup> will participate if the fluid temperature decreases from 350 °C to 200 °C by heat conduction [28].

**Figure 3.** Mineralizing zones in the Shizhuyuan ore-field. Inner zone: W-Sn-Mo-Bi; Middle zone: Pb-Zn; and Outer zone: Hg-Sb (modified after [14]).

In summary, based on the mineralization temperatures, the Shizhuyuan ore field can be classified into three parts: (1) a high-to moderate-temperature part, including complex skarn mineralization in Shizhuyuan (W-Sn-Mo-Bi zone) and sphalerite-galena mineralization in Chaishan (Pb-Zn zone); (2) a moderate- to low-temperature part, composing simple skarn in Shizhuyuan (W-Sn-Mo-Bi zone) and sphalerite-galena mineralization in Shexingping (Pb-Zn zone); and (3) low-temperature stibnite mineralization in Wutongping (Hg-Sb zone).

#### 3. Sampling and Analytical Methods

This study collected six samples from three mineralization zones (Table 1). Samples 490-28, 490-13, and S3-2 were obtained from the W-Sn-Mo-Bi zone. Samples 490-28 and 490-13 were acquired from Tunnel 490 of the Shizhuyuan W-Sn-Mo-Bi deposit. The former is a complex skarn (skarn overprinted with greisenization), and the latter is a skarn. Sample S3-2, a complex skarn, was collected from the Chaishan deposit ~1 km from the Qianlishan

granite. In the Pb-Zn zone, Sample QX-1 represents the Pb-Zn ore in the Shexingping deposit. In the Hg-Sb zone, Sample WTP-4 is a Hg-Sb ore in the Wutongping deposit located ~6 km from the Qianlishan granites.

Table 1. Samples collected	from three mineralizing	z zones in the Shizhu	vuan ore-field.
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Sample	Mineralizing Zone	Location	Location	Longitude	Latitude	Sample
490-28	W-Sn-Mo-Bi	Shizhuyuan	Tunnel 490–516	25°44′	113°10′	Complex Skarn
490-13		Shizhuyuan	Tunnel 490 P2C2 eastern 10 m	25°44′	113°10′	Simple Skarn
S3-2		Chaishan	Tunnel 500 in Chaishan	25°43′	113°09′	Complex Skarn
S8-2	Pb-Zn	Chaishan	Tunnel 640 in Chaishan	25°43′	113°09′	Pb-Zn Ore
QX-1		Shexingping	81-3 Ore Tunnel 450 in Shexingping	25°43′	113°08′	Pb-Zn Ore
WTP-4	Hg-Sb	Wutongping	Wutongping	$25^{\circ}40'$	113°09′	Hg-Sb Ore

#### In Situ Trace Element Analyses of Pyrite

These six samples were cut into 25-mm-wide circular pucks. They were set in epoxy and polished for in situ analyses of pyrite. Before in situ analysis, three samples (490-28, 490-13, and S8-2) were etched by NaOCl (sodium hypochlorite solution, 6–14% w/v active chlorine) to reveal the internal texture. The sample surface was soaked in the solution for 30–120 s. Once a noticeable color change occurred on the surface, the samples were rinsed with cold tap water. After rinsing, they were allowed to dry. The color on the pyrite surface varied according to the pyrite composition and the time of etching. In situ trace element analyses of pyrite were carried out using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Center of Excellence in Ore Deposits (CODES), University of Tasmania, Hobart, Australia. For a detailed description of the analysis, please refer to [29]; a brief introduction to the methodology is presented below.

The laser ablation spot diameter was 19  $\mu$ m, and the repetition rate was 5 Hz. The laser beam energy ranged between 4 and 5 J/cm<sup>2</sup>. The analysis time for each sample was 100 s, including background analysis (30 s with the laser off). The acquisition time was mostly set to 0.02 s with a total sweep time of ~1.5 s. Data reduction followed the method of [30], with an internal standard of Fe. The calibration was conducted using standards STDGL2, GSD-1G, and PeruPy [29,31].

Imaging was performed using a set of parallel lines arranged in a square. The laser beam was 13 to 20  $\mu$ m in size, and the repetition rate was 10 Hz with a constant speed (covering the size of the beam in 1 s). The sweep time was ~0.2 s, and the image speed was 15 or 25  $\mu$ m/s. The acquisition time for most elements was set to 0.002 s, while those for Ag, Te, and Au were strongly prolonged (0.04 s) to improve their detection limits. Similarly, Se was measured for 0.004 s. Background and sulfide standards were measured at the start and end of each image. Images could be corrected for drift using standard analysis; however, sensitivity drift was negligible due to the long duration of analysis (1–2 h). The effect of redeposition was insignificant due to the pre-ablation of each line.

#### 4. Results

#### 4.1. Petrography

Previous studies have indicated that the QGC (~10 km<sup>2</sup>) comprises two parts: the QGC and a series of mafic dikes. The mafic dikes are much younger (~10 Ma) than the QGC and the associated W-Sn-Mo-Bi mineralization; thus, they are not genetically related to the mineralization. The QGC, which is closely related spatially and temporally to the W-Sn-Mo-Bi mineralization, can be subdivided into five sections [1,2,14,15,24–26,32]. The first section (S<sub>1</sub>) is a fine-grained porphyritic biotite granite (GL-13, Figure 4) located on the northern edge of the plutons, with an outcrop area of ~4.0 km<sup>2</sup>. The second section (S<sub>2</sub>) is a gray-white, microfine-grained porphyritic biotite granite (315-36, Figure 4) that occurs in the southern part of the pluton, with an outcrop area of ~1.1 km<sup>2</sup>. The third section (S<sub>3</sub>) is a gray-white, medium- to coarse-grained (mainly 0.3–0.8 mm in diameter) equigranular biotite granite (490-21, Figure 4) with an outcrop area of 4.4 km<sup>2</sup>. The fourth section (S<sub>4</sub>) is

a gray-white, fine-grained (mostly 0.1–0.3 mm in diameter) equigranular biotite (two-mica) granite ( $\sim$ 0.1 km<sup>2</sup>) (490-10, Figure 4). This section has intruded into the first three sections, and pegmatite belts are often found on its top. The fifth section (S<sub>5</sub>) represents a series of NE-striking (25–65°) granite porphyry dikes (490-2, Figure 4).



**Figure 4.** Photographs of the Qianlishan granites. S<sub>1</sub> (Sample GL-13): porphyritic biotite granite; S<sub>2</sub> (Sample 315-36): microfine-grained porphyritic biotite granite; S<sub>3</sub> (Sample 490-21): middle- to large-grained equigranular biotite granite; S<sub>4</sub> (Sample 490-10): fine-grained equigranular biotite granite; S<sub>5</sub> (490-2): granite porphyry dikes (Sample 490-2). Abbreviations [33]: Qz, Quartz; Pl, Plagiarize; Bt, Biotite; Ms, Muscovite; Kfs: potassium feldspar.

#### 4.2. Mineralization

The samples and mineralization assemblage of each mineralized zone are presented in Figure 5 and Table 2.

The mineralization assemblage of the W-Sn-Mo-Bi zone contains pyrite, molybdenite, and scheelite (chalcopyrite in Sample 490-28) (Figure 5b). Sample 490-28 includes molybdenite, pyrite, chalcopyrite, and scheelite. Molybdenite consists mostly of fine- to medium-grained (50–200  $\mu$ m) gray lamellar aggregates. They are commonly bent and kinked. It appears to be pale yellow to deep reddish brown in transmitted light. Pyrite is ubiquitous in this zone and occurs as yellow, subhedral to anhedral grains with sizes of 50–300  $\mu$ m. By comparison, chalcopyrite is rare. These grains are brassy, lamellar, and 50–150 in size. Sample 490-13 and Sample S3-2 have metal mineral assemblages similar to that of 490-28, while the total content is less. This assemblage comprises molybdenite and minor pyrite. Pyrite is distributed sporadically as yellow, subhedral grains with sizes ranging from 30 to 150  $\mu$ m. Molybdenite is present as gray lamellar aggregates with widely ranging sizes of 50–200  $\mu$ m.

# (a)

 $\begin{array}{c} 490-28 \\ \hline \\ 88-2 \\ \hline \\ 60 \\ \hline \\ \\ 60 \\ \hline \\ 60 \\ \hline$ 

(b)



**Figure 5.** The samples (**a**) and their mineral assembly (**b**) collected from three mineralizing zones. W-Sn-Mo-Bi zone: 490-28, 490-13 and S3-2; Pb-Zn: S8-2; and QX-1; Hg-Sb: WTP-4. Abbreviations: Py: pyrite; Mol: molybdenite; Ccp: chalcopyrite; Sp: sphalerite; Gn: galena; Stb: stilbite.

Zone	Sample	Rock	Mineral Assembly	Extreme Enrichment (1000–500 ppm)	Strong Enrichment (500–100 ppm)	Middle Enrichment (100–10 ppm)	Slight Enrichment (10–1 ppm)
W-Sn-	490-28	Complex Skarn	Ру+Сру+Мо			As-Bi -Co-Pb-Ni- Cu-Sn-Mn-Ti	Sb-Cr-Se-Zr-Te-Tl- Ag-Zn
Mo-Bi 490-13 S		Simple Skarn	Py+Mo	As	Ni	Pb-Co-Sb-Mn-Mo- Bi-Cu	Ti-Se-Tl-Čr-Zn-W-Te- Sn-Ag
	S3-2	Complex Skarn	Py+Mo	As	Cu	Pb-Th-Bi-Co	Mn-Te-Se-Mo-Sb-Ti- Ag-Ni-Zn-Zr-U
Pb-Zn	S8-2	Ore	Py+AsPy+Ga+Sp	Ta	Cu-Co-Mn- Sn-As	Ti-Zn-Th-Bi-W- Se-Ni	Pb-Mo-Cr-V-Ag-Te
	QX-1	Ore	Ga+Sp+Py			Mn	Pb -Ti-Zr-Ag-Se-Cu- As-Sn
Hg-Sb	WTP-4	Ore	Ga+St+Py		As-Mn-Ni	Cu-Sb-Co-Ti-Pb- Zn-Cr-Se	Mo-Zr-V-Tl

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<b>Table 2.</b> Trace element characteristic of pyrites from the Shizhuyuan ore-field.												

Notes: Py denotes pyrite; Ccp denotes Chalcopyrite; Mol denotes Molybdenite; Gn denotes Galena; Sp: Sphalerite; Stb: stibnite.

The metal mineral assemblage of Sample S8-2 and Sample QX-1 (the Pb-Zn zone) is composed of pyrite, galena, and sphalerite. Additionally, minor arsenopyrite is found in Sample S8-2. Pyrite in S8-2 is yellow, euhedral to subhedral, and 50–230  $\mu$ m in size. Arsenopyrite consists of pale-yellow grains with sizes of 50–120  $\mu$ m. It shows strong anisotropy (red-violet). Pyrite, present as anhedral grains, is rare in Sample QX-1. The ores in the Hg-Sb zone include stibnite, galena, and pyrite. Stibnite is gray-white, lamellar and elongated, metallic luster, and <20  $\mu$ m in size. It is opaque with perfect cleavage on [10], showing strong anisotropy. Pyrite is rare, subhedral to anhedral, and <100  $\mu$ m (mostly < 20  $\mu$ m, ); it is disseminated and dispersed.

#### 4.3. In Situ Spot Analysis

Pyrite is the shared mineral of the three mineralized zones; therefore, it is chosen as the target mineral for in situ analysis to reveal its compositional features in each zone. Analyzing their genetic relationship will promote interpreting the formation of the mineralization zones in the Shizhuyuan ore field.

After etching with the NaOCl solution, none of the pyrites collected from the three zones exhibited color zones (Figure 5b: 490-28, 490-13 and S8-2), which suggests that pyrite has no obvious overgrowths.

The results of the pyrite in situ analyses are presented in Tables 2–4.

Sample	No	Minimum	Maximum	Average	Median
490-28	37	0.3	10	4	4
490-13	20	0.02	3	0.4	0.2
S3-2	23	1	535	69	15
S8-2	20	0.04	289	21	2
QX-1	19	0.04	0.4	0.2	0.1
WTP-4	29	0.01	3	0.4	0.09

**Table 3.** Co/Ni ratio of pyrites.

Note: No denotes the number of the analyzed spots.

Samples 490-28, 490-13, and S3-2 were obtained from the W-Sn-Mo-Bi zone.

Pyrites from Sample 490-28 are moderately enriched (with contents of 10–1000 ppm) in Bi > As > Co > Pb > Ni > Cu > Sn > Mn and slightly enriched (with contents of 1–10 ppm) in Ti > Sb > Cr > Se > Te > Tl > Zr > Ag (Table 2). In the time-solved profile (Figure 6), the trends of the counts for Co, Ni, and As are parallel to those of Fe and S, suggesting that they enter pyrite crystals via stoichiometric substitution. The counts of Co are approximately one order of magnitude higher than those of Ni, revealing that the content of Ni is much higher than that of Ni. This result is consistent with the Co/Ni ratio of 4, indicating its

magmatic origin [34] (Table 3). The spikes of Bi, Pb, Ag, Tl, and Te are similar to each other (Figure 7), indicating that they are probably present as Bi-Pb-Tl-Te inclusions in pyrite. Similarly, Figure 8 shows the presence of Pb-Tl-Sb inclusions. These inclusions might be galena enriched in Tl and Sb. The enrichment in Tl is likely due to the replacement of Pb<sup>2+</sup> by 2Tl<sup>+</sup> [35].



Figure 6. Time-resolved depth profiles of Co, Ni and As in Sample 490-28.



Figure 7. Time-resolved depth profiles of Bi, Pb, Tl, Te, and Ag in Sample 490-28.

Sample	Parameter	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	As	Se
490-28	Median	2	0.04	0.5	0.9	465,341	48	13	1	0.7	3	7
	Average	12	0.12	7	15	464,380	54	27	21	1	79	7
	Minimum	0.1	0.01	0.03	0.04	458,563	0.3	0.07	0.02	0.2	0.02	0.3
	Maximum	247	0.87	136	193	465,431	429	432	348	4	494	13
490-13	Median	1.5	0.06	1.3	2	464,733	8.7	39	12	2	288	8
	Average	9.8	0.07	4.5	26	464,233	67	348	16	5	654	8
	Minimum	0.3	0.01	0.23	0.36	460,809	1	4	0.58	0.01	20	3
	Maximum	158	0.23	32	187	465,410	462	3466	51	15	4294	17
S3-2	Median	3	0.01	0	2	464,921	30	0.5	174	0.6	167	7
	Average	3	0.04	0.26	11	464,245	47	2	270	2	1045	7
	Minimum	0.12	0.01	0.02	0.15	454,416	0.1	0.07	0.01	0.02	0.28	0.32
	Maximum	6.8	0.16	1.4	134	465,461	254	16	1348	15	5914	16
S8-2	Median	9	0.5	0.48	6	462,168	3.6	1	2	5	58	13
	Average	53	2	2.3	261	457,515	275	11	289	45	109	12
	Minimum	1	0.02	0.03	0.04	408,641	0.1	0.09	0.02	0.3	1.8	2.4
	Maximum	624	18	15	2152	465,448	3803	142	2699	364	817	19
QX-1	Median	1	0.03	0	21	465,450	0.04	0.2	1	0.34	1	2
~	Average	3	0.14	0.29	62	465,104	0.04	0.3	2	0.55	1	2
	Minimum	0.3	0.01	0.07	5	459,566	0.01	0.09	0.1	0.01	0.06	0.1
	Maximum	7	0.5	2.08	485	465,467	0.07	0.77	5.1	2.2	3	2.9
WTP-4	Median	24	0.3	3.02	2	464,997	8.8	101	11	0.64	43	9.8
	Average	42	2	12	185	463,936	43	119	76	15	188	10
	Minimum	1	0.01	0.02	0.02	457,672	0.04	1.1	1.1	0.01	10	0.66
	Maximum	306	14	133	1687	465,407	387	473	1490	214	2801	19
Sample	Parameter	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Te	Gd	Hf	Ta
490-28	Median	0.04	0.1	0.08	0.4	0.09	0.2	0.2	0.2	0.06	0.03	0.01
	Average	7	1	0.2	2	0.1	17	9	5	0.06	0.4	0.07
	Minimum	0.02	0.03	0.03	0.03	0.05	0.01	0.02	0.03	0.04	0.01	0.01
	Maximum	56	4	0.6	11	0.2	330	243	83	0.06	2	0.18
490-13	Median	0.04	0.01	0.2	0.7	0.06	0.2	9	0.3	0.02	0.01	0.01
	Average	0.5	0.1	26	1	0.07	2	35	3	0.03	0.04	0.01
	Minimum	0.01	0.01	0.01	0.07	0.01	0.04	0.3	0.03	0.02	0.01	0.01
	Maximum	1.8	0.60	217	6	0.17	33	295	20	0.05	0.11	0.01
S3-2	Median	0.2	0.02	0.05	1	0.1	0.5	3	3	0.2	0.03	0.03
	Average	2	0.07	6	2	0.1	0.7	5	10	1	0.3	0.04
	Minimum	0.03	0.01	0.01	0.02	0.02	0.01	0.08	0.01	0.02	0.01	0.01
	Maximum	4	0.2	35	11	0.4	2	39	113	3	0.71	0.09

**Table 4.** Trace element content of pyrite from each zone (unit: ppm).

Table 4. Cont.

Sample	Parameter	Zr	Nb	Мо	Ag	Cd	Sn	Sb	Te	Gd	Hf	Ta
S8-2	Median	0.2	0.09	0.07	0.3	0.1	1	0.2	1	0.1	0.02	0.01
	Average	0.4	0.2	3	2	0.2	135	0.4	1	0.11	0.04	613
	Minimum	0.04	0.04	0.03	0.02	0.05	0.03	0.02	0.01	0.05	0.02	0.01
	Maximum	1	0.7	10	6	0.54	1425	2	4	0.20	0.08	4900
QX-1	Median	0.1	0.02	0.1	0.9	0.1	0.1	0.4	0.3	0.15	0.2	0
	Average	2	0.02	0.1	2	0.1	1	0.8	0.3	0.15	0.2	0
	Minimum	0.03	0.02	0.02	0.13	0.08	0.01	0.06	0.01	0.15	0.09	0
	Maximum	8	0.02	0.2	8	0.3	7	3	0.56	0.15	0.3	0
WTP-4	Median	0.3	0.08	0.7	0.07	0.3	0.2	2	0.2	0.05	0.05	0.02
	Average	6	0.1	9	0.7	0.6	0.6	47	0.2	0.2	0.5	0.02
	Minimum	0.02	0.01	0.02	0.01	0.05	0.01	0.2	0.03	0.04	0.01	0.01
	Maximum	115	0.6	136	7	4	2	736	0.43	0.9	4	0.05
Sample	Parameter	W	Pt	Au	Tl	Pb206	Pb207	Pb208	Bi	Th		U
490-28	Median	0.04	0.02	0.03	0.2	2	2	2	3	0.01	0	.01
	Average	0.3	0.02	0.05	4	41	35	37	79	0.04	(	).1
	Minimum	0.01	0.01	0.01	0.01	0.05	0.01	0.1	0.09	0.01	0	.01
	Maximum	3	0.02	0.21	90	403	378	386	937	0.27	(	).7
490-13	Median	0.1	0.02	0.06	1	31	30	30	5	0.03	0	.03
	Average	4	0.02	0.08	8	76	71	74	17	0.03	(	).1
	Minimum	0.01	0.01	0.01	0.02	0.5	0.3	0.6	0.05	0.01	0	.01
	Maximum	26	0.06	0.29	88	519	488	496	131	0.04	(	).4
S3-2	Median	0.03	0.02	0.06	0.4	38	27	19	24	0.17	0	.02
	Average	0.1	0.02	0.11	0.4	73	59	60	47	66		1
	Minimum	0.01	0.01	0.02	0.01	0.4	0.01	0.02	0.05	0.01	0	.01
	Maximum	0.69	0.03	0.34	0.95	456	361	397	288	372	e	5.2
S8-2	Median	0.05	0.01	0.03	0.09	2	2	2	5	2	0	.03
	Average	16	0.01	0.03	0.3	6	9	8	21	26	(	).1
	Minimum	0.01	0.01	0.01	0.01	0.2	0.3	0.05	0.2	0.01	0	.01
	Maximum	248	0.02	0.08	1.8	40	53	50	125	100	0	.51
QX-1	Median	0.02	0.02	0.01	0.01	2	2	3	0.1	0.01	0	.03
	Average	0.03	0.02	0.02	0.02	5	3	4	0.1	0.02	0	.05
	Minimum	0.02	0.02	0.01	0.01	0.5	0.1	0.7	0.04	0.01	0	.01
	Maximum	0.06	0.02	0.03	0.03	35	14	14	0.17	0.03	0	.14
WTP-4	Median	0.05	0.02	0.03	0.2	17	18	17	0.05	0.03	0.	025
	Average	0.1	0.02	0.06	1	22	21	21	0.2	0.07	0	.22
	Minimum	0.01	0.01	0.01	0.01	1	1.6	1	0.01	0.01	0	.01
	Maximum	0.6	0.02	0.27	20	81	78	81	1	0.5		2



Figure 8. Time-resolved depth profiles of Pb, Tl, and Sb in Sample 490-28.

As presented in Table 4, the pyrite in Sample 490-13 is highly enriched in As and Ni (100–500 ppm), followed by Pb > Co > Sb > Mn > Mo > Bi > Cu. The parallel trends of the counts for As, Fe, and S indicate that As enters the pyrite lattice via isomorphic substitution (Figure 9). Additionally, the trends for Co, Ni, and As are parallel to those for Fe and S. This result suggests that they exist in pyrite as isomorphisms or micro-inclusions (such as cobaltite and CoAsS). The similar spikes of Pb, Tl, and Sb are probably due to the existence of Pb-Sb inclusions. The pyrite in Sample 490-13 has a low Co/Ni ratio with a median of 0.24.



Figure 9. Time-resolved depth profiles of Co, Pb, Ni, As, Sb, and Tl in Sample 490-13.

The pyrite in Sample S3-2 has extremely elevated As with an average of 999 ppm. The content of Cu (270 ppm) is strongly enriched. In order of concentration, the other elements are Pb > Co > Bi > Th. The pyrite Co/Ni ratio of S3-2 with a median of 15 is the highest among all the samples. In Figure 10, the parallel trends for Co, Fe, and S are flat, indicating that Co enters pyrite by isomorphism. The trend for As is nearly parallel to that of Co, except for a bulge in the middle. This result implies that in addition to isomorphism, As is present as inclusions in pyrite. Although Bi counts have a profile similar to those of Fe and S, it increases at the end of the curve, which suggests that Bi is present as both isomorphisms and inclusions. The spike in Bi is similar to that in Pb, which indicates that Bi and Pb are combined within inclusions in pyrite.



Figure 10. Time-resolved depth profiles of Bi, Pb, As, and Co in Sample S3-2.

In summary, the presence of elements with high contents in pyrite from each sample is exhibited in Table 5.

Table 5	. The present forms of trace elements in pyrite.

<b>Mineralizing Zones</b>	Sample	Isomorphism	<b>Micro-Inclusion</b>	Inclusion
	490-28	Co, Ni, As		Bi, Pb, Ag, Tl, Te
W-Sn-Mo-Bi	490-13	Co, Ni, As		Pb, Sb, Tl
	S3-2	As, Co	Pb, Bi	Bi, Pb, As
	S8-2	Co, Ni, As	Pb, Bi	
Pb-Zn	QX-1	Mn, Pb		Pb, Ag
Hg-Sb	WTP-4	Mn, Pb	Pb-Zn-Cu	Pb, Zn, Cu, Sb; V, As

S8-2 and QX-1 are ores collected from the Pb-Zn zone.

These two samples have distinctive pyrite content features. The pyrite for Sample S8-2 has various elements above the detection limits. Co > Mn > Ta > Cu > Sn > As are strongly enriched, followed by Ti-Zn-Bi-W-Se. This sample also has slight enrichments in Ni > Pb > Th > Cr > V > Ag > Te. Based on the time-resolved LA-ICP-MS depth profile of Sample S8-2 (Figure 11), the parallel trends for Co, Ni, and As suggest that these elements enter pyrite via a substitution mechanism. The parallel trends for Pb and Bi mirror those of Fe and S, indicating that Pb and Bi may occur as Pb-Bi micro-inclusions.

By comparison, pyrite from QX-1 contains minor elements above the detection limits. It has only moderate enrichment in Mn and slight enrichments in Pb and Ag. Its Co/Ni (0.12) ratio is the lowest. The trends for Mn and Pb are parallel to those of Fe and S, suggesting that they occurred in pyrite in the form of a solid solution (Figure 12). However, Pb displays spike summation, indicating the occurrence of a Pb solid solution.

Sample WTP-4 was collected from the Hg-Sb zone. Unlike those from the W-Sn-Mo-Bi and Pb-Zn mineralized zones, pyrite from Sample WTP-4 contains abundant low-temperature elements As, Mn, and Ni and is moderately enriched in Cu, Sb, Co, Ti, Pb, Zn, Cr, and Se. It also has small amounts of Mo, Zr, and V. As presented in Figure 13, the trend for Mn is parallel to those of Fe and S, indicating its presence as a solid inclusion in pyrite. The V spike nearly mirrors that of As, indicating the occurrence of a V-As solid inclusion in the pyrite. The trends for Pb, Zn, and Cu are parallel to each other, implying that they are probably present as a solid inclusion. In addition, their curves are parallel to those of Fe and S, indicative of the possible occurrence of galena micro-inclusions with elevated Cu.



Figure 11. Time-resolved depth profiles of Co, Ni, As, Bi, and Pb in Sample S8-2.



Figure 12. Time-resolved depth profiles of Pb and Mn in Sample QX-1.



Figure 13. Time-resolved depth profiles of Mn, V, As, Pb, Zn, and Cu in Sample WTP-4.

# 4.4. Mapping Analysis

As shown in Figure 14, pyrite from Sample 490-28 has an obvious core-rim texture. The core has elevated Co and Ni, while the rim is enriched in Bi, Pb, Ag, and As. Meanwhile, some areas of the pyrite core are extremely enriched in Co and Ni (red areas in Co mapping and green area in Ni mapping). These parts are probably relicts of sedimentary pyrite.



Figure 14. Mapping of pyrite from Sample 490–28.

Pyrite from Sample S8-2 has abundant Co and As in the core, while Pb, Bi Ag and minor Sb, Te, As, Co, and Ni are enriched in the rim (Figure 15). Pb-Bi-Sb inclusions occur occasionally in the pyrite. The sporadic distribution of Cu indicates that Cu occurs as inclusions.



Figure 15. Mapping of pyrite from Sample S8-2.

Pyrite from Sample QX-1 has few trace elements (Figure 16). Only minor Mn and Pb and trace amounts of Cu are detected.

Collectively, the results of pyrite mapping analyses are presented in Table 6.

![](_page_17_Figure_1.jpeg)

Figure 16. Mapping of pyrite from Sample QX-1.

Table 6. The core-rim texture of pyrites.

Mineralizing Zones	Sample	Core	Rim
W-Sn-Mo-Bi	490-28	Co, Ni	Pb, Ag, Sb, Bi
Dh 7n	S8-2	As, Co	Co, Ni, As, Te, Sb, Ag, Pb, Bi, Cu
PD-Zn	QX-1	Pb, Mn, Cu	Mn, Sb, Pb, Ag

Note: The content unit is ppm.

#### 5. Discussion

#### 5.1. Element Combinations and Features

Pyrite is one of the most common minerals in nature and a ubiquitous mineral in the Shizhuyuan ore field. In addition to cubes, pyrite crystals are present as octahedra and pyritohedra. Octahedra usually form at high temperatures (>600 °C), such as the pyrite occurring in the Ni ore in Norway; in contrast, pyritohedra are commonly present in low-temperature or sedimentary deposits rather than in high-temperature or metamorphic deposits [36]. The composition, texture and electrical properties are variable, leading to its ability to capture various minor and trace elements, such as Ag, As, Au, Bi, Cd, Co, Cu, Hg, Mo, Ni, Pb, Pd, Ru, Sb, Se, Sb, Sn, Te, Tl, and Zn [37]. These minor and trace elements are present in pyrite crystals in three forms: (1) metamorphism; (2) microinclusions or nanometer-sized inclusions; and (3) mineral inclusions that fill in the fractures. Isomorphous substitution commonly occurs between ions/anions with similar charges and radii. Co, Ni, As, Se, and Te mostly enter the pyrite crystal lattice by isomorphism. Isomorphous substitution can be classified into two forms: (a) stoichiometric substitution, such as Co or  $Ni^{2+}$  substituting for  $Fe^{2+}$  in pyrite and Se/Te replacing S<sup>2-</sup> in pyrite crystals, and (b) nonstoichiometric substitution, such as  $AsS^{3-}/AsS_2^{4-}$  substituting for S in pyrite crystals [37].

According to the relationships among their variations, trace elements are divided into several groups: (1) Bi, Pb, Te, and Tl; (2) Sb, Cu, Pb, Tl, and Zn; and (3) Mn and V.

# 5.1.1. Bi, Pb, Te and Tl

As shown in Figure 16, the Bi content has a strong correlation with temperature: the pyrites from Samples 490-28, S3-2, and S8-2 corresponding to the high-temperature zone have the highest Bi contents (average contents are 79, 47, and 17 ppm, respectively); those from the low-temperature zone (Sample WTP-4) have the lowest Bi concentration of 0.2

on average; those from the moderate-temperature zone have a moderate Bi content of 21 ppm. Bi probably occurs as native bismuth in high-temperature (>350 °C) reductive fluids [38]. This inference is consistent with the unusually high Bi contents of Samples 490-28 (937 ppm) and S3-2 (288 ppm), which probably correspond to the occurrence of native bismuth inclusions in pyrite.

Based on the Te-Bi binary diagram (Figure 17), in the low-temperature Hg-Sb zone, the small variations in Bi and Te contents and their strong correlation indicate that Bi is mostly present in pyrite as bismuth telluride (BiTe). In contrast, in the W-Sn-Mo-Bi and Pb-Zn zones, Pb and Te contents show weak correlations. The Bi/Te ratio ranges widely, with a minimum of 0.05 and a maximum of 1000, which suggests that bismuth telluride (BiTe) is not the main occurrence of Bi in these two zones.

![](_page_18_Figure_3.jpeg)

Figure 17. Cont.

![](_page_19_Figure_2.jpeg)

Figure 17. Cont.

![](_page_20_Figure_2.jpeg)

Figure 17. Binary plots of trace element in pyrites. Unit: ppm.

Actually, in the W-Sn-Mo-Bi and Pb-Zn zones, the Bi content is strongly correlated with the Pb content. As shown in Figure 7, Figure 10, and Figure 11, which display the time-resolved depth profiles of Samples 490-28, S3-2, and S8-2, respectively, the similar spikes of Bi and Pb imply their strong correlation and the possible occurrence of Bi-Pb mineral inclusions. For instance, as shown in Figure 11 for Sample S8-2, the trends of Pb, Bi, and S are parallel to each other, indicating the presence of lillianite (Pb<sub>3</sub>Bi<sub>2</sub>S<sub>6</sub>), aikinite (CuPbBiS<sub>3</sub>), or cosalite (Pb<sub>2</sub>Bi<sub>2</sub>S<sub>5</sub>) as micro-inclusions; in the time-resolved depth profile of Sample S3-2 (Figure 10), the Bi spike is similar to that of S, which is probably attributed to the occurrence of bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) micro-inclusions. The Pb/Bi ratio in the W-Sn-Mo-Bi zone (Sample 490-28) is 1.5. In the Pb-Zn zone, Sample S8-2 has a distinctive Pb/Bi ratio of 5. These values are consistent with the presence of Bi-Pb mineral inclusions in these two zones. Moreover, the Pb concentration in each mineralized zone is entirely distinct. The Pb contents in the W-Sn-Mo-Bi zone are the highest of the three zones, with a maximum of 519 ppm. The average Pb concentrations of samples 490-28, 490-13, and S3-2 are 41 ppm, 76 ppm, and 73 ppm, respectively. The Pb-Zn zone has the lowest Pb contents

(0.19–40 ppm); the Pb concentrations of pyrites from Sample S8-2 and Sample QX-1 average 6 and 5 ppm, respectively. With respect to the Hg-Sb zone, the Pb content corresponding to Sample WTP-4 is 22 ppm on average, and 81 ppm at its maximum. The discrepancy in Pb concentrations among the three zones might be attributed to the differences in the quantity of galena. Specifically, in the Pb-Zn zone, Pb preferentially enters galena, resulting in a decrease in Pb in pyrite, and vice versa.

As shown in the time-resolved depth profiles of Sample 490-28 in Figure 7, the parallel trends of Tl, Pb, Bi, and Te indicate their strong correlations. These correlations probably result from the replacement of  $Pb^{2+}$  by  $2Tl^+$  in lillianite ( $Pb_3Bi_2S_6$ ) or other minerals composed of Bi and Pb [39].

In the Tl-Bi and Pb-Bi binary diagrams, three regions with different temperatures (the high-T, moderate-T and low-T regions) are apparent according to Pb/Bi and Bi/Tl; in Samples 490-28, S3-2, and S8-2, representing the high-T region, the Pb/Bi ratios are higher than 1.5. In contrast, Pb/Bi in the low-T region (Sample WTP-4) is lower than 0.01. Samples 490-13 and QX-1 have intermediate Pb/Bi ratios. Similarly, Bi/Tl is higher than 20 in the high-T region and lower than 2 in the low-T region. The moderate-T region corresponds (Sample 490-13 and QX-1) to Bi/Tl ratios ranging from 2 to 20. In summary, Pb/Bi and Bi/Tl are effective factors for distinguishing mineralization zones with various mineralization temperatures.

#### 5.1.2. Au, Ag, Te, and As

The Au contents are low in the Shizhuyuan ore field and hardly depend on temperature: the inner W-Sn-Mo-Bi zone (averages, Sample 490-13: 0.08 ppm; S3-2: 0.06 ppm; 490-28: 0.05 ppm) > the outer zone (WTP-4: 0.06 ppm) > the middle Pb-Zn zone (S8-2: 0.03 ppm; QX-1: 0.02 ppm). As shown in Figure 17, based on the Au saturation line of  $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$  [40], Au is unsaturated and present in pyrite as microinclusions [41,42]. Au has a positive correlation with Ag (Figure 17), indicative of the occurrence of electrum (AuAg) inclusions. Furthermore, Ag/Au ranges widely from 1 to 200, suggesting the existence of minerals containing Au and Ag. As illustrated in Figure 17, Au is also positively associated with Te. Au is inferred to be present also as tellurides, such as calaverite (Au<sub>2</sub>Te) and petzite (AuAg<sub>3</sub>Te<sub>2</sub>) inclusions.

The Ag contents in the W-Sn-Mo-Bi and Pb-Zn zones reach 11 ppm on average and 1.2–2.1 ppm on average, respectively. By comparison, the Ag concentration (0.7 ppm) of the Hg-Sb zone is one order of magnitude less than those of the other zones. As presented in Figure 17, not all of the data have a good correlation. These results suggest that Ag combines with other elements to form mineral inclusions, in addition to the aforementioned Au and Te. As shown in Figure 17, according to their strongly positive association, Ag and Sb are likely combined into minerals such as stephanite (Ag<sub>2</sub>SbS<sub>3</sub>), pyrargyrite (Ag<sub>3</sub>SbS<sub>3</sub>), miargyrite (AgSbS<sub>2</sub>) and polybasite ((Ag, Cu)16Sb<sub>2</sub>S<sub>11</sub>) [19]. Additionally, Ag demonstrates a positive relationship with Pb, indicating that minor Ag probably enters galena micro-inclusions. Foord et al. [43] reported that Ag combined with Sb/Bi can enter galena by replacing Pb in the mineral lattice. The replacement mechanism is Ag<sup>+</sup> + (Sb, Bi)<sup>3+</sup> = 2Pb<sup>2+</sup>. This substitution is likely the cause of the parallel trends of Pb, Sb, and Ag in the time-resolved depth profiles for Sample 490-28 (Figure 7).

### 5.1.3. Sb, Cu, Pb, Tl, and Zn

The distributions of Sb differ in each zone from each other. The Sb concentration in the Hg-Sb zone is much higher than those in other zones, with a maximum of 736 ppm and an average of 47 ppm. In contrast, the maximum (3 ppm) and average (0.8 ppm) Sb concentrations in the Pb-Zn zone are two orders of magnitude less than those in the Hg-Sb zone. With respect to the W-Sn-Mo-Bi zone, the Sb concentration reaches a maximum of 295 ppm, with an average ranging from 5 to 35 ppm.

The similar spikes of Sb, Tl, and Pb (Figure 8) indicate their strong correlations. This observation agrees with the positive association of Sb and Tl (Pb) in the Tl (Pb)-Sb

binary diagram (Figure 17), which probably results from the replacement of Pb in Pb-Sb mineral inclusions by Tl, such as jamesonite (Pb<sub>2</sub>Pb<sub>2</sub>FeSb<sub>6</sub>S<sub>14</sub>) and boulangerite (Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>). Furthermore, Sb-Cn and Pb-Cu present sound correlations as well, implying the occurrence of bournonite (PbCuSbS<sub>3</sub>).

#### Mn and V

Mn and V have extremely contrasting values: the maximum Mn content is 1687 ppm, while V has a maximum of 14 ppm. They share the same variation tendency of increasing from the inner zone (W-Sn-Mo-Bi) to the outer zone (Hg-Sb).

In summary, the abovementioned distribution characteristics of trace elements are presented in Table 7.

Element	Content vs. Temperature	Comparison	Combination	DV	HT(ppm)	MT(ppm)	LT(ppm)
Bi	Positively related		LT and OZ: Te-Bi; MT-HT: Pb-Bi	Tl/Bi	>20	2< and <20	<2
Pb		IZ>OZ>MZ	Bi, Sb, Cu, Tl	Pb/Bi	>1.5	0.01< and <1.5	< 0.01
Cu Co/Ni Au	Positively related	IZ >OZ>MZ IZ >OZ>MZ	Pb, Zn, Sb Ag, Te, As	Co/Ni	>1	<1	<1
			0, ,		IZ (ppm)	MZ(ppm)	OZ(ppm)
Ag	Variation in orders	IZ>MZ>OZ	Au, Te, Sb, Pb	Average	1.2	2–2.1	0.5
Sb	Variation in orders	MZ <iz <oz<="" td=""><td>Sb, Tl, Pb, Cu</td><td>Average</td><td>4-8.3</td><td>0.3</td><td>44.1</td></iz>	Sb, Tl, Pb, Cu	Average	4-8.3	0.3	44.1
Mn		IZ <mz<oz< td=""><td></td><td>Average</td><td>16</td><td>102</td><td>166</td></mz<oz<>		Average	16	102	166
V				Average	0.03	0.54	1.54

Table 7. Distribution characteristics of trace element in pyrites.

Notes: IZ is inner zone; MZ is middle zone; OZ is outer zone; LT is low temperature; MD is middle temperature; HT is high temperature; DT is discrimination value.

#### 5.2. Ore Forming Environment

Co/Ni is an important discriminating tool for ore diagenesis [18,39,44]. In the three zones, Ni is most enriched in the Hg-Sb zone (the Ni content of Sample WTP-4 has a median value of 101 ppm). In contrast, the enrichment in Co is the highest in the W-Sn-Mo-Bi zone corresponding to the high-temperature region. This result is consistent with the fact that the Co/Ni ratio has a strongly positive association with the temperature of mineralization. As shown in Table 3, each zone has a distinct Co/Ni ratio. Co/Ni in the high-temperature region is the highest. Specifically, Sample S3-2 (15 ppm) > Sample 490-28 (4 ppm) > Sample S8-2 (2 ppm). In the moderate-temperature zone, Sample 490-13 (0.2 ppm) > Sample QX-1 (0.1 ppm), which is closely followed by Sample WTP-4 (median value: 0.09 ppm) in the low-temperature zone. As presented in Figure 17, the data are separated into two sections by the line where Co/Ni = 1:1) data higher than the line represent the high-temperature zone, and (2) data lower than the line represent the moderate- to low-temperature zones. In Figure 17, the data of the high-, moderate- and low-temperature zones can be discriminated by the distinct regions they occupied. Moreover, Sample S3-2 in the high-temperature zone is outstanding due to its extremely high Co/Ni ratio, which suggests that Sample S3-2 was subjected to the strongest magmatic-hydrothermal alteration.

As mentioned above, Bi is an indicative factor of high temperature, and the Co/Ni ratio reflects the degree of hydrothermal alteration. Therefore, the Bi-Co/Ni binary diagram can discriminate these mineralization zones. As presented in the Bi-Co/Ni binary diagram (Figure 16), all five samples are located in distinct regions. According to temperature, all the samples can be divided into three groups: (1) for the high-temperature group, Samples 490-28 and S3-2 from a complex skarn in the W-Sn-Mo-Bi zone and Sample S8-2 in the Pb-Zn zone all plot in the high Co/Ni and high Bi region (1 < Co/Ni < 100, 0.1 < Bi < 1000), implying a magmatic-hydrothermal genesis; (2) for the moderate-temperature group,

Sample 490-13 collected from a simple skarn in the W-Sn-Mo-Bi zone has high Bi and low Co/Ni (Co/Ni < 1, 0.1 < Bi < 1000); and (3) for the low-temperature group, Sample WTP-4 acquired from the antimony ore in the Hg-Sb zone has characteristics of low Bi and low Co/Ni.

# 5.3. *Trace Element Distribution Characteristics* 5.3.1. W-Sn-Mo-Bi zone

As demonstrated by Tables 5 and 6, in Sample 490-13, the trace element composition is simple: (1) Co, Ni, and As enter pyrite by isomorphism, and (2) mineral inclusions mostly contain Pb, Bi, and Tl. Moreover, its Co/Ni ratios are 0.02–3, with a median of 0.2. By comparison, Samples 490-28 and S3-2 collected from the complex skarn have more variable pyrite trace element compositions: (1) Co, Ni, and As enter the pyrite lattice by isomorphism; (2) Pb-Bi mineral inclusions occur as both micro-inclusions and mineral inclusions in the pyrite lattice fraction; and (3) mineral inclusions are composed of Bi, Pb, Ag, Tl, Te, and Sb. Pyrite Co/Ni ratios of the complex skarn are high. Specifically, Sample S3-2 acquired from the complex skarn in Chaishan has a median Co/Ni of 15 (ranging from 1.29 to 534.97). Similarly, the Co/Ni ratios of Sample 490-28 in the Shizhuyuan complex skarn range from 0.3 to 10 with a median value of 4. Accordingly, a complex skarn results from a simple skarn superimposed by a hydrothermal process that adds Bi and Ag. The Co/Ni ratios of complex skarn are far higher than that of simple skarn. Based on field work and petrological observations, a simple skarn overlaid by greisenization leads to the formation of a complex skarn. This process is in accordance with the trace element distributions in these two kinds of skarn. These results provide evidence for the suggestion that the Co/Ni ratio is an effective tool to indicate the degree of hydrothermal alteration. As a result, Sample S3-2 with the highest Co/Ni reflects the strongest hydrothermal impact.

#### 5.3.2. Pb-Zn zone

On the basis of the spot analysis and mapping of pyrite (Tables 5 and 6), Sample 8-2 has a trace element assemblage similar to that of the skarn in the W-Sn-Mo-Bi zone: (1) Co, Ni, and As enter pyrite by isomorphism; (2) Pb and Bi form micro-inclusions; and (3) Pb, Bi, Te, and Sb are found in mineral inclusions. Except for a value of 0.04, the other sixteen Co/Ni ratios of Sample S8-2 are higher than 1.67, with a maximum of 289 and a median of 2.44. These results provide evidence that the Pb-Zn deposit has a hydrothermal genesis. Interestingly, Sample QX-1 from Shexingping has apparently distinct characteristics of trace element combinations: (1) Mn, Pb, and Cu occur in the form of isomorphism, and (2) mineral inclusions are mainly composed of Mn, Sb, Pb, and Ag. Compared with Sample S8-2, Sample QX-1 has much more Mn and much less Bi. Moreover, the Co and Ni concentrations of Sample QX-1 are mostly lower than the detection limits. Five groups of Co and Ni content data range from 0.04 to 0.4 with a median value of 0.12. The trace element assemblage and Co/Ni ratios of Sample QX-1 are in contrast to those of Sample S8-2, indicating that they were impacted by two distinct hydrothermal fluid processes. The Co/Ni ratios and Bi contents of Sample QX-1 are lower than those of Sample S8-2, indicative of the lower temperature of the hydrothermal fluids. This inference is in accordance with the previous fluid inclusion study. The homogenization temperatures of fluid inclusions in Samples S3-2 and S8-2 are 299–344 °C and 187–362 °C, respectively [17]. The high Mn concentration of Sample S8-2 suggests higher oxygen fugacity. Moreover, the Mn content reaches 485.1 (Table 4), indicating a hydrothermal genesis [45].

# 5.3.3. Hg-Sb zone

Sample WTP-4 was collected from an ore in Wutongping. Its pyrite trace element characteristics are elucidated as follows: (1) Mn and Pb are present as isomorphisms; (2) Pb, Zn, and Cu occur as micro-inclusions; and (3) mineral inclusions contain Pb, Zn, Cu, and As. The pyrite of sample WTP-4 has high Ni concentrations with an average of 119 ppm and a maximum of 473 ppm. Its Co/Ni ratios are low, with a median of 0.09. Except for

two data points (3.04 and 2.6 ppm), the other twenty-six Co/Ni ratios are lower than 1. Consequently, pyrites from Sample WTP and those from Sample QX-1 (Pb-Zn zone) have similar Co/Ni ratios and trace element combinations.

In summary, the pyrite trace element assemblage varies in each mineralized zone. The assemblages exhibit a continuing regular variation from the inner zone to the outer zone (Figure 18; Table 8). (1) Inner zone: the simple skarn from the inner zone has element assemblages of Co-Ni-As and Pb-Sb-Tl, while the complex skarn from the inner zone corresponds to the combinations of Co-Ni-As and Pb-Bi-Ag-Sb-Tl-Te. (2) Middle zone: the Chaishan Pb-Zn ore (S8-2) in the inner part has element combinations of As-Co and Pb-Bi-Te-Sb, and the Shexingping Pb-Zn ore in the outer part has element assemblages of Mn-Pb-Cu and Ag-Sb. (3) Outer zone: the element assemblages of the Hg-Sb ore are Mn-Pb-Cu and Sb-Zn. In the inner zone, the Bi content increases from the simple skarn to the complex skarn, but decreases from the inner zone through the inner and outer parts of the middle zone to the outer zone. Meanwhile, Mn and Sb show the opposite trend, increasing from the inner zone to the outer zone. Pb and Cu concentrations decrease from the inner zone to the outer zone. Thus, the element assemblages and regular variations in pyrite contents among mineralized zones reflect the gradual changes in ore-forming hydrothermal fluids.

![](_page_24_Figure_3.jpeg)

Figure 18. The regular variation from the inner zone to the outer zone in the Shizhuyuan ore-field.

Rim	Location	Sample	Rock	Combination	Variation
W-Sn-Mo-Bi	Shizhuyuan	490-13 490-28	Simple Skarn Complex Skarn	Co-Ni-As, Pb-Sb-Tl Co-Ni-As,	Bi: gradually increase
	Chaishan	S3-2	Complex Skarn	Pb-Bi-Ag-Sb-Tl-Te	Rie gradually dagraage Mr.
Pb-Sb	Chaishan Shexingping	S8-2 QX-1	Galena Ore Galena Ore	As-Co, Pb-Bi-Te-Sb Mn-Pb-Cu, Ag-Sb	Sb: gradually increase; Pb, Cu:
Hg-Sb	Wutongping	WTP-4	stibnite Ore	Mn-Pb-Cu, Sb-Zn	decrease after increase

Table 8. Combination and variation of trace elements in pyrites among each zone.

# 6. Conclusions

- 1. The gradual changes in pyrite trace elements from the inner mineralization zone to the outermost zone reflect the compositional variations in the corresponding hydrothermal fluids.
- 2. Pyrites in each mineralized zone are distributed in distinct regions in the Co/Ni-Bi binary diagram, suggesting that this diagram is an effective discrimination tool for the degree of hydrothermal alteration.
- 3. All three mineralized zones probably constitute a whole ore-forming hydrothermal system, and the hydrothermal fluids originated from the Qianlishan granites.

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