Genesis of the Giant Huoshaoyun Non-Sulfide Zinc–Lead Deposit in Karakoram, Xinjiang: Constraints from Mineralogy and Trace Element Geochemistry

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Abstract: The Huoshaoyun zinc–lead deposit, a giant non-sulfide deposit in Xinjiang, is one of the most significant discoveries of zinc–lead deposit in China and globally in recent years. The deposit is dominated by zinc–lead non-sulfides, with minor occurrences of sulfides such as sphalerite, galena, and pyrite. The non-sulfide minerals include smithsonite, cerussite, anglesite, and Fe-oxide. This study focuses on the mineralogical characteristics of sulfide and non-sulfide ores, as well as the trace element characteristics of sphalerite, smithsonite, and Fe-oxide. Mineralogical analysis reveals that smithsonite is derived from the oxidation of primary sulfide minerals and can be classified into three types that are generated during different stages of supergene oxidation. The three types of smithsonite are formed through replacing the sphalerite and host limestone, as well as directly precipitating in the fissures and vugs. Trace element analysis of sphalerite indicates that it is rich in Cd, Ti, and Ge, but poor in Fe and Mn. The ore-forming temperature, calculated using the GGIMFis geothermometer, is mostly within the range of 100–150 °C. Moreover, the trace element characteristics, ore-forming temperature, and S and Pb isotope compositions of the sulfide ores of the Huoshaoyun deposit are similar to those of the Jinding and Duocaima MVT lead–zinc deposits, which are also located in the Eastern Tethyan zinc–lead belt. This suggests that the sulfide orebody in the Huoshaoyun Zn-Pb deposit could also be the MVT deposit. Study of the trace element of the non-sulfide minerals shows that the Mn and Cd are relatively enriched in smithsonite, while Ga, Ge, and Pb are enriched in Fe-oxide. This can be attributed to distinct geochemical properties of the trace elements in the non-sulfide minerals of the Huoshaoyun deposit and is consistent with those of the other oxidized MVT deposits, thus indicating the supergene oxidation process of this deposit.

Keywords: sphalerite; smithsonite; trace elements; ore deposit genesis; supergene oxidation; Huoshaoyun deposit

1. Introduction

Non-sulfide zinc–lead deposits are one of the important sources of lead, zinc, and other metals globally [1–3]. In the early 20th century, lead and zinc were primarily sourced from sulfide ores [4]. In recent years, the development of beneficiation technologies has enabled the reutilization of non-sulfide zinc–lead resources, particularly those dominated by smithsonite [5,6]. The economic viability of non-sulfide deposits has significantly improved, making them a major potential source of lead and zinc metals in the 21st century [1,6]. The Xinjiang Huoshaoyun deposit, located in the northwestern part of the Qinghai-Tibet Plateau, is one of the most important recent discoveries of zinc–lead deposits in China and globally. As of 2016, the Huoshaoyun deposit had a total lead and zinc metal resource of 18 million tons [7], making it the largest zinc–lead deposit in China. The
The Huoshaoyun zinc–lead deposit is mainly composed of non-sulfide zinc–lead ores (Zn-Pb carbonates: smithsonite and cerussite), which account for more than 95% of the zinc–lead reserves, with a small amount of sulfide ores. However, there is currently a hot debate regarding the genesis of both the zinc–lead carbonate and zinc–lead sulfide ore bodies at the Huoshaoyun deposit. Some scholars believe that both the non-sulfide and sulfide zinc–lead ores are of SEDEX (sedimentary exhalative) type related to the deep-seated magmatic-hydrothermal fluids [8–11], while others suggest that the Huoshaoyun deposit was formed through the oxidation of primary MVT (Mississippi Valley type) deposit [12]. Gao et al. (2020) proposed that the Huoshaoyun deposit was neither an oxidized MVT deposit nor a SEDEX deposit, but rather a type of hypogene hydrothermal deposit [13].

Extensive research has demonstrated that the trace element composition of sphalerite is a reliable indicator for distinguishing the genesis types of zinc–lead deposits and for revealing the physicochemical conditions of ore formation [14–18]. Furthermore, during the oxidation process of zinc–lead sulfides, certain trace elements (e.g., Cd, Ge, Ga, and TI) show distinctive patterns of selective enrichment. For example, the decomposition of Ge-bearing sphalerite can lead to Ge enrichment in Fe-oxy-hydroxide minerals during the supergene process at relatively high pH values [19].

These findings provide evidence for elucidating the potential oxidation process and determining the genesis of the Huoshaoyun deposit.

In this study, the mineralogical research was conducted using an optical microscope, cathodoluminescence (CL), and TIMA (TESCAN Integrated Mineral Analyzer) analyses, to define the mineral paragenesis. Moreover, we performed laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) to reveal the trace element compositions of both sulfide (sphalerite) and non-sulfide minerals in the Huoshaoyun deposit. The results, combined with previous studies, provide evidence of the genesis of both the Zn-Pb sulfide and Zn-Pb carbonates orebodies of the Huoshaoyun deposit.

2. Regional Geology

The Huoshaoyun zinc–lead deposit is situated in the Karakorum area, Xinjiang, in the northwestern part of the Qinghai-Tibet Plateau. It is located at 79°00′00″ E, 35°00′00″ N in Hetian County, Xinjiang, approximately 300 km north of Hotan City. It is a giant zinc–lead deposit located in the western region of the eastern Tethyan zinc–lead metallogenic belt in China (Figure 1) [8,20–22]. The main zinc–lead deposits of this metallogenic belt are distributed within the Paleogene to Neogene basins in the Lanping-Simao and Tianshuihai North Qiangtang terranes. The Huoshaoyun Zn-Pb deposit occurs within the Linjitang Basin of the Tianshuaihai North Qiangtang Terrane, bounded by the Altyrn fault to the southeast, the Jinsha River fault zone to the north, the Karakorum fault to the south, and the Qiaoertianshan fault passing through the basin (Figure 2) [23–27]. The exposed strata in the region consist mainly of Triassic and Jurassic formations, from bottom to top: the Middle Triassic Heweitan Formation, the Upper Triassic Keleqinghe Formation, and the Middle Jurassic Longshang Formation [8]. This area is characterized by well-developed fault structures, including several sets of faults trending NW, NE, and nearly EW. Among them, the NW-trending faults, represented by the Qiaoertianshan and Karakorum deep faults, are the largest in scale (Figure 2). The Qiaoertianshan Fault is not only a regional tectonic boundary but also could be the main ore-controlling structure for copper, zinc–lead, and other polymetallic deposits in the area [11,27]. Along with the Qiaoertianshan Fault and its secondary faults, several medium- to large-sized deposits have been discovered, including the Duobaoshan zinc–lead deposit, Baotashan zinc–lead deposit, and Tianshuihai zinc–lead deposit (Figure 2). The regional intrusive rocks are not developed and mostly consist of small-sized, intermediate-acidic intrusions. The volcanic activity in the region is weak [7,8,28].
3. Geology of the Huoshaoyun Deposit

The Huoshaoyun deposit is the largest zinc–lead deposit in China. It has over 18 Mt Zn-Pb metal reserves at an average grade of 23.58% zinc and 5.63% lead, as well as significant cadmium reserves [30]. It is noteworthy that the estimated resources of the studied deposit consist of 62 million tonnes of zinc–lead carbonate ore and 3 million tonnes of...
lead–zinc sulfide ore [22]. Based on these figures, the ratio of sulfidic to non-sulfidic ore in the deposit is relatively low, approximately 4.8%. This indicates that the majority of the ore deposit comprises zinc–lead carbonate ores, with a smaller proportion of lead–zinc sulfide ores. The mining area consists of the Upper Triassic Keleqinghe Formation, the Middle Jurassic Longshan Formation, and the Quaternary sedimentary group (Figure 3). A total of five Zn-Pb orebodies have been discovered in this deposit, with ore body I dominated by zinc–lead sulfide minerals and the others mainly composed of zinc–lead carbonate minerals. The orebodies are mainly stratiform, with dip angles ranging from 3° to 7° [26]. The ore-bearing host rocks of the deposit are mainly the Middle Jurassic Longshan Formation, with the second and fourth lithologic sections being the ore-bearing strata of the III and IV ore belts, and I and II ore belts, respectively. The second lithologic section of the Longshan Formation is composed mainly of argillaceous limestone, followed by bioclastic argillaceous limestone, oolitic limestone, and brecciated limestone, with occasional hematite mineralization. The fourth lithologic section is composed mainly of fine-grained limestone, with occasional hematite mineralization, and interbedded with bioclastic limestone, marly limestone, and mudstone. The underlying Keleqinghe Formation mainly consists of quartz sandstone and mudstone (Figures 3 and 4).

Figure 3. Geological structure, stratigraphy, and boundaries of the Huoshaojun area [30].
Figure 4. Distribution of ore bodies and their contact relationships with surrounding rocks in the Huoshaoyn zinc–lead deposit [30].

In the open pit of Huoshaoyn, mineralization can be classified into two parts: an upper sulfide orebody and a lower non-sulfide orebody (zinc–lead carbonates) (Figure 5a). The upper massive sulfide orebody is predominantly composed of galena, with small amounts of sphalerite and traces of pyrite (Figure 5b). The lower non-sulfide orebody is further divided into two parts: the upper part is composed of massive ore containing smithsonite as the primary mineral with rare cerussite (Figure 5d), while the lower part consists of a layered orebody composed of interbedded smithsonite and cerussite (Figure 5c,d). Near the fault, brecciated smithsonite ores are developed, containing cerussite, anglesite, and residual galena (Figure 5e). Moreover, gypsum, calcite, and other minerals can be observed locally within the smithsonite orebody (Figure 5f). The alteration of the wall rocks around the ore bodies is weak, mainly including calcification, pyritization, silicification, kaolinization, and hematite alteration [7,8,14,27].
smithsonite orebody in the middle of the Huoshaoyun open-pit mine, underlying interbedded smithsonite and cerussite with minor galena remnant and anglesite. (e) Breccia of smithsonite ore near the fault with anglesite, cerussite, and galena remnant. (f) Gypsum developed in the cavity. Abbreviations: SZ—sulfide zone; SmtZ—smithsonite zone; SCZ—smithsonite and cerussite zone; Gn—galena; Smt—smithsonite; Cer—cerussite; Ang—anglesite; Gp—gypsum.

4. Sampling and Analytical Methods

The samples were collected from the open pit in the Huoshaoyun deposit. The collected samples were processed into thin sections, and representative thin sections and minerals were chosen for microscopic observation. Additionally, mineral automated quantitative analysis (TESCAN Integrated Mineral Analyzer—TIMA) and cathodoluminescence (CL) analysis were conducted, and LA-ICP-MS in situ trace element analysis was performed on selected minerals.

Microscopic observation was conducted under a Carl Zeiss Axio Scope.A1 microscope at the Hubei Key Laboratory of Petroleum Geochemistry and Environment, Yangtze University. Cathodoluminescence was performed using a CL8200MK5-2 cathodoluminescence instrument at the State Key Laboratory of Geological Processes and Mineral Resources at China University of Geosciences (Wuhan). The acceleration voltage of the cathodoluminescence instrument was set at 10–15 kV, with an electron beam current of 220–280 uA. The exposure time was set between 7 and 15 s, the gain was between 5 and 7, the saturation was 1.2, and the gamma value was between 1.3 and 1.8.

The TESCAN Integrated Mineral Analyzer (TIMA3 X GHM) system at the Xi’an Kuangpu Geological Exploration Technology Co., Ltd. (Xi’an, China) has obtained quantitative mineral abundances of these samples. The TIMA system comprises a TESCAN MIRA3 Schottky field emission SEM and nine detectors, including four high flux EDS detectors (EDAX Element 30) arranged at 90° intervals around the chamber. In this study, the dot mapping analysis mode was used with X-ray counts set to 1200, pixel spacing of BSE set to 3 µm, and dot spacing of EDS set to 9 µm. The measurements were conducted in a high vacuum environment, with an acceleration voltage of 25 kV, electricity of 9 nA, and a working distance of 15 mm. The electricity and BSE signals were calibrated by platinum Faraday cup and EDS signals by Mn standard. TIMA can automatically compare the measured BSE and EDS data of each different phase with the database and then distinguish their mineral phases and compute mineral abundances.

The LA-ICP-MS analysis was performed at Xi’an SampleSolution Analysis Technology Co., Ltd. (Wuhan, China). The laser beam spot size and frequency used in the analysis were 32 µm and 250 Hz, respectively. The single mineral trace element content was processed using multi-external standard without internal standard correction, with the use of NIST 610 and NIST 612 glass standard reference materials [31]. The USGS sulfide standard reference material MASS-1 was used as a monitoring standard to verify the reliability of the calibration method. Each time-resolved analysis data included approximately 20–30 s of blank signal and 50 s of sample signal. The offline processing of the analysis data, including the selection of sample and blank signals, correction for instrument sensitivity drift, and calculation of elemental content, was performed using the software ICPMSDataCal10.9 [31].

5. Results

5.1. Type and Texture of the Zn-Pb Ores

The Huoshaoyun deposit comprises three primary ore types: sulfide ore, mixed ore, and non-sulfide ore.

The sulfide ores are predominantly composed of massive fine-grained galena (Figure 6a) and oolitic sphalerite (Figure 6b). Galena commonly occurs as fine-grained in black massive ores (Figure 6a). It generally shows euhedral–subhedral granular texture and is intergrown with calcite (Figure 6c), locally replaced by anglesite when observed under the microscope (Figure 6c). Sphalerite appears as oolitic grains in hand specimens (Figure 6b) and frequently displays colloform textures in the microscope, with galena occurring
frequently at both the edges and centers (Figure 6d). In addition, some samples also contain colloform galena and are enclosed by sphalerite (Figure 6f).

Figure 6. Textural features of sulfide ores in Huoshaoyun Zn-Pb deposit. (a) Massive fine-grained galena ore. (b) Oolitic sphalerite ore, with abundant oolitic sphalerite and galena. (c) Euhedral–subhedral fine-grained galena in the massive galena ore, which is partially replaced by anglesite. (d) Fine-grained galena enclosed by the colloform sphalerite. (e) Euhedral–subhedral galena intergrown with calcite. (f) Colloform galena is enveloped by colloform sphalerite. Abbreviations: Sp — sphalerite; Gn — galena; Ang — anglesite.

The mixed ore is predominantly composed of non-sulfide minerals, including smithsonite, cerussite, and Fe-oxide, with a minor amount of primary sulfides. The majority of these non-sulfide minerals are produced through direct replacement of sulfides or the host limestone (Figure 7a). Smithsonite, which exhibits gray oolitic textures under the microscope, is the most abundant non-sulfide mineral (Figure 7a). A small amount of extremely fine-grained smithsonite directly replaces sphalerite (Figure 7b). Galena and sphalerite occur together, with early-stage galena taking the form of dendritic–skeletal (Figure 7c) or massive blocks (Figures 6d and 7d) and being enveloped by colloform sphalerite (Figure 7d). A later shell of galena often forms in the outer part of the colloform sphalerite (Figures 6d,e and 7c,d). Anglesite appears relatively dull under the microscope and is usually
distributed inside or on the edge of galena (Figure 7e,f). Cerussite is brighter and appears pale gray under the microscope, with a relatively complete crystal structure (Figure 7e,f).

The replacement of galena by anglesite and cerussite is also observed (Figure 7e,f). Pyrite displays a euhedral–subhedral structure (Figure 7g,h) and is usually oxidized to form Fe-oxide, which is surrounded by cerussite (Figure 7e).

Figure 7. Textural features of the mixed ore. (a) Smithsonite replaces host limestone, forming the texture of dark cores with bright rims. (b) TIMA image shows smithsonite replacing sphalerite. (c) Dendritic–skeletal galena enclosed by colloform sphalerite. (d) Colloform sphalerite is intergrown with galena. (e) TIMA image shows anglesite replace galena directly, and both the anglesite and

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**Figure 7** Textural features of the mixed ore. (a) Smithsonite replaces host limestone, forming the texture of dark cores with bright rims. (b) TIMA image shows smithsonite replacing sphalerite. (c) Dendritic–skeletal galena enclosed by colloform sphalerite. (d) Colloform sphalerite is intergrown with galena. (e) TIMA image shows anglesite replace galena directly, and both the anglesite and
galena are replaced by later cerussite. (f) Microscopic image corresponding to (e). (g) TIMA image shows Fe-oxide and cerussite replacing pyrite. (h) Microscopic image corresponding to (g). Abbreviations: Smt1—grey smithsonite; Smt—smithsonite; Sp—sphalerite; Gn—galena; Py—pyrite; Ang—anglesite; Cer—cerussite; Fe-Ox—Fe-oxide.

Non-sulfide ore mainly consists of smithsonite, which occurs commonly as breccia, massive or banded ore. Under the microscope, smithsonite can be classified into three types: grey smithsonite (Smt1), yellow smithsonite (Smt2), and colorless smithsonite (Smt3).

Smt1 appears as light grey to dark grey on thin sections and appears grey under the microscope. It generally exhibits a bright rim with dark core (Figure 7a), with a small amount appearing in the form of small particles (Figure 8a). CL images show a dark red color (Figure 8c,f).

Smt2 appears light to dark brown-yellow and shows bright red color in CL images (Figure 8c). It is generally dominated by a banding structure (Figure 8b) or small grains (Figure 8d), and has poor translucency. Grey smithsonite (Smt1) is often observed as an inclusion within it (Figure 8b,c).

Smt3 appears colorless on thin sections and mainly fills the fracture of the ores in a vein-like form (Figure 8b), growing symmetrically towards the center on both sides of the fractures (Figure 8e). The grey smithsonite (Smt1) and yellow smithsonite (Smt2) are often replaced by Smt3 (Figure 8b). CL images also show a dark red color (Figure 8f).

In addition to smithsonite, small amounts of Fe-oxide, cerussite, and anglesite (Figure 8g,h) are present. Occasionally, euahedral–subhedral greenockite also developed (Figure 8i).

**Figure 8.** Textural features of the non-sulfide ore from the Huoshaojun Zn-Pb deposit. (a) Small grains of Smt1. (b) Smt2 enclosing Smt1 and replaced by Smt3. (c) CL image corresponding to (b). (d) Smt2 enclosing Smt1. (e) Smt3 is growing symmetrically along the fractures from both sides toward the center. (f) CL image corresponding to (e). (g) Coexistence of smithsonite, anglesite, and cerussite. (h) Cerussite replacing anglesite and galena. (i) Microscopic image of greenockite. Abbreviations: Smt1—grey smithsonite; Smt2—yellow smithsonite; Smt3—colorless smithsonite; Gn—galena; Ang—anglesite; Cer—cerussite; Gnk—Greenockite.
Based on the above studies, the mineralization of the Huoshaoyun deposit underwent a primary sulfide period and a subsequent supergene oxide period (Table 1). According to the occurrence characteristics of the different types of smithsonite, which is the most important ore mineral of this deposit, the supergene oxide period can be further divided into three stages. The main mineral paragenesis sequence of the Huoshaoyun deposit is determined and listed in Table 1.

Table 1. Main mineral paragenesis sequence of the Huoshaoyun deposit.

<table>
<thead>
<tr>
<th>Period</th>
<th>Sulfide</th>
<th>Supergene</th>
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<tr>
<td>Stage</td>
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<td>Stage2</td>
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<tr>
<td>Galena</td>
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</tr>
<tr>
<td>Sphalerite</td>
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<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Grey Smithsonite (Smt1)</td>
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<tr>
<td>Yellow Smithsonite (Smt2)</td>
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</tr>
<tr>
<td>Colorless Smithsonite (Smt3)</td>
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</tr>
<tr>
<td>Anglesite</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Cerussite</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Fe-oxide</td>
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<td>++</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Gypsum</td>
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</table>

Note: “+” indicates their relative abundance.

5.2. The Results of LA-ICP-MS

The trace element content of the sphalerite, various types of smithsonite, and Fe-oxide was analyzed using LA-ICP-MS in this study. The results are presented in Tables 2 and 3.

The results for the sphalerite are as follows:

1. Sphalerite has low Fe and Mn element contents, with Mn content ranging from 10 ppm to 23.7 ppm and an average content of 13.2 ppm. The Fe content varies greatly, ranging from 10.7 ppm to 1540 ppm, with an average content of 248 ppm.

2. Test on sphalerite reveals that Cd is the most enriched element among the rare dispersed elements, followed by Tl and Ge, while the contents of Ga and In are relatively low. Some measurement points of Ge, Ga, and In are below the detection limit. The Cd content in sphalerite is high and varies greatly, ranging from 3130 ppm to 6282 ppm with an average content of 4962 ppm. The Tl content ranges from 17.2 ppm to 52.5 ppm with an average content of 29.7 ppm. The Ge content is unevenly distributed, with some samples having low content ranging from 0.06 ppm to 1.12 ppm, while some samples have higher content ranging from 9.45 ppm to 28.4 ppm. The Ga content is generally low, ranging from 0.02 ppm to 1.65 ppm with an average content of 0.35 ppm. The In content is only detected in a few measurement points, ranging from 0.01 ppm to 0.55 ppm with an average content of 0.05 ppm.

3. The sphalerite has relatively high Pb content and low As content. The Pb content ranges from 3954 ppm to 9057 ppm, with an average content of 5613 ppm. The distribution of As content is uneven, ranging from 5.24 ppm to 269 ppm, with an average content of 66.5 ppm.

In summary, sphalerite from the Huoshaoyun deposit enriches rare dispersed elements Cd and Tl, and some samples also enrich Ge, while Fe and Mn are depleted in sphalerite.
Three types of smithsonite were analyzed. The trace element characteristics of the smithsonite samples are summarized as follows:

(1) The smithsonite enriches Fe and Mn elements, with Fe content ranging from 4849 ppm to 27,649 ppm and an average content of 14,748 ppm, and Mn content ranging from 1598 ppm to 5646 ppm with an average content of 3542 ppm.

(2) Cd is the most abundant rare dispersed element in smithsonite, while Tl, Ga, and Ge are of lower concentrations. The Cd content significantly varies among the different types of smithsonite. In Smt1, Cd content is relatively high, ranging from 994 ppm to 1302 ppm, with an average content of 1002 ppm. In Smt2, Cd content is lower, ranging from 183 ppm to 1067 ppm, with an average content of 748 ppm. In Smt3, Cd content is the lowest, ranging from 83.9 ppm to 580 ppm, with an average content of 258 ppm. Tl and Ga contents are low, ranging from 0.12 ppm to 1.66 ppm and 0.01 ppm to 0.31 ppm, respectively, while Ge content is the lowest, with only 8 points detected, ranging from 0.17 ppm to 3.75 ppm.

(3) Pb content is relatively high, ranging from 4646 ppm to 48,890 ppm, with an average content of 12,713 ppm.

In summary, smithsonite from the Huoshaoyun deposit enriches Cd, Fe, Mn, and Pb, and depletes Ge, Ga, and Tl.

Fe-oxide relatively enriches Cd, Ga, Ge, and Pb elements, while the contents of the Tl and Mn are low. Cd content ranges from 31.8 ppm to 40.6 ppm, Ga content ranges from 3.35 ppm to 5.74 ppm, and Ge content ranges from 4.1 ppm to 60 ppm.

### Table 2. LA-ICP-MS testing results of sphalerite from the Huoshaoyun deposit, Xinjiang.

<table>
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<th>Simple</th>
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<th>Mn</th>
<th>Cu</th>
<th>Cd</th>
<th>Ga</th>
<th>Ge</th>
<th>Ti</th>
<th>Pb</th>
<th>In</th>
<th>As</th>
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<td>6282</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
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<td></td>
<td>59.4</td>
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<td>0.02</td>
<td>6035</td>
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<td>0.41</td>
<td>26.9</td>
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<td>5.24</td>
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<td>10.7</td>
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<td>12.8</td>
<td>17.2</td>
<td>4560</td>
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<td>81.48</td>
<td>1.27</td>
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<tr>
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<td>3130</td>
<td>1.65</td>
<td>9.45</td>
<td>17.3</td>
<td>9057</td>
<td>0.01</td>
<td>65.65</td>
<td>1.23</td>
<td>141</td>
<td></td>
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<tr>
<td></td>
<td>5531</td>
<td>0.76</td>
<td>10.1</td>
<td>17.9</td>
<td>6772</td>
<td>0</td>
<td>67.37</td>
<td>1.71</td>
<td>115</td>
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<tr>
<td></td>
<td>584</td>
<td>15.6</td>
<td>1.36</td>
<td>5416</td>
<td>0.38</td>
<td>12.8</td>
<td>17.2</td>
<td>4560</td>
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<td>81.48</td>
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<td>9.45</td>
<td>17.3</td>
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<td>18.2</td>
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<td>6772</td>
<td>0</td>
<td>67.37</td>
<td>1.71</td>
<td>115</td>
</tr>
</tbody>
</table>

Note: trace elements in ppm in the data table. "-" represents unable to calculate. For the meaning of “PC1” see below; “T” is the temperature calculated according to “PC1” parameters.

### Table 3. LA-ICP-MS results of smithsonite and Fe-oxide from the Huoshaoyun deposit, Xinjiang.

<table>
<thead>
<tr>
<th>Simple</th>
<th>Mineral</th>
<th>Fe</th>
<th>Mn</th>
<th>Cd</th>
<th>Ga</th>
<th>Ge</th>
<th>Ti</th>
<th>Pb</th>
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<tr>
<td></td>
<td>Smt1</td>
<td>12,189</td>
<td>3328</td>
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<td>8429</td>
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<tr>
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<td>3267</td>
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<tr>
<td></td>
<td>Smt1</td>
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<td>Smt1</td>
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<td>Smt1</td>
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### 6. Discussion

#### 6.1. Genesis of the Sulfide Ores

6.1.1. Characteristics of Trace Elements in Sphalerite and Ore-Forming Temperature

Numerous previous studies have shown that trace elements (e.g., Fe, Mn, Cd, Ge, Ga, In, and Tl) are commonly present in the form of isomorphism in sphalerite via direct and coupled substitutions, as well as using crystal vacancy [15,16,32–34]. Consequently, the characteristics of the trace elements in sphalerite can record the signature of the ore-forming fluids and discriminate the different genetic types of Zn-Pb deposits [15,16,18,35].

The Fe and Mn contents in sphalerite of the Huoshaoyun deposit are significantly lower than those in magmatic/volcanic hydrothermal-related Zn-Pb deposits (e.g., skarn and VMS (volcanogenic massive sulfide) deposits) and SEDEX deposits (Figure 9a,b). Instead, they are consistent with those of MVT deposits, especially the Jinding and Duocaima deposits, as well as other MVT deposits, the Fe content in the Huoshaoyun deposit is slightly lower. This may be related to the exceptionally enriched Cd content in the sphalerite of the deposit (Figure 9c), since Fe$^{2+}$ and Cd$^{2+}$ may have competitive substitution of the Zn$^{2+}$ in sphalerite, i.e., (Fe$^{2+}$; Cd$^{2+}$) ↔ Zn$^{2+}$ [15,16]. The Ge content of sphalerite in the Huoshaoyun deposit is unevenly distributed, with some points showing high concentrations, which is consistent with the findings of Yuan et al. (22.3 ppm on average) [14]. In contrast, the In content is generally low, typically below 0.1 ppm. The characteristic of high Ge and low In is distinct from magmatic/volcanic hydrothermal-related Zn-Pb deposits and SEDEX deposits, but similar to MVT deposits (Figure 9d,e). The sphalerite from the Huoshaoyun deposit enriched the rare dispersed element Tl (Figure 9f). Although some VMS and SEDEX deposits also have high Tl contents in the ores, the majority of Tl is enriched in pyrite and marcasite, while the enrichment of Tl in sphalerite is limited (Figure 9f) [36–39]. Additionally, Tl-enriched sphalerite is mainly found in MVT deposits (e.g., the Wiesloch deposit in Germany, the Upper Silesia ore field in Poland, and the Jinding and Duocaima deposits in the Eastern Tethyan zinc-lead belt) [39–41].

In summary, the trace element characteristics of sphalerite in the Huoshaoyun deposit are similar to those of MVT deposits, especially the Jinding and Duocaima deposits, while they differ significantly from those of magmatic/volcanic hydrothermal-related Zn-Pb deposits (e.g., Skarn and VMS deposits) and SEDEX deposits.

<table>
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<tr>
<th></th>
<th>Smt2</th>
<th>5261</th>
<th>1598</th>
<th>1062</th>
<th>0.16</th>
<th>0.17</th>
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</tr>
<tr>
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<tr>
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<td>5.74</td>
<td>60</td>
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<tr>
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<td>0.02</td>
<td>31.8</td>
<td>4.4</td>
<td>26.7</td>
<td>3.17</td>
<td>300,398</td>
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</table>

Note: trace elements in ppm in the data table.
Figure 9. Box–whisker plots of the trace element compositions of sphalerite from Huoshaoyun, Jinding, Duocaima, MVT, VMS, Skarn, and SEDEX deposits. Note: the plots are based on data from this study, Yuan et al. [14], Ye et al. [15], Cook et al. [16], and Zhang [42].

Studies have revealed that sphalerite formed at high temperatures typically enriches Fe, Mn, and In, while sphalerite formed at medium–low temperatures commonly enriches Ge and Cd but depletes Fe, Mn, and In [43]. The sphalerite from the Huoshaoyun deposit is distinct from high-temperature sphalerite in that it depletes Fe and Mn but enriches Cd and Ge. Recently, Frenzel et al. (2016) conducted a comparative analysis of the trace element compositions of sphalerites from various types of Zn-Pb deposits against measured fluid homogenization temperatures. They systematically synthesized the data and proposed a series of calculation formulas (GGIMFis) that establish a relationship between the trace elements Ga, Ge, Fe, Mn, and In in sphalerite and ore-forming temperatures [44]:

$$PC1 = \ln(\frac{C_{Ga}^{0.22} \cdot C_{Ge}^{0.22} \cdot C_{Fe}^{0.37} \cdot C_{Mn}^{0.20} \cdot C_{In}^{0.11}}{C_{Fe}}),$$

$$T = -54.4 \times PC1 + 208$$

In Equation (1), $C_{Fe}$ denotes the weight percent concentration of Fe, $C_{Ga}$ denotes the parts per million concentration of Ga, and the concentration of all other elements is equivalent to that of Ga.

The ore-forming temperature of the sphalerite (sulfide mineralization) in the Huoshaoyun deposit was calculated to be within the range of 103–206 °C using the GGIMFis (Table 2). The results indicate that the formation temperature of sphalerite in this deposit is comparatively low and significantly distinct from that of magmatic-hydrothermal deposits, but falls within the typical temperature range (70–180 °C) of MVT zinc–lead deposits [45].

6.1.2. Genesis of the Sulfide Ores in the Huoshaoyun Deposit

The binary plots of trace elements (or the ratios of different elements) in sphalerite have been demonstrated to be the reliable discrimination of the genetic types of Zn-Pb deposits [46–49]. The sphalerite samples of the Huoshaoyun deposit all plot within the field of the MVT deposit in the In/Cd-Mn, Mn-In/Ge, Mn-Cd, Mn-Fe, Mn-In, and Mn-Ge...
discrimination diagrams, indicating the sulfide ores in this deposit could be of the MVT deposit (Figure 10). Moreover, the sphalerite samples of the Huoshaoyun deposit are overlapped with those of the Jinding and Duocaima MVT deposits in these diagrams (Figure 10), further suggesting that they could have similar ore-forming material/fluids source, metallogenic environment, and origins. In order to further elucidate the genetic type of the sulfide ore body in the Huoshaoyun deposit, this study compares the S-Pb isotopic compositions, metallogenic temperature, and the typical texture of the sulfide ores in the Huoshaoyun deposit with those of the Jinding and Duocaima MVT deposits.

The sulfur isotopic compositions of sulfides from the Huoshaoyun, Jinding, and Duocaima deposits in the Eastern Tethyan zinc–lead belt show similarity (Figure 11). The sulfides in these deposits all have a wide range of sulfur isotopic compositions, with the δ34S values ranging from −33.2‰ to 31.6‰ for the Huoshaoyun deposit [22,50,51], −48.6‰ to 7.7‰ for the Jinding deposit [52,53], and −26.34‰ to −3.52‰ for the Duocaima deposit [42] (Figure 11). This characteristic distinguishes them from Zn-Pb deposits associated with magmatic-hydrothermal fluids (δ34S = −5‰ to −5‰) [54]. The δ34S values of most of the sulfides from these deposits fall within the range of δ34S values related to bacteriogenic sulfate reduction (BSR) (very low δ34S values), indicating that the sulfur in sulfide minerals mainly originated from BSR of seawater sulfates. This is consistent with that of some MVT Zn-Pb deposits worldwide (Figure 11).

Moreover, the sulfide ores from the Huoshaoyun (Figures 6d and 7c), Duocaima, and Jinding deposits contain abundant colloform sphalerite and skeletal, fine-grained galena [42,52,53], suggesting the rapid precipitation of zinc–lead sulfides from supersaturated fluids under far-from-equilibrium conditions, while the mixing of the hot Zn-Pb bearing fluids with low-temperature H2S-rich brine is an efficient way to lead the rapid precipitation of sulfides in the carbonate-hosted Zn-Pb deposits [39,55]. Therefore, these deposits could be formed through the mixing between a hot metal-bearing (Zn, Pb, etc.) fluid and a low-temperature brine containing BSR-derived H2S, while some sulfides with positive sulfur isotope values in these deposits can be attributed to the involvement of the
thermochemical sulfate reduction (TSR)-related reduced sulfur and/or the sulfate-limited conditions during the sulfide precipitation process [50,52].

The $^{206}$Pb/$^{204}$Pb ratios of sulfides in the Huoshaoyun Zn-Pb deposit range from 18.525 to 18.563, the $^{207}$Pb/$^{204}$Pb ratios range from 15.673 to 15.710, and the $^{208}$Pb/$^{204}$Pb ratios range from 38.879 to 39.005 [7,58]. These ratios are very similar to those of the Jinding Zn-Pb deposit ($^{206}$Pb/$^{204}$Pb ratios range from 18.410 to 18.523, $^{207}$Pb/$^{204}$Pb ratios range from 15.620 to 15.662, and $^{208}$Pb/$^{204}$Pb ratios range from 38.569 to 38.714) [59], and also close to the range of Pb isotopic composition of the Duocaima Zn-Pb deposit [42] (Figure 12). Additionally, the plot field of the sulfide date from these deposits in $^{206}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb diagrams indicates that the metal source of these deposits is derived from upper crustal rocks, which is consistent with the typical MVT deposits worldwide.

**Figure 11.** Sulfur isotope compositions of zinc-lead sulfides from the Huoshaoyun zinc-lead deposit. Note: $\delta^{34}$S values for H$_2$S from BSR from Chen et al. [56]; SEDEX and MVT zinc-lead deposits from Leach et al. [57]. Date for Huoshaoyun deposit from Yuan [50], Li et al. [22], Wu et al. [51]; dates for Jinding deposit from Tang et al. [52], Dai [53]; dates for Duocaima deposit from Zhang [42].

**Figure 12.** Correlative diagrams of $^{206}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb (modified from Xiong et al. [60]) for the Huoshaoyun, Jinding, and Duocaima deposits. Note: the plots are based on data from Gao et al. [7], Wu, [58], Zhang [59], Zhang [42]. U—upper crust; O—orogene; M—mantle; L—lower crust. The region shaded grey represents the extent of MVT deposits.
In addition, most of the ore-forming temperatures of the Huoshaoyn Zn-Pb deposit were determined to be about 100–150 °C using the GGIMFis geothermometer. These temperatures are consistent with those of the Jinding Zn-Pb deposit, which were mainly at 100–130 °C based on fluid inclusion measurements in sphalerite [61], and the Duocaima Zn-Pb deposit, which were mainly at 120–180 °C [62]. These results suggest that these deposits formed from the low-temperature hydrothermal fluids, which is consistent with the metallogenic temperature of the MVT deposits [57].

In summary, the trace-element signatures of sphalerite, ore-forming temperatures, S-Pb isotopes, and some special texture of the sulfide ores all indicate that the sulfide ores in the Huoshaoyn deposit are the MVT deposit and may have similar ore-forming processes to the Jinding and Duocaima deposits in the Eastern Tethyan Zn-Pb belt.

6.2. Trace Element Characteristics of the Non-Sulfide Minerals and Implications for Their Origins

During the supergene oxidation of zinc–lead sulfides, variations in the geochemical properties of the trace elements and/or physicochemical conditions (pH, temperature, etc.) can lead to the enrichment of distinct trace elements in different non-sulfide minerals [63].

The concentration of Fe and Mn in smithsonite from the Huoshaoyn Zn-Pb deposit is significantly greater than that in sphalerite (Figure 13a). This can be explained by the decomposition of both the Fe-bearing sphalerite and the pyrite during supergene oxidation (Figure 7), which released abundant Fe and Mn into the fluid. The capture of Fe and Mn by smithsonite occurred through isomorphic substitution.

Although the concentration of Cd is relatively high in smithsonite, it is significantly lower compared to that in sphalerite. This indicates that some Cd may have been lost during the oxidation process. Moreover, the development of the greenockite (CdS) in the non-sulfide ores (Figure 8f) suggests that a part of the Cd\(^{2+}\) in the oxidizing fluids, resulting from oxidation of the Cd-bearing sphalerite, formed its own independent mineral (e.g., via CdSO\(_4\) + ZnS\(_4\) → ZnSO\(_4\) + CdS) [64] rather than entered the smithsonite structure. On the other hand, compared to Fe-oxide, Cd is enriched in smithsonite (Figure 13b). This shows that Cd\(^{2+}\) tends to enter smithsonite instead of being adsorbed by Fe-oxide during the supergene oxidation process, which could be attributed to the very similar geochemical properties of Cd\(^{2+}\) and Zn\(^{2+}\).

Ga and Ge are enriched in Fe-oxide compared to smithsonite (Figure 13c,d). During supergene oxidation, the large amount of sulfuric acid generated from the alteration of pyrite could have caused the pH of the fluid to decrease and become acidic, leading to the incorporation of Ga into Fe-oxide when the pH of the metal-bearing solution is extremely low (pH < 4) [65]. Ge can not only octahedrally coordinate with oxygen and co-precipitate with Fe-oxide, but can also be adsorbed by Fe-oxide [19,66]. Therefore, Fe-oxide formed through the oxidation of the Ge- and Ga-bearing sulfide ores commonly has high contents of Ga and Ge (e.g., crystal non-sulfide Zn prospect, northern Peru) [19].

All type of smithsonites from the Huoshaoyn deposit have a relatively high content of Pb (Figure 13e), suggesting that during the oxidation process of zinc–lead sulfides, besides forming the cerussite and anglesite, Pb\(^{2+}\) in the oxidizing fluid can also enter into smithsonite [67]. In comparison, Fe-oxide has much higher Pb content than the smithsonite and sphalerite (Figure 13e). This could be because Pb\(^{2+}\) can not only coprecipitate with Fe-oxide but also can be continuously adsorbed by Fe-oxide [68].

Compared to sphalerite, both smithsonite and Fe-oxide exhibit significant depletion in Tl (Figure 13f), with the highest content being less than 4 ppm and the majority being less than 1 ppm. It is speculated that Tl was released into the surrounding environment during the oxidation process and underwent significant loss.
In summary, compared with sphalerite, the contents of Fe and Mn increase significantly in smithsonite. Ge and Ga are less concentrated in smithsonite but are more enriched in Fe-oxide. These features are consistent with the characteristics of the trace element migration and enrichment during the oxidizing process of the MVT deposits. For instance, Stavinga observed significantly higher Fe and Mn concentrations in oxidized smithsonite compared to primary sphalerite in the Prairie Creek MVT deposit [67], while Santoro et al. found that Ga and Ge were mainly enriched in Fe-oxide minerals during the supergene oxidation process of four MVT Zn-Pb deposits [65]. These findings indicate significant oxidation of sulfide ores in the Huoshaoyun Zn-Pb deposit.

6.3. From MVT Deposits to Non-Sulfide Ores

Zn-Pb-Fe sulfides not only occur in sulfide ores but also in the mixed ores of the Huoshaoyun deposit. These minerals, i.e., sphalerite, galena, and pyrite, are typically replaced by anglesite, cerussite, smithsonite, and Fe-oxide (Figure 7b,e–h), providing clear evidence of the oxidation process of the Zn-Pb-Fe sulfides. Therefore, combined with the other results of this study, we argued that the Huoshaoyun Pb-Zn deposit is a supergene MVT deposit and its formation process can be summarized as follows:

The sulfide ores are formed thought the mixing between a hot metal-bearing (Zn, Pb, etc.) fluid and a low-temperature brine containing BSR-derived H₂S.

The continuous periodic uplift of the Qinghai-Tibet Plateau since the Cenozoic provided long-term uplift, erosion, rapid exhumation of the sulfide ores, and exposure to oxygenated surface waters. Pyrite has quicker oxidation rates and contributes Fe³⁺, SO₄²⁻, and H⁺ to the fluid, which led to acidification of the fluids and formation of Fe-oxide. (Figure 7g,h).

Oxidation of sphalerite and galena also generated Zn²⁺, Pb²⁺, H⁺, and SO₄²⁻. The high sulfate and low pH condition, created by the oxidation of these sulfides, is conducive to the formation of anglesite from galena: Pb²⁺ + SO₄²⁻ → PbSO₄ (Anglesite) (Figure 7e,f), while sulfates also react with the host rocks to form gypsum and liberate CO₃²⁻:SO₄²⁻ +
CaCO₃ → CaSO₄ (Gypsum) + CO₂. The termination of the certain oxidation stage and/or depletion of the sulfides can cause the decreasing of SO₄²⁻ in the fluids and increasing in its pH. This can lead the anglesite to become unstable and alter to cerussite: PbSO₄ + CO₂ → PbCO₃ (Cerussite) + SO₂ (Figure 7f). Occasionally, the galena could be directly replaced by cerussite, i.e., PbS + H₂O + CO₂ + 2O₂ → PbCO₃ (Cerussite) + SO₂ + 2H⁺ (Figure 7b).

The formation of smithsonite can be divided into three main stages.

1. Smt1: Sphalerite oxidation generates Zn²⁺ which migrates through fractures and reacts with host rocks, replacing the calcite and forming grey smithsonite: Zn²⁺ + CaCO₃ → ZnCO₃ (Smithsonite) + Ca²⁺. The oolitic textures (Figure 7a) indicates its replacement of the host limestone, while a small amount of fine-grained grey smithsonite (Figure 8a) suggests that a portion of Zn²⁺ in the fluid could have directly crystallized into smithsonite: Zn²⁺ + H₂O + CO₂ → ZnCO₃(Smithsonite) + 2H⁺.

2. Smt2: The second-stage supergene oxidizing fluids formed this yellow smithsonite (Smt2) through replacing the host rock (Figure 8d), filling the cavities, and enclosing the grey smithsonite (Smt1) as banding-shaped or replacing Smt1 (Figure 8b,c).

3. Smt3: The colorless smithsonite was formed by the third-stage fluid carrying Zn²⁺ filling along the fractures from both sides to the center, or replacing Smt1 and Smt2.

7. Conclusions

1. The Huoshaoyun zinc–lead deposit is composed of sulfide and non-sulfide ores. The former is mainly composed of sphalerite, galena, and pyrite, whereas the latter is primarily composed of smithsonite, with minor cerussite, anglesite, and Fe-oxide. The non-sulfide minerals clearly replaced the sulfides, suggesting the oxidation of the primary sulfide ores.

2. The trace element analysis of sphalerite indicates that it is rich in Cd, Ti, and Ge, but poor in Fe and Mn. The ore-forming temperature, calculated using the GGIMFis geothermometer, is most within the range of 100–150 °C. Moreover, the trace element characteristics, ore-forming temperature, and S and Pb isotope compositions of the sulfide ores of the Huoshaoyun deposit are similar to those of the Jinding and Duocaima MVT lead–zinc deposits, which are also located in the eastern Tethyan zinc–lead belt. This suggests that the sulfide orebody in the Huoshaoyun Zn-Pb deposit could be also the MVT deposit.

3. The trace element of the non-sulfide minerals shows that the Mn and Cd are relatively enriched in smithsonite, while Ga, Ge, and Pb are enriched in Fe-oxide. This characteristic is consistent with that of the other oxidized MVT deposits worldwide, thus indicating the supergene oxidation process of the precursor MVT ores in the Huoshaoyun deposit.

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