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A review of the Zn-Pb deposits in Sichuan-Yunnan-Guizhou metallogenic region with emphasis on the enrichment mechanism of Ge, Ga, and In

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ABSTRACT

The low-medium temperature Zn-Pb deposits in the Sichuan-Yunnan-Guizhou (SYG) metallogenic region contain not only Pb and Zn but also abundant critical metals such as Ge, Ga, and In. The majority of previous studies focus on the genesis of Pb and Zn metals, and the research on Ge, Ga and In in the SYG region has become a topic in recent years due to economic importance of these metals. In this review, the distribution, occurrence, and enrichment mechanism of Ge, Ga, and In in Zn-Pb deposits in the SYG region is summarized. Sphalerite is the main host mineral of Ge, Ga, and In, with contents of up to ~1300 ppm, ~600 ppm, and ~1191 ppm, respectively. Pyrite from the Fule Zn-Pb deposit is also rich in Ge (up to 340 ppm), which may be due to involvement of magmatic components in the ore-forming fluids. Germanium, Ga, and In mainly appear in the form of isomorphism in sphalerite. Independent minerals of Ge such as ruizhongite ($Ag_2\square)Pb_3Ge_2S_8$), are only found in the Wusihe Zn-Pb deposit. Copper is the main coupling ions for substitution of Ge, Ga, and In in sphalerite. However, the positive correlation of Ge with Pb, Mn and Ag in the sphalerite of Huodehong, Shaojiwan, Shanshulin, and Qingshan Zn-Pb deposits may indicate other means of substitution or existence of nanometer Ge minerals with similar composition to the ruizhongite. The substitution mechanisms of Ge and Ga vary with layers in the zoned sphalerite from the Nayongzhi Zn-Pb deposit, possibly indicating that physical or chemical variations in fluids will affect the substitution ways of Ge and Ga in sphalerite.

The growth direction and crystal structure of ZnS also exert control over the contents of Ge, Ga, and In. The enrichment degree of Ge, Ga, and In changes between (1 1 0) and (1 1 1) crystal planes, and the wurtzite structure is beneficial to the infiltration of large ions (Ge, Ga, and In). Compared to sphalerite with euhedral texture, colloform sphalerite is conducive to the enrichment of Ge. For zoned sphalerite such as the rhythmic banding and the conventional zone, the former lacks zoning of Ge, Ga and In but the latter shows elemental zonation and Ge is enriched in the black domains. The correlation between the contents of Ge, Ga, and possible In in sphalerite and Pb or Zn isotopes of sulfides indicates the significant contribution of basement rocks for the enrichment of these metals. During the mineralization process, Ge tends to be enriched in dark or early sphalerite, including the Daliangzi, Tianbaoshan, Huize, Nayongzhi, Fule, Fuli, Wusihe, and Maoping deposits, which may be due to the variations in temperature or fluid evolution. The opposite variation trend of Ge and Ga with sphalerite color or stage in the Daliangzi, Nayongzhi, Maoping, Shaojiwan, and Wusihe Zn-Pb deposits indicates that Ge and Ga may behave differently during precipitation of sphalerite.

1. Introduction

Research on critical metals such as Ge, Ga, and In has been paid numerous attention in recent years due to their unique use in green energy and high-technology fields. These metals have high economic value and supply scarcity (Wang et al., 2013; Guberman, 2015; Wen

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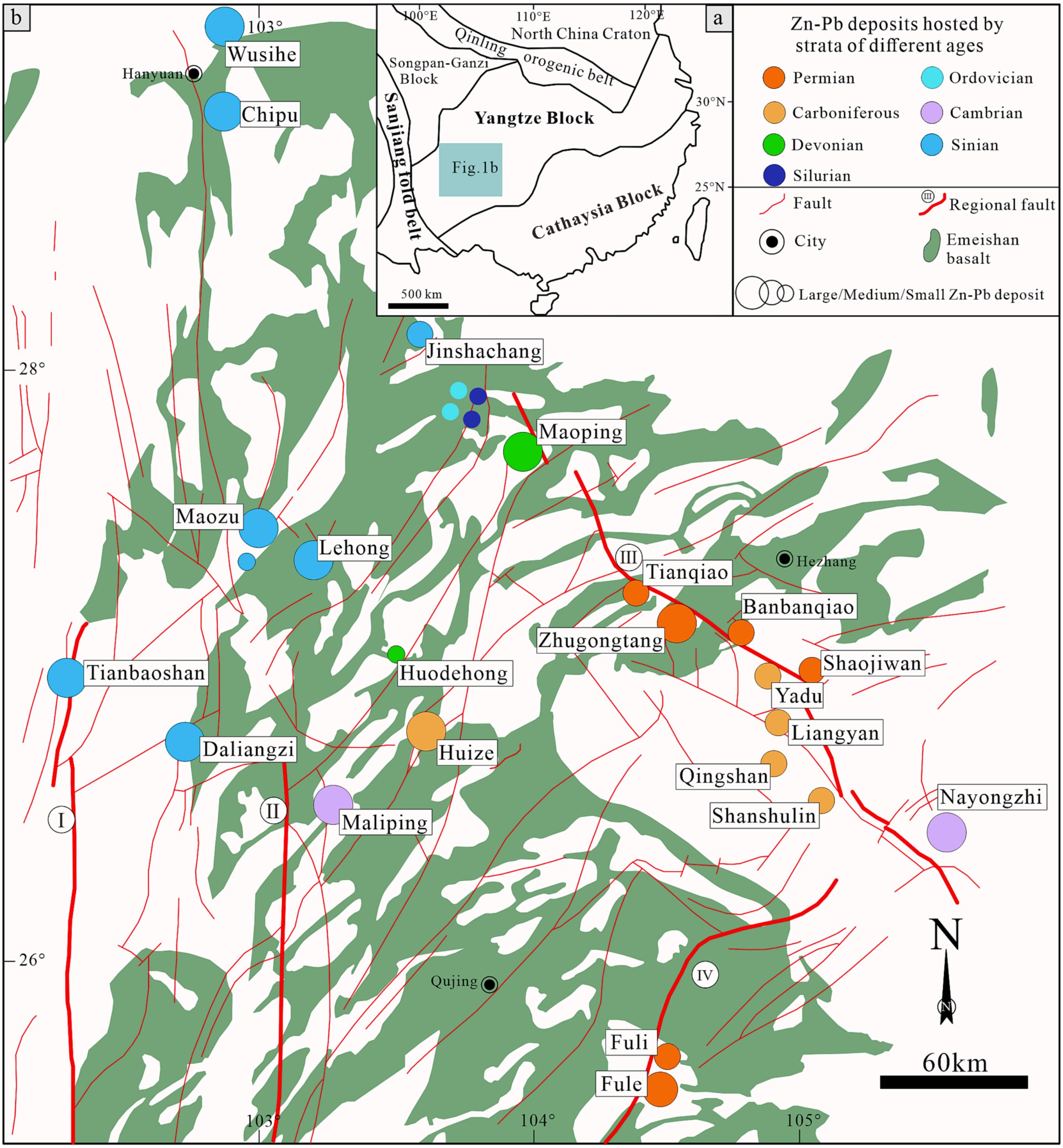

Fig. 1. Regional geology map of the SYG region and the distribution of Zn-Pb deposits. Faults I to IV are Anning River, Xiaojiang, Weining-Shuicheng, and Mile-Shizong faults, respectively (Modified from Wu et al., 2023; Liu and Lin, 1999; Luo et al., 2020).

et al., 2020). Among them, Ga and Ge are widely used in the semiconductor industry, whereas In is commonly used in smart devices and solar cells. There is also a trend with significant increase in demand for these metals in the future (Frenzel et al., 2016; Schulz et al., 2017; Wen et al., 2020). Recycling is an important source of Ge supply, but to guarantee future metal availability, the exploration for new deposits as well as the evaluation of known deposits for these elements is still a matter of considerable importance. The average contents of Ge, Ga, and In in the continental crust are 1.4 ppm, 15 ppm, and 0.05 ppm, respectively (Hans Wedepohl, 1995). The disperse features of these elements make them rarely form independent metal deposits, but typically associated with mineral deposits such as Zn-Pb sulfide and coal deposits (Wen et al., 2020), and their reserves are significantly lower compared to other common metals (Bernstein, 1985; Cook et al., 2009; Wen et al., 2020). All over the world, associated Ge in Zn-Pb deposits account for 75% of the total Ge resource (USGS, 2020). Therefore, understanding the distribution, occurrence, and enrichment mechanisms of Ge, Ga, and In in Zn-Pb deposits is crucial for the exploration and utilization of these critical metals.

The adjacent area among Sichuan, Yunnan, and Guizhou (SYG) provinces hosts over 400 Zn-Pb deposits and occurrences with more than 26 million tons (Mt) of Pb and Zn metals, grading at 5 wt% Pb and 10 wt % Zn, forming the prominent SYG Pb-Zn metallogenic region (Zhou et al., 2018c). The SYG region provides 27% of the total Pb + Zn resource in China, making it one of the largest Zn-Pb producers in the world (Fig. 1) (Hu et al., 2017; Zhou et al., 2018a, b, c). In addition to Pb and Zn, associated metals such as Ge, Ga, In, Cd, and Tl in the SYG region are also economic products and have become an important source of dispersed elements in China (Hu et al., 2021; Luo et al., 2022b; Wei et al., 2021a,b; Wen et al., 2020). Due to the economic significance of this metallogenic region, numerous studies have been carried out on the genesis of the Zn-Pb deposits. These Zn-Pb deposits share some similar features: 1) occurrence of associated dispersed elements in most deposits; 2) relatively simple mineral assemblages with sphalerite and galena being main ore minerals; 3) carbonate rocks being the mainly host rock; 4) the ore body is primarily controlled by reverse fault and fold systems; 5) ore-forming fluid dominated by low-medium temperature (120–250 °C) and middle to high salinity (<20 wt% $NaCl_{equiv}$); 6) sulfur derivation from thermochemical reduction of marine sulfate and/or evaporite; 7) spatially associated with the ~260 Ma Emeishan flood basalts; 8) mainly formed in the Indosinian period, which is closely related to the post-collisional orogeny of the Indosinian block and the Yangtze block (Appendix A Table 1; Huang et al., 2004 and references therein; Meng et al., 2015, 2019; Zhou et al., 2015; Zhou et al., 2023). Based on these studies, the Zn-Pb deposits in the SYG region are considered as Mississippi Valley-type (MVT) type (Hu et al., 2017; Zhou et al., 2018a, b; Yang et al., 2019, 2022b). However, most studies mainly focus on the genesis of Pb and Zn, research on associated metals such as Ge, Ga, and In is not enough.

In recent years, the research on Ge, Ga, and In has become an international hot topic. These studies include favorable deposit types of Ge, Ga, and In (Cook et al., 2009; Ye et al., 2011), independent minerals and nanoclusters (Fougerouse et al., 2023; Meng et al., 2023b), the valence state and the substitution mechanism (Belissont et al., 2016, 2019; Bonnet et al., 2017; Liu et al., 2023). In addition, the relationship between the enrichment of Ge, Ga and In and crystal structure (Johan, 1988; Belissont et al., 2014, 2016; Pring et al., 2020), mineral textures (Barrie et al., 2009; Belissont et al., 2014; Cook et al., 2015), source of ore-forming materials (Torró et al., 2023), physical–chemical condition (Bauer et al., 2019), and deposit types (Cook et al., 2009; Ye et al., 2011; Zheng et al., 2023) has been illustated. Compared to international studies on Ge, Ga, and In, studies of these elements in the SYG region are limited and mainly focus on sulfide textures (Luo et al., 2022a), mineral chemistry (Hu et al., 2019, 2021; Li et al., 2020; Meng et al., 2019, 2022, 2023a; Wei et al., 2018, 2019, 2021b, c; Yang et al., 2022b), sphalerite type and Ge isotopes (Meng et al., 2015), aiming to understand the main host minerals, the occurrences, and the possible factors controlling the enrichment of Ge, Ga, and In.

In this review, we summarize the research progress on Zn-Pb deposits in the SYG region and focus on the genesis of critical metals such as Ge, Ga, and In in these deposits. The main contents include: 1) basic geological features of Ge-, Ga- and In-bearing Zn-Pb deposits; 2) the distribution of Ge, Ga, and In in minerals such as sphalerite at the scale of deposit, mineralization stages, and textures; 3) the occurrence of these critical metals and related substitution mechanism; 4) the controlling factors for the enrichment of Ge, Ga and In. This review provides a comprehensive understanding of Ge, Ga, and In in the Pb-Zn deposits in the SYG region and has significant implication to ore genesis, mineral exploration and utilization of these critical metals.

2. Regional geology

The southwest China comprises the Yangtze and Cathaysia blocks, and the Sanjiang fold belt system (Fig. 1a; John et al., 1990). The SYG region, situated on the southwestern margin of the Yangtze block, is part of a the low-medium temperature metallogenic province in SW China (Hu et al., 2017). The SYG region is a triangular area bounded by three regional faults, the NS-trending Anning River fault, the NE-trending Mile-Shizong fault, and the NW-trending Weining-Shuicheng fault (Fig. 1b). In addition to the three regional faults, the Xiaojiang fault is also developed in SYG region (Fig. 1b). Several NE and NW secondary faults and fold belts have emerged (Fig. 1b; Huang et al., 2004; Zhou et al., 2018c). The distribution of Zn-Pb deposits in the SYG region is predominantly controlled by reverse faults and anticlines, with some deposits influenced by normal faults (such as the Yinchanggou deposit) (Tan et al., 2017). The SYG region is an important MVT Zn-Pb metallogenic region in China and even the world. In addition to Pb and Zn (>20 Mt), dispersed elements such as Ge, Ga, and In are present in most deposits. For example, the Fule deposit in NE Yunnan province contains ~ 329 t Ge and 177 t Ga, whereas the Huize deposit contains ~ 525 t Ge. The Tianbaoshan deposit in the SE Sichuan contains ~ 258 t Ga, and 122 t Ge (Appendix A Table 2; Liu et al., 2022a; Zhou et al., 2018a; Zhu et al., 2016b,a). The Ge, Ga, and In reserves in the SYG region were estimated based on the Zn grade and reserve and the average content of Ge, Ga and In in sphalerite. It is estimated that the Ge resource in the SYG region are greater than 3500 t, the Ga resource are greater than 800 t, and the In resource in the main In-rich Maliping Zn-Pb deposit are greater than 60 t. According to the scale classification of Ge, Ga and In deposits, the SYG region hosts abundant large-scale Ge deposits (≥200 t), and small-scale Ga and In deposits (<400 t; <100 t) (Appendix A Table 2).

The strata in the SYG region primarily consist of pre-Sinian basement rocks unconformably covered by sediments that are mainly carbonate (Liu and Lin, 1999; Zhao et al., 2010; Zhou et al., 2013a, d, 2015). The basement of the Yangtze Block mainly consists of Proterozoic to Archean crystalline and folded basement rocks, including the migmatite and gneiss of the Kangding Group, the metamorphic clastic rocks and spilite-keratophyre of the Dahongshan Group, and clastic rock with minor carbonate rocks of the Kunyang/Huili Group from the bottom to top (Zhao et al., 2010; Li et al., 2013; Zhu et al., 2020). The Zn-Pb deposits in the SYG region are mainly found in the Sinian, Cambrian, Ordovician, Silurian, Devonian, Carboniferous, and Permian carbonate strata (Fig. 1b). The Permian Emeishan flood basalts as the primary igneous rock in this region host magmatic deposits such as Fe-Ti-V oxide and Ni-Cu-(PGE) sulfide deposits (Xiong et al., 2023; Zhou et al., 2018c; Zhu et al., 2020).

3. Critical metal-bearing Zn-Pb deposits in the SYG region

The SYG region is predominantly characterized by Zn-Pb deposits that are widely distributed in the NE and NW directions, which are mainly controlled by the regional NE-trending Shizong-Mile fault and NW-trending Yadu-Shuicheng faults (Fig. 1b). The deposits in the northeastern Yunnan and southern Sichuan provinces are located in the NE direction, including the Jinshachang, Maoping, Huodehong, Huize, Maozu, Lehong, and Tianbaoshan deposits, whereas those in northwestern Guizhou are located in the NW direction including the Shanshulin, Qingshan, Shaojiwan, Yadu, and Zhugongtang deposits (Fig. 1b) (Zhou et al., 2013a, b, d, 2015). The ore-hosting strata in the NE-direction deposits are usually older than those in the NW direction. In the NE direction, the ore-hosting strata are mainly of Sinian age, followed by the Permian and Cambrian strata, whereas those of NW direction mainly range from Devonian to Permian in age (Fig. 1b; Appendix A Table 2). In both directions, the dominant magmatic rocks are Permian Emeishan basalts with a few diabase dykes occurring in the Qingshan and Shanshulin deposits in the NW direction (Zhou et al., 2018b). The deposits in the NE direction are typically large in size in terms of Pb and Zn compared to those in the NW direction (Appendix A Table 2). There are no significant differences in ore types, structures and textures between deposits in NW and NE directions. The geological features of deposits in these two directions are summarized in Appendix A Table 1 and represented deposits are described below.

3.1. Zn-Pb deposits in the NE direction of the SYG region

3.1.1. Daliangzi

The Daliangzi deposit is situated in the southwestern part of the SYG region. The Daliangzi deposit has Pb + Zn reserves of ~ 4.5 Mt grading at 10.5% Zn and 0.75% Pb. The ore bodies are related to a carbonized structural breccia belt in the mining area. The ore minerals are mainly sphalerite, galena, and chalcopyrite. Calcite, quartz, pyrite and dolomite are the main gangue minerals. Bitumen is also found in massive and brecciated ores (Li et al., 2022b).

Sphalerite in the Daliangzi deposit is the main host mineral of Ge, Ga, and In (Li et al., 2022a, b). Germanium, Ga and In exist in the form of isomorphism in sphalerite, and no Ge, Ga, and In independent minerals are found. Dark sphalerite is relatively rich in Ge (average 61 ppm), whereas light sphalerite is relatively rich in Ga (average 57 ppm) (Li et al., 2022b). The Ga content of sphalerite is positively correlated with Cu and Ag, whereas the Ge is positively correlated with Cu (Li et al., 2022b).

3.1.2. Maoping

The Maoping Zn-Pb deposit is situated in the northeastern part of Yunnan Province (Yang et al., 2019, 2022b). The total Pb + Zn resource of this deposit exceeds 3 Mt with Pb + Zn grades ranging from 12% to 30% (Tan et al., 2019b). The Maoping deposit includes three ore bodies hosted in the Devonian Zaige Formation, the Lower Baizuo Formation, and the Lower Weining Formation, respectively (Han et al., 2007b; Tan et al., 2019b). Sphalerite and galena are the main ore minerals, whereas dolomite, quartz, pyrite and calcite are the main gangue minerals (Han et al., 2007b; Wu et al., 2021).

In the Maoping Zn-Pb deposit, sphalerite is the primary host mineral of Ge, Ga, and In (Wei et al., 2021b; Yang et al., 2022b). Germanium, Ga, and In were considered to be present in the form of isomorphism in sphalerite, which possily substitutes Zn directly or via coupled substitution with Cu and other elements (Wei et al., 2021b; Yang et al., 2022b; Wang et al., 2023a). Germanium is relatively enriched in brown sphalerite (average 141 ppm), whereas Ga is detected in light sphalerite (average 4 ppm) (Wang et al., 2023a). There is no difference in In content between the brown and light sphalerite (average 12 ppm). The differential enrichment of Ge, Ga, and In in sphalerite of different ore bodies is controlled by the different contents of these elements in the ore-bearing strata, temperature and sulfur fugacity (Wei et al., 2021b; Niu et al., 2023; Wang et al., 2023a).

3.1.3. Huize

The Huize Zn-Pb deposit is situated in the western part of the Yunnan-Guizhou junction. The proven reserves of Pb + Zn are approximately 7 Mt, with average grades of around 25–35 % for Pb + Zn (Bao et al., 2017). The deposit mainly includes two mining areas: Kuangshanchang and Qilinchang. The ore bodies primarily occur within the Lower Carboniferous Baizuo Formation (Li et al., 2006; Meng et al., 2019; Zhang et al., 2022). Ore minerals are mainly sphalerite and galena, whereas gangue minerals are mainly calcite, pyrite, and dolomite with minor quartz, barite, and gypsum (Han et al., 2007a; Oyebamiji et al., 2020, 2023).

Sphalerite is the main host mineral of Ge, Ga and In, mainly in the form of isomorphism (Ye et al., 2011; Oyebamiji et al., 2020). Independent Ge mineral was observed in the deposit, which is mainly composed of Ge and Al (Zhang et al., 2008). Germanium, Ga, and In are mainly hosted in the early sphalerite with average contents of 12 ppm, 35 ppm, 3 ppm, respectively (Oyebamiji et al., 2020). Moreover, Ge is mainly enriched in the dark zone of the zoned sphalerite with contents up to 1000 ppm (Liu et al., 2022a). Correlation analysis shows that Ge and In in sphalerite are mainly coupled with Cu (Oyebamiji et al., 2020; Liu et al., 2022a).

3.1.4. Maliping

The Maliping Zn-Pb deposit is located in the southwest of the SYG region. It is a large Zn-Pb deposit newly discovered in recent years (Hu et al., 2019; Luo et al., 2019). The Pb + Zn reserves of the Maliping deposit are more than 2 Mt, and the average grades of Pb and Zn are 4.18% and 9.38%, respectively (Luo et al., 2019). The main ore-hosting rock of the deposit is dolostone and shale of lower Cambrian Meishucun Formation. Ore minerals mainly include sphalerite and galenite, and gangue minerals mainly include quartz, dolomite, pyrite, and calcite (Luo et al., 2019).

The Maliping Zn-Pb deposit is abnormally rich in In in the SYG region (up to 342 ppm, average 78 ppm) (Appendix A Table 2 and 3). Germanium, Ga and In have no independent minerals, and mainly exist in the form of isomorphism in sphalerite. The In enrichment in the deposit may be related to the intermediate-acid magmatic rocks in the basement rocks (Hu et al., 2019).

3.2. Zn-Pb deposits in the NW direction of the SYG region

3.2.1. Nayongzhi

The Nayongzhi Zn-Pb deposit is located in the southeastern limb of the Wuzhishan anticline. The main ore-hosting strata is the dolostone of the Qingxudong Formation. No exposed magmatic rocks were found in this mining area (Chen et al., 2017; Zhou et al., 2018b). The Nayongzhi Zn-Pb deposit consists of four mining areas: Lumaolin, Jinpo, Yuhe, and Shayan. The reserves and average grades of Pb + Zn in Lumaolin, Jinpo, and Shayan mining areas are 0.38 Mt (4.06%), >0.44 Mt (6.24%), and > 0.53 Mt (6.61%), respectively (Yang et al., 2018b). The ore minerals consist of sphalerite and galena, and gangue minerals are mainly calcite and dolomite (Zhou et al., 2018b).

Gallium and Ge in sphalerite mainly appear in the form of isomorphism, and no inclusions or independent minerals are found. In the zoned sphalerite, the brown cores have relatively high Ge content (average 547 ppm), whereas pale-yellow and light color rims have elevated Ga (average 159 ppm) and the content of In is very low (average < 1 ppm) (Wei et al., 2021c). Correlation analysis shows that Ga is coupled with Cu and Ag, whereas In is coupled with Sn (Wei et al., 2018).

3.2.2. Tianqiao

The Tianqiao Zn-Pb deposit is located in the east-central part of the SYG region, within the northwestern area of the Yadu-Mangdong tectonic belt. The distribution of ore bodies in this deposit is primarily controlled by the fault and anticline. The ore bodies are mainly hosted in the dolomitic limestone in the upper part of the Lower Carboniferous Dapu Formation and coarse-grained dolostone in the middle and lower part of the Baizuo Formation (Zhou et al., 2009; Yang et al., 2022b). The identified Pb + Zn metal reserve is 0.4 Mt, with the average grades of Pb and Zn are 5.5 % and 16.7 %, respectively (Zhou et al., 2013d, 2014b). The primary metallic minerals are sphalerite and galena, with calcite and pyrite being the predominant gangue mineral (Zhou et al., 2009, 2013d, 2014b).

Sphalerite is the main host mineral of Ge, Ga and In compared with pyrite (Meng et al., 2022; Yang et al., 2022b). Galena is another host mineral of Ge with average Ge content of 23 ppm (Zhao et al., 2011). Germanium, Ga, and In in sphalerite mainly exist in the form of isomorphism. At present, no independent minerals of Ge, Ga, and In have been found in the deposit. Light sphalerite is richer in Ge and Ga (average 91 ppm and 25 ppm, respectively) than dark sphalerite (average 76 ppm and 14 ppm, respectively). Correlation analysis shows that Ga and Ge are coupled with Cu, whereas Ag also be involved in the substitution of Ga or Ge by Cu (Yang et al., 2022b).

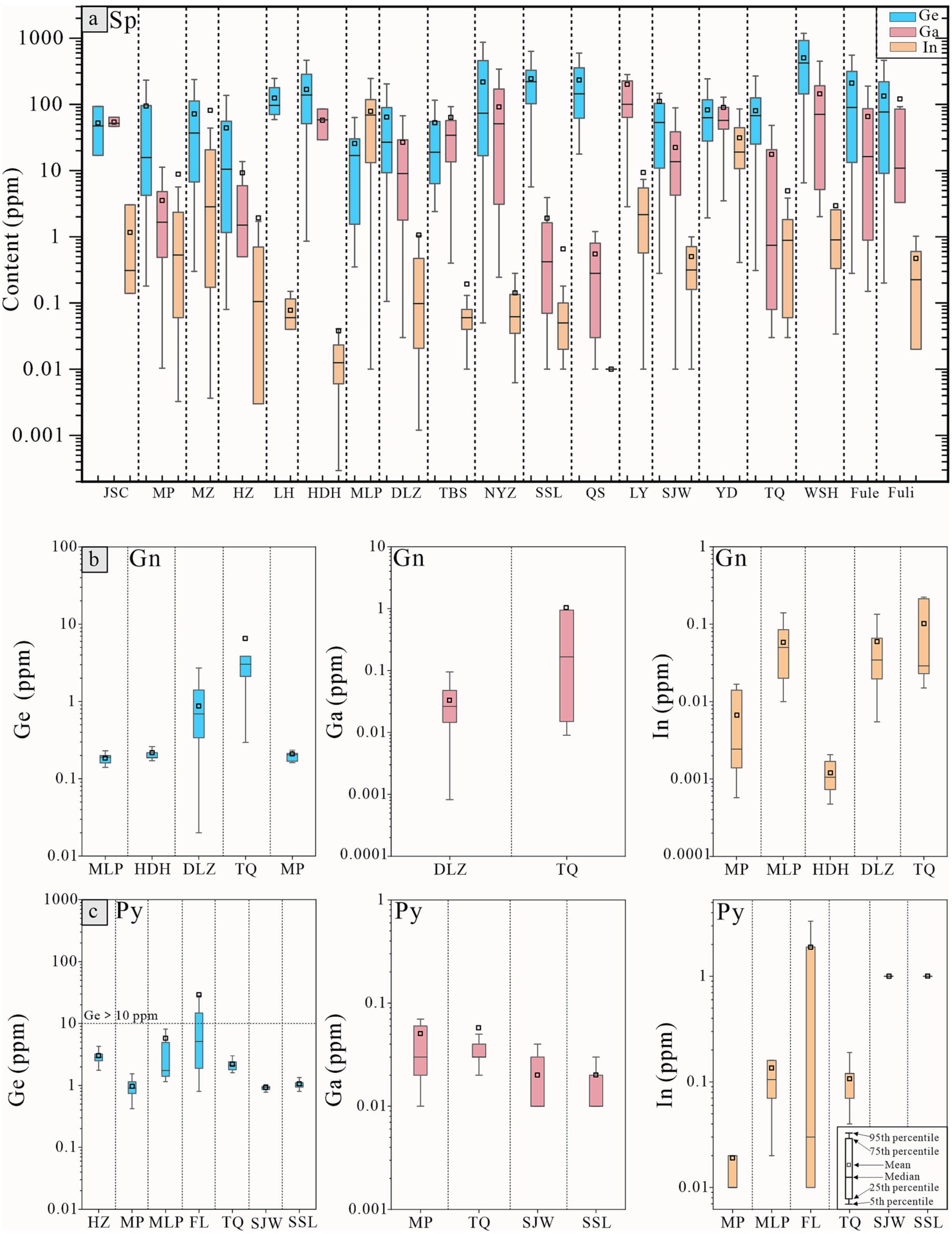

Fig. 2. The contents of Ga, Ge and In in sphalerite (a), galena (b) and pyrite (c) in Zn-Pb deposits in the SYG region. Data sources of sphalerite: Jinshachang (JSC) (Li, 2019; Wu et al., 2019b); Maoping (MP) (Wei et al., 2021b; Yang et al., 2022b; Niu et al., 2023; Wang et al., 2023a); Maozu (MZ) (Li et al., 2020); Huize (HZ) (Ye et al., 2011; Wu et al., 2019b; Oyebamiji et al., 2020; Oyebamiji et al., 2023); Lehong (LH) (Wei et al., 2019); Huodehong (HDH) (Hu et al., 2021; Luo et al., 2022b); Maliping (MLP) (Hu et al., 2019); Daliangzi (DLZ) (Yuan et al., 2018; Wu et al., 2019b; Li et al., 2022b); Tianbaoshan (TBS) (Ye et al., 2016; Yu et al., 2022); Nayongzhi (NYZ) (Wei et al., 2021c); Shanshulin (SSL), Qingshan (QS), Yadu (YD), Tianqiao (TQ) and Shaojiwan (SJW) (Yang et al., 2022b); Liangyan (LY) (Wang et al., 2023b); Wusihe (WSH) (Luo et al., 2020); Fule (Li, 2016); Fuli (Liang et al., 2023). Data sources of galena and pyrite: Daliznzgi (Li et al., 2022a); Tianqiao (Meng et al., 2022); Maliping (Hu et al., 2019); Hudodehong (Hu et al., 2021; Luo et al., 2022b); Maoping (Wei et al., 2021b; Yang et al., 2022b); Shaojiwan, Shanahulin (Yang et al., 2022b); Huize (Meng et al., 2019); Fule (Li et al., 2019).

3.2.3. Qingshan

The Qingshan Zn-Pb deposit is located in the Weining-Shuicheng Zn-Pb metallogenic belt, close to the junction of the SYG region. The main ore-bearing surrounding rock is limestone of the Upper Maping Formation and sandstone and shale of the Middle Permian Liangshan Formation (Meng et al., 2023a). The Emeishan basalts and diabase are the main igneous rocks. The mining district is divided into two mining areas, namely the Qingshan and Hengtang. The Zn-Pb ore bodies predominantly occur as steeply dipping veins and frequently exhibit intensive of Zn-Pb mineralization. Proven reserves of Pb + Zn exceed 0.3 Mt, with Pb and Zn grades of 3.76 % to 9.92 % and 34.96 % to 37.58 %, respectively (Yang et al., 2022b; Meng et al., 2023a). The main ore minerals are sphalerite and galena. Gangue minerals mainly include dolomite, calcite, barite, pyrite, and quartz (Zhou et al., 2013b; Yang et al., 2022b).

Sphalerite is the main host mineral of Ge, Ga and In, and Ge may also be enriched in pyrite and marcasite (Yang et al., 2022b; Meng et al., 2023a). No independent minerals and inclusions of Ge, Ga and In are found. There are also a large number of oxidized ores in the Qingshan deposit, which also show the enrichment of Ge, Ga and In (Zhang et al. unpublished). Germanium is relatively enriched in brown sphalerite of the Qingshan deposit (average 233 ppm), and the contents of Ga and In in sphalerite are very low. Gallium is coupled with Cu, but the linear correlation between Ge and Cu is poor (Yang et al., 2022b).

3.3. Other Zn-Pb deposit of the SYG region

The Wusihe Zn-Pb deposit is located in the north of SYG region. The main ore-hosting rocks of the deposit are breccia dolostone, black siliceous rock of the Upper Sinian Dengying Formation and carbonaceous shale of the Lower Cambrian Qiongzhusi Formation (Xiong et al., 2016, 2018). Igneous rocks and metamorphic rocks of basement strata are developed in the mining area, and Emeishan basalt is not exposed. The reserves of Pb + Zn are more than 5.4 Mt, and the average grades of Pb and Zn are 2.0 % and 8.6 %, respectively (Luo et al., 2021). The main ore minerals of the deposit include sphalerite and galena, and gangue minerals include quartz, dolomite, calcite, pyrite, and apatite.

The Wusihe Zn-Pb deposit is the deposit most rich in Ge and Ga of sphalerite in the SYG region. There are possibly two forms of Ge in sphalerite: isomorphism (Luo et al., 2021) and independent minerals (Meng et al., 2023b). The isomorphism is inferred from the positive correlation between Ge and Cu, Fe, and Ag. The Ge independent mineral is the newly discovered Ruizhongite, $(Ag_2\square)Pb_3Ge_2S_8$, in sulfide matrix (Meng et al., 2023b). The differential enrichment of Ge in the zoned sphalerite is possibly controlled by the precipitation rate and crystallization process of sphalerite (Luo et al., 2021).

4. The distribution and occurrence of Ge, Ga and in

4.1. Distribution of Ge, Ga and in in different types of minerals

Understanding the main host minerals of Ge, Ga, and In in Zn-Pb deposits is essential for exploring and utilizing these metals. Sphalerite is a significant host mineral of Ge, Ga, and In (Cook et al., 2009; Ye et al., 2011). Studies indicate that Ga and In are predominantly enriched in non-recrystallized sphalerite, while the content of Ga and In in chalcopyrite increases after recrystallization (220–800 °C) (George et al., 2016). Research on the Arre deposit suggests that the form of Ge in sphalerite can be transferred and form discrete minerals or nanoparticles when exposed to the conditions of metamorphism, deformation, and high temperature (below 400 °C) (Fougerouse et al., 2023). This indicates that apart from sphalerite, other minerals in the deposit may also serve as hosts for elements such as Ge, Ga, and In. The deposits in the SYG region typically form within a temperature of 120–250 °C (Zhou et al., 2018c), obviously lower than recrystallization (220-800 °C) and metamorphic temperature (400-800 °C). Moreover, there is no metamorphic modification after Pb-Zn ore formation. Therefore, Ge, Ga, and In transfer during recrystallization due to metamorphism and deformation cannot be used to explain the enrichment of these metals in the SYG region.

Sphalerite is the main mineral hosting Ge, Ga, and In in the Zn-Pb deposits of the SYG region, with contents up to ~ 1300 ppm, ~600 ppm, and ~ 1191 ppm, respectively (Appendix A Table 2 and 3; Fig. 2a). Galena and pyrite are commonly associated with sphalerite in the SYG region. Whether galena and pyrite are also important host minerals of Ge, Ga, and In remains controversial. In galena, the contents of Ge, Ga, and In are very low, ranging from below detection limit to 6.49 ppm, 5.55 ppm, and 0.25 ppm, respectively (Appendix A Table 2 and 3; Fig. 2b). The contents of Ge, Ga, and In in pyrite are similar to those in galena, ranging from below detection limit to 61.8 ppm, 0.32 ppm, and 13.7 ppm, respectively (Appendix A Table 2 and 3; Fig. 2c). Germanium is only relatively rich in pyrite from the Fule Zn-Pb deposit (Appendix A Table 2 and 3; Fig. 2c), with content of 0.8–340 ppm, which was interpreted as the involvement of Emeishan basalts in the ore-forming fluids (Zhou et al., 2018a). Pyrite in the Zn-Pb deposits associated with magmatic activity could serve as a potential vector mineral for Ge enrichment, aiding future exploration for Ge.

4.2. The occurrences of Ge, Ga, and in

4.2.1. The valences of Ge, Ga, in and their common coupling elements in sphalerite

Several studies have investigated the valences of Ge in sphalerite from various environments by the micro-X-ray absorption near-edge structure (μ-XANES), including the Tres Marias MVT Zn deposit in Mexico (Cook et al., 2015), the vein-type Saint-Salvy deposit in France (Belissont et al., 2016), the super-giant carbonate-hosted Zn-Pb-Ag deposits of the MacArthur River in Australia, Fule Zn-Pb deposit in SYG region (Wei, 2022), and simulated sphalerite under MVT deposit conditions (Liu et al., 2023). These studies indicate that Ge^{4+} is the main valance in sphalerite. However, in the world-class MVT deposits of central Tennessee, United States, Ge^{2+} was found only in the banded sphalerite with low Fe content (701–3607 ppm), which was interpreted to be due to variations in oxygen fugacity (Bonnet et al., 2016, 2017). Germanium in other minerals, such as pyrite and chalcopyrite, is also present as Ge^{4+} (Etschmann et al., 2017; Belissont et al., 2019).

Gallium predominantly exists in the form of Ga^{3+} (Gray et al., 2005), with occasional occurrences of Ga^{2+} and Ga^{+} (Schulz et al., 2017). Indium occurs as In^{3+} in sphalerite (Alfantazi and Moskalyk, 2003). In aqueous solutions, both Ga^{3+} and In^{3+} are the primary forms of these ions (Wood and Samson, 2006).

Based on the substitution mechanism and Ab initio quantum chemical simulation, the most probable coupling elements for Ge and Ga entering into sphalerite crystal structure are Cu and Fe (Liu et al., 2023). Copper typically exists in geological fluids as Cu(I) chloride and hydrogen sulfide complexes (Seward et al., 2000; Cook et al., 2012). It has been confirmed that Cu in In-rich sphalerite from the Toyoha deposit in Japan, which was formed below 300 °C, exists in the form of Cu^{+} (Cook et al., 2012). Copper is present as Cu^{+} and Fe is present as Fe^{2+} in sphalerite from the vein-type Saint-Salvy deposit in France, which was formed between 80 and 580 °C. Cu^{+} was also observed in sphalerite synthesized under simulated MVT conditions (Liu et al., 2023). However, Fe-rich sphalerite (>6 mol.% Fe) possibly containing minor amount of Fe^{3+} (Belissont et al., 2016). In summary, Cu^{+} and Fe^{2+} are main forms of Cu and Fe, respectively, in sphalerite. The primary mechanism of incorporating In in the sphalerite is to couple with Cu and Sn for substitution. Tin can exist in the forms of Sn^{2+}, Sn^{3+}, and Sn^{4+}. However, the valence of Sn was not reported in sphalerite (Cook et al., 2009; Belissont et al., 2014; Torró et al., 2023).

4.2.2. Isomorphic substitution

The most common form of Ge, Ga, and In in sphalerite in SYG region

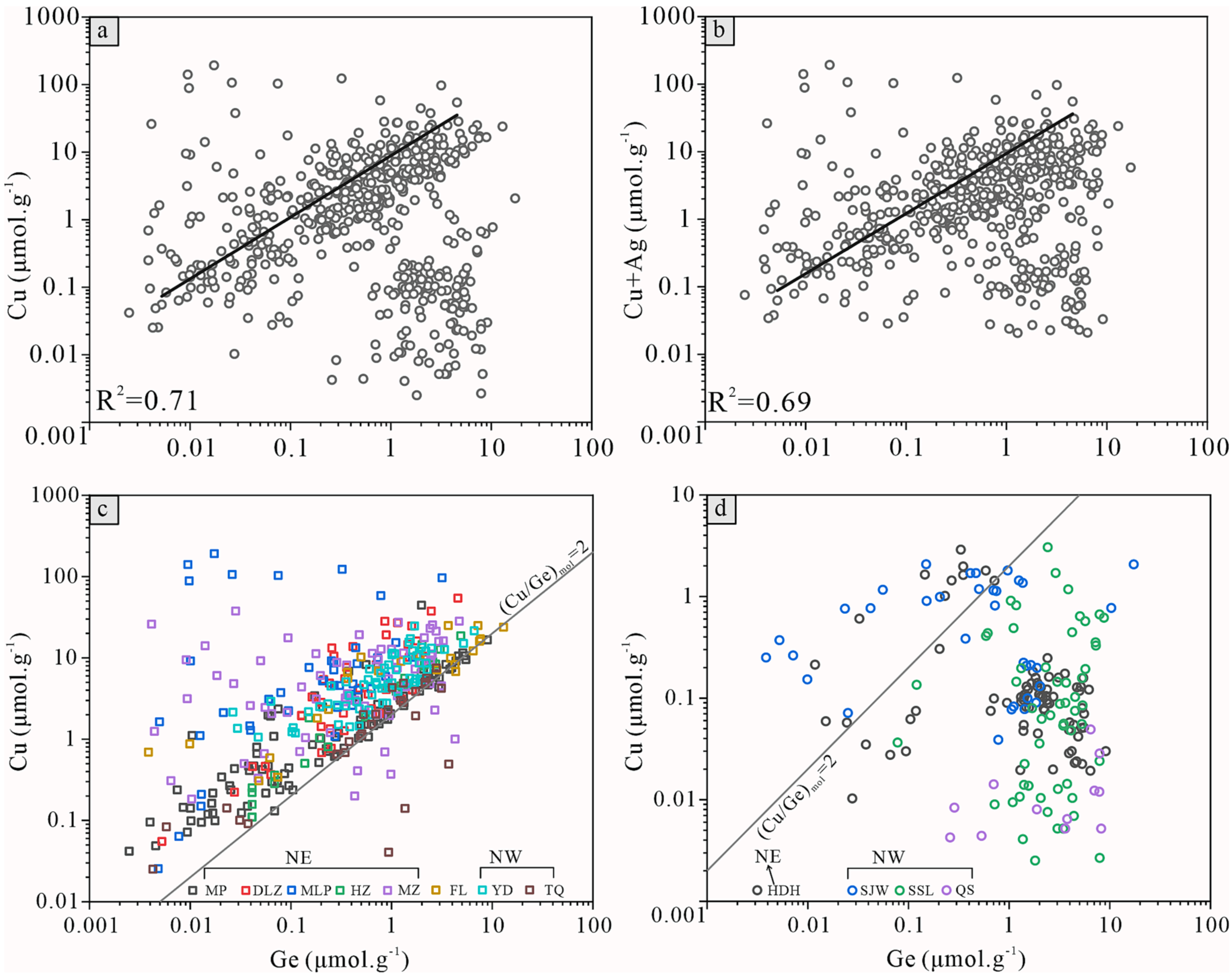

Fig. 3. The correlation diagrams of Ge versus Cu (a, c, d) and Ge versus Cu + Ag (b) in sphalerite of Zn-Pb deposits. Sphalerite samples with $(Cu/Ge)_{mol} = 2$ are plotted in c, whereas those deviated from the line of $(Cu/Ge)_{mol} = 2$ are plotted in d. Data sources: Maoping (MP), Yadu (YD), Tianqiao (TQ), Shaojiwan (SJW), Shanshulin (SSL) and Qingshan (QS) (Yang et al., 2022); Maozu (MZ) (Li et al., 2020); Maliping (MLP) (Hu et al., 2019); Huize (HZ) (Ye et al., 2011); Huodehong (HDH) (Luo et al., 2022); Fule (FL) (Ren et al., 2019); Daliangzi (DLZ) (Li et al., 2022b).

is isomorphism (Wei et al., 2018, 2019, 2021b, c; Hu et al., 2019, 2021; Li et al., 2019, 2020, 2022b). The proposed substitution mechanism of Ge includes Ge^{4+} and Ge^{2+}: $Ge^{4+} + 2(Cu, Ag)^{+} \leftrightarrow 3Zn^{2+}$ (Yuan et al., 2018; Hu et al., 2019; Wei et al., 2019; Li et al., 2022b; Yang et al., 2022a), $Ge^{4+} + \square$($\square$ represents vacancy) $\leftrightarrow 2Zn^{2+}$ (Cook et al., 2015; Luo et al., 2021; Liu et al., 2023), $Ge^{4+} + 2Fe^{2+} + \square \leftrightarrow 4Zn^{2+}$ (Yuan et al., 2018; Liu et al., 2023), $4(Cu^{+} + Sb^{3+}) + (Ge^{4+} + 2Ag^{+}) + 2\square \leftrightarrow 13Zn^{2+}$ (Li et al., 2020), $Ge^{4+} + Mn^{2+} \leftrightarrow 3(Zn, Cd)^{2+}$ (Hu et al., 2021), $Ge^{4+} \leftrightarrow 2Fe^{2+}$, $nCu^{2+} + Ge^{2+} \leftrightarrow (n + 1)Zn^{2+}$ (Ye et al., 2016; Li et al., 2022b), $Ge^{2+} \leftrightarrow Zn^{2+}$ (Luo et al., 2021), $2Cu^{+}+Ge^{2+} \leftrightarrow 2Zn^{2+}$, $Ge^{2+} \leftrightarrow Fe^{2+}$, $Ge^{2+} + Mn^{2+} \leftrightarrow 2(Zn, Cd)^{2+}$ (Hu et al., 2021). The proposed substitution mechanism of Ga in sphalerite in the SYG region mainly includes: $Cu^{+} + Ga^{3+} \leftrightarrow 2Zn^{2+}$ (Wei et al., 2018; Li et al., 2022b; Yang et al., 2022b). The possible substitution ways for In in sphalerite are as follows: $2In^{3+} + Sn^{4+} + 2\square \leftrightarrow 5Zn^{2+}$ (Li et al., 2020), $In^{3+} + Sn^{3+} + \square \leftrightarrow 3Zn^{2+}$ (Wei et al., 2018; Yuan et al., 2018), $Cu^{+} + In^{3+} \leftrightarrow 2Zn^{2+}$ (George et al., 2016; Xu et al., 2021a, b). $Cu^{+} + (Ga, In)^{3+} + Sn^{4+} \leftrightarrow 4Zn^{2+}$ (Torró et al., 2023). Cu^{+} and Sn^{n+} are the main coupling ions of In.

Both Ag^{+} and Cu^{+} are monovalent ions. Some studies have also suggested that Ag can serve as a coupling element for Ge (Li et al., 2020, 2022b). To understand the incorporation mechanism, we investigate the correlation between Cu and Ge, as well as Cu + Ag and Ge in sphalerite from Zn-Pb deposits in the SYG region. The similar correlation coefficients between Cu and Ge, and between Cu + Ag and Ge (Fig. 3a, b), indicate that Ag^{+} has minor impact on the Ge substitution in sphalerite. The majority of deposits in the SYG region, including Maoping, Daliangzi, Maliping, Huize, Maozu, Fule, and Yadu (Fig. 3c), plot above or near the line of $(Cu/Ge)_{mol} = 2:1$, which may be dominated by $Ge^{4+} + 2Cu^{+} \leftrightarrow 3Zn^{2+}$. The Huodehong, Shaojiwan, Shanshulin, and Qingshan deposits are obviously below the line of $(Cu/Ge)_{mol} = 2:1$ (Fig. 3d), which suggests other occurrences of Ge in sphalerite from these deposits. In the Huodehong, Shaojiwan, and Qingshan deposits, Ge shows a positive correlation with Pb, Ag, or Mn (Fig. 4a-d). The correlation between Ge, Pb, and Ag is consistent with the composition of the new discovered ruizhongite in the Wusihe deposit of the SYG region. Therefore, Ge-bearing minerals or nanoclusters may also exist in other Zn-Pb deposits in the SYG region. For Ga and In, nearly all Zn-Pb deposits in the SYG region plot above the lines of $(Cu/Ga)_{mol} = 1$ (Fig. 4e) and $(Cu/In)_{mol} = 1$ (Fig. 4f), consistent with the substitution mechanism of $(In, Ga)^{3+} + Cu^{+} \leftrightarrow 2Zn^{2+}$.

In addition to the different substitution mechanism of Ge, Ga, and In

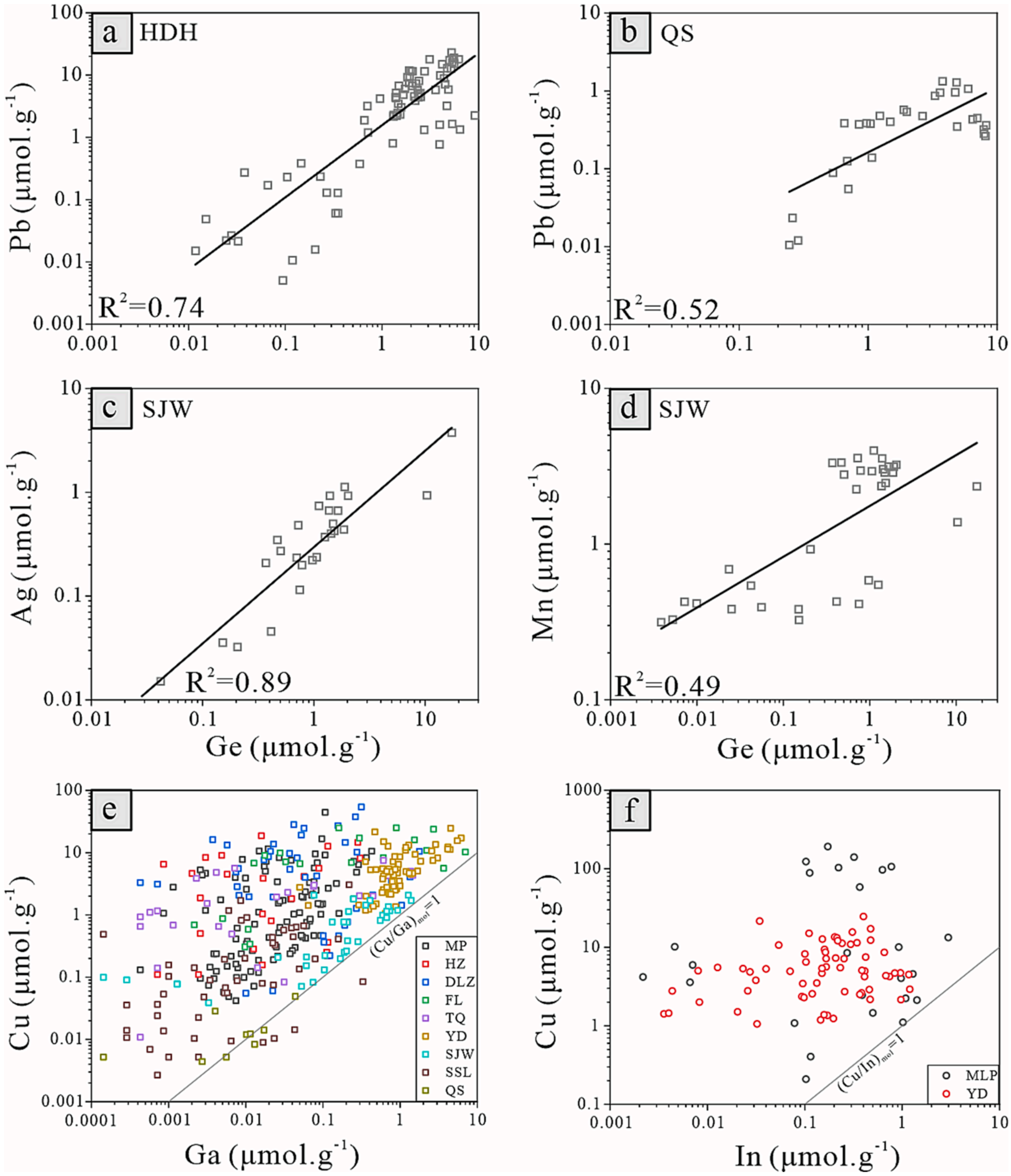

Fig. 4. (a-d) Binary correlation between Ge and Pb, Ag, and Mn of sphalerite in Huodehong (HDH), Qingshan (QS), and Shaojiwan (SJW) Zn-Pb deposits in the SYG region. (e-f) The correlation of Cu versus Ga and In in sphalerite of Zn-Pb deposits in the SYG region. The data source is the same as Fig. 3.

in sphalerite on deposit scale, substitution mechanism of these elements also varies on single sphalerite grain scale. In the zoned sphalerite from the Nayongzhi Zn-Pb deposit, the brown core has higher Ge, whereas the yellow and pale rims have higher Ga and In (Wei et al., 2021c). The brown cores show positive correlation between Ge and Cu with $(Cu/Ge)_{mol}$ ratios less than 2 (Fig. 5a). But the correlation between Cu and Ge is not obvious for yellow and pale rims (Fig. 5a). Germanium shows a positive correlation with Fe for both brown cores and yellow and pale rims, but the latter shows higher correlation (Fig. 5b). The positive correlation between Ga and Cu is only observed for yellow and light rims with $(Cu/Ga)_{mol}$ ratios close to 1 (Fig. 5c). The brown cores lack correlation between Ga and Cu and have higher $(Cu/Ga)_{mol}$ ratios than yellow and light rims (Fig. 5c). No obvious correlation between Ga and Sb for both cores and rims (Fig. 5d), but the cores have lower Ga and Sb contents than rims. Previous study shows that changes in temperature, oxygen fugacity and fluid composition between cores and rims of sphalerite are possibly the key factors controlling the distribution of Ge, Ga, and other trace elements (Wei et al., 2021c). Therefore, the physicochemical condition of ore-forming fluids may have a stronger influence on the substitution mechanism of Ge, Ga and In at the mineral grain scale.

4.2.3. Nature minerals of Ge, Ga and in

Germanium also forms numerous independent minerals in Zn-Pb-Cu deposits. These include argyrodite (Ag_8GeS_6), germanite ($Cu_{13}Fe_2Ge_2S_{16}$), renierite ($(Cu, Zn)_{11}(Ge, As)_2Fe_4S_{16}$), and briartite ($Cu_2(Fe, Zn)GeS_4$) (Schulz et al., 2017). Recently, a new independent Ge mineral, ruizhongite, $(Ag_2\square)Pb_3Ge_2S_8$, was discovered in the Wusihe Zn-Pb deposit in the SYG region (Meng et al., 2023b). The structure comprises a non-centrosymmetric arrangement of $[GeS_4]^{4-}$ tetrahedra (Meng et al., 2023b). Germanium-rich minerals, mainly composed of Ge and Al (GeO_2 39.84 % and Al_2O_3 49.96 %), were also reported in the Huize Zn-Pb deposit (Zhang et al., 2008), but the chemical formula was not given. Independent Ga-containing minerals were rarely reported in

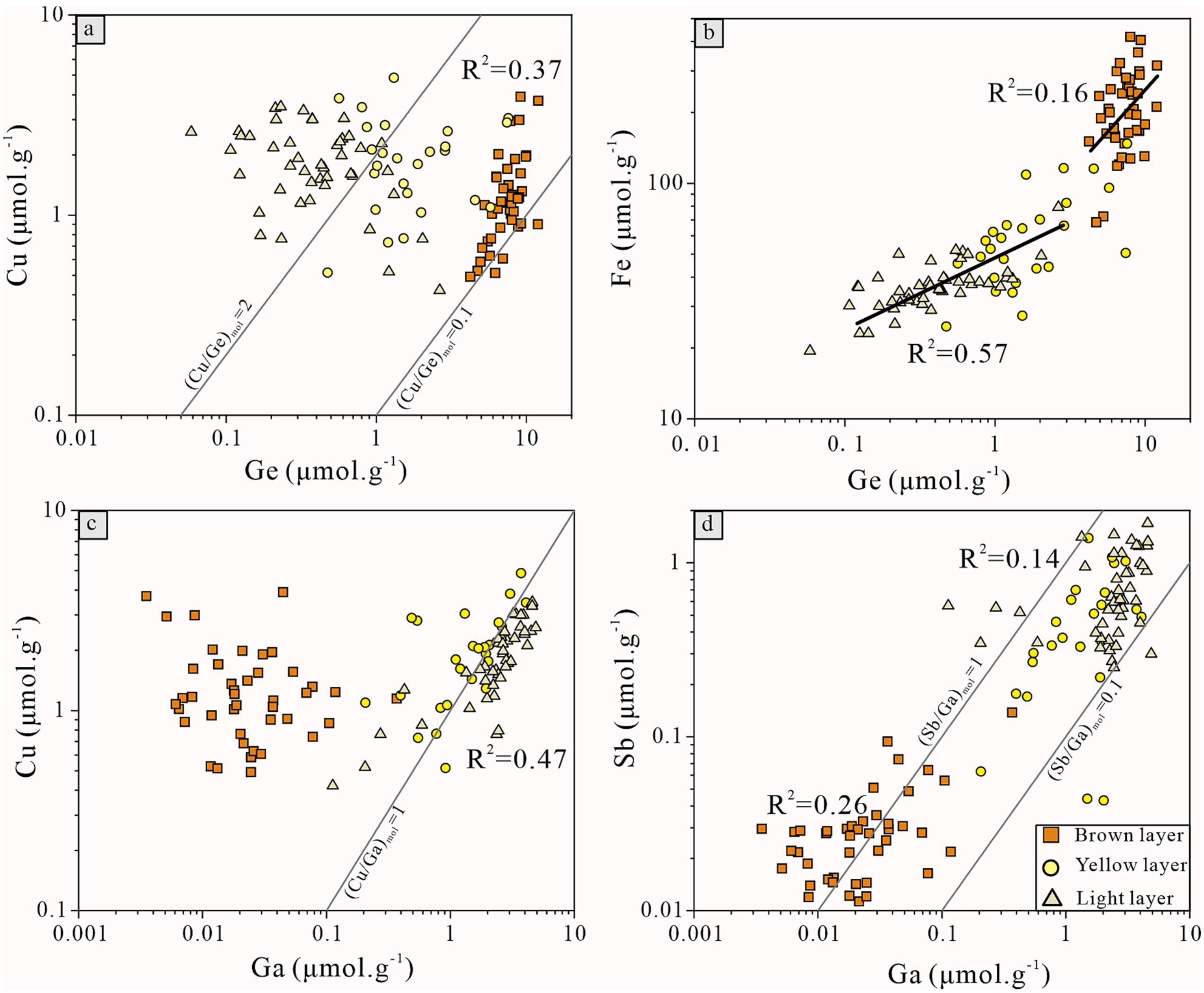

Fig. 5. The correlation of Ge with Cu (a) and Fe (b), and the correlation of Ga with Cu (c) and Sb (d) in different layers in zoned texture of sphalerite from the Nayongzhi deposit (Data are from Wei et al., 2021c).

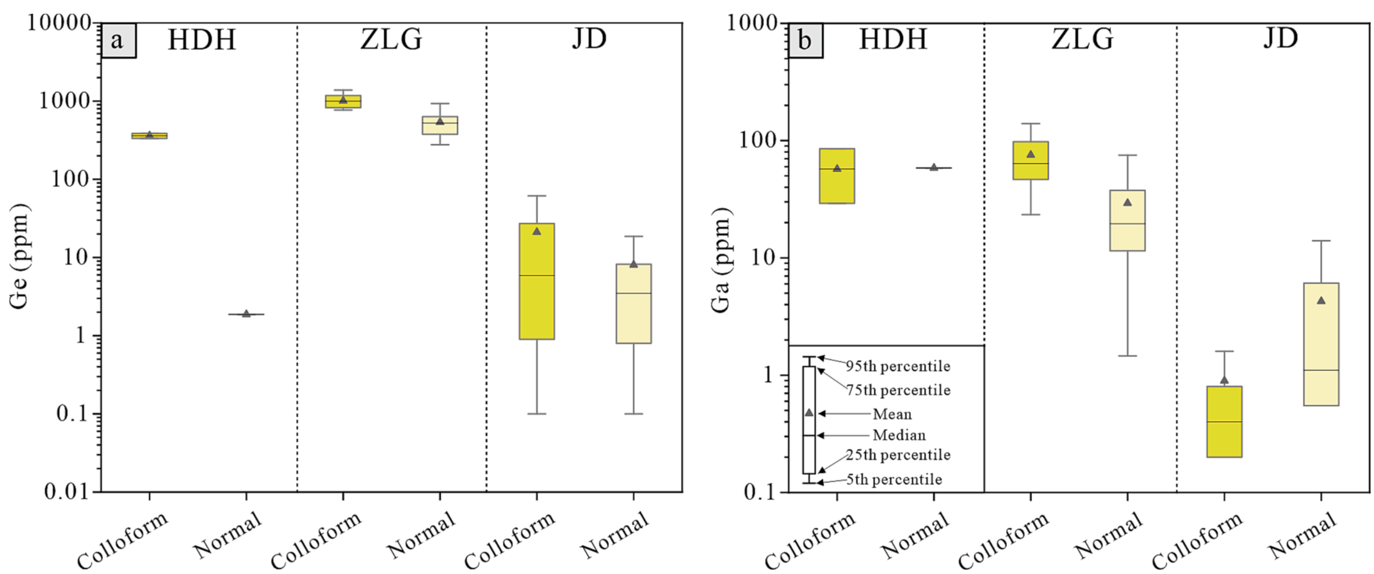

Fig. 6. The contents of Ge and Ga in sphalerite with colloform and normal textures. Data sources: Huodehong (HDH) (Luo et al., 2022b); Zhulingou (ZLG) (Luo et al., 2022a); Jinding (JD) (Mu, 2021).

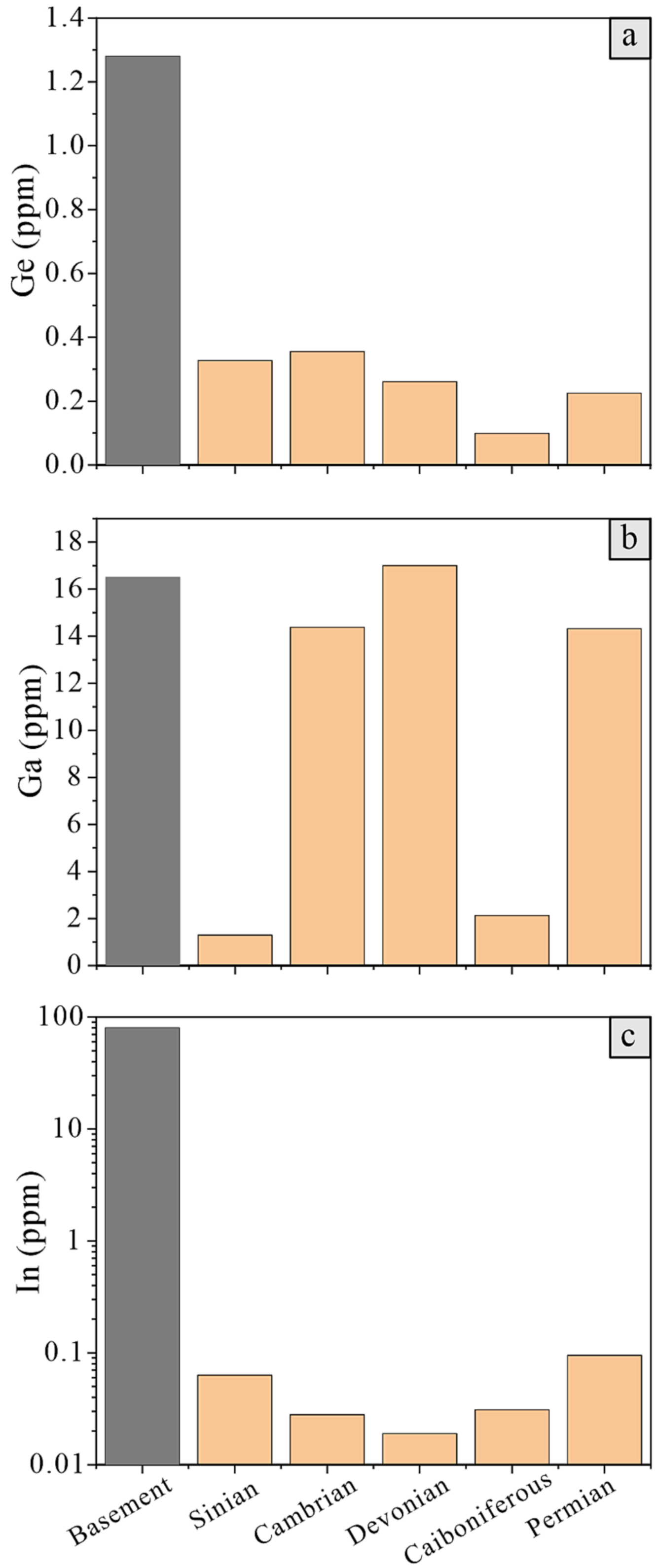

Fig. 7. The contents of Ge (a), Ga (b), and In (c) in basement rocks and common ore-hosting strata with different ages in the SYG region. Data sources: Du et al., 2019; Mo et al., 2013.

global Zn-Pb deposits. These include Gallite ($CuGaS_2$), Gallobeudantite ($PbGa_3[(AsO_4), (SO_4)]_2(OH)_6$), Sohngeite (Ga $(OH)_3$), and Tsumgallite (GaO(OH)), found in Tsumeb Mine in Namibia (Cu-Zn-Pb) (Schulz et al., 2017). There are 15 named independent minerals containing In as a main component, such as dzhalindite (In $(OH)_3$), indite ($Fe^{2+}In_2S_4$), and $Zn_{1.5}Fe_{0.5}CuInS_4$ from Dulong deposit, of which roquesite ($CuInS_2$) is the most widespread (Schulz et al., 2017; Xu et al., 2021a). However, In-bearing and Ga-bearing minerals were not reported in the SYG region until now.

The smooth time profile curves of Ge, Ga, and In during LA-ICP-MS analysis was commonly use to indicate no contaminated micro inclusions (Wei et al., 2019, 2021b, c; Li et al., 2020; Hu et al., 2021). However, nano-particles/inclusions are still possibly present, which represents another occurrence of independent minerals of Ge, Ga, and In. For example, Ge oxide (GeO_2) nanoparticles (<500 nm) are present in sphalerite from the world-class MVT deposit in the central and eastern mining areas of Tennessee, United States (Bonnet et al., 2017). In addition, Ge also occurs as briartite nano inclusions in sphalerite from the Arre deposit (Fougerouse et al., 2023), which was considered to be due to the dissolution of Cu and Ge at temperatures below 400 °C. In the SYG region, transmission electron microscopy was used to analyze the occurrence of Ge, Ga, and In in zoned sphalerite from the Nayongzhi Zn-Pb deposit, but no nano inclusions were found (Wei et al., 2021c).

5. Controlling factors for differential enrichment of Ge, Ga, and in

5.1. Crystal structure

Zinc sulfide (ZnS) has a close-packed structure, which can be classified into the cubic sphalerite and the hexagonal wurtzite (Chen and Chen, 2010; Yang et al., 2022c). The crystal structure of minerals was affected by external physical and chemical conditions. For example, experiments have shown that higher temperature and supersaturation can cause pyrite to transform from a cube to an octahedron to a pyritohedron (Murowchick and Barnes, 1987). The conversion from sphalerite to wurtzite is more common under high-temperature conditions. Under low temperature conditions, such a conversion may require a strict condition of sulfur fugacity and redox environment (Allen et al., 1912; Scott and Barnes, 1972; Leleu et al., 1975).

The crystal structure of zinc sulfide significantly influences the distribution of trace elements. Both sphalerite and wurtzite and its derived minerals show significant enrichment of Ge (Bernstein, 1985; Höll et al., 2007; Bonnet et al., 2016; Pring et al., 2020; Voudouris et al., 2022). In the MVT Zn-Pb deposits in Tennessee, the enrichment of Ge and Cu is associated with the wurtzite structure, while the enrichment of Fe and Cd is related to the sphalerite structure (Bonnet et al., 2016). The intensive interaction between the cations in the wurtzite structure, resulting in better accommodation of large cations such as Ge, Ga, and In, may explain the enrichment of these elements in the wurtzite structure (O'Keeffe and Hyde, 1978). However, contrary to these findings, Pring et al. (2020) reports higher concentrations of Ga and In in sphalerite than wurtzite. This disparity may be due to various degrees of effects by hydrothermal fluid conditions during crystallization, M:S ratios, and coexisting minerals (Pring et al., 2020; Kisi and Elcombe, 1989).

A study on the Saint-Martin-la-Sauvete District deposit revealed preferential enrichment of In in sphalerite within the (111) growth zone, whereas Cd mainly occurs in the (110) growth zone (Johan, 1988). The sphalerite exhibits rhythmic banding and sector zoning textures aligned with the (110) and (111) crystal planes. Rhythmic banding exhibits higher In concentration, whereas sector zoning shows higher Cu, Ge, Ag, and Ga concentration (Belissont et al., 2014). Sector zoning in sphalerite is commonly influenced by imbalanced kinetic control factors, such as the atomic arrangement of the growth plane and crystal growth under constrained conditions (Di Benedetto et al., 2005). It was found that Ge and Cu in sphalerite from the MVT deposit of Tennessee are enriched along the growth direction of [010], which corresponds to (110) crystal plane (Bonnet et al., 2016). In addition to the (110) crystal plane, Ge is also enriched in the (111) crystal plane

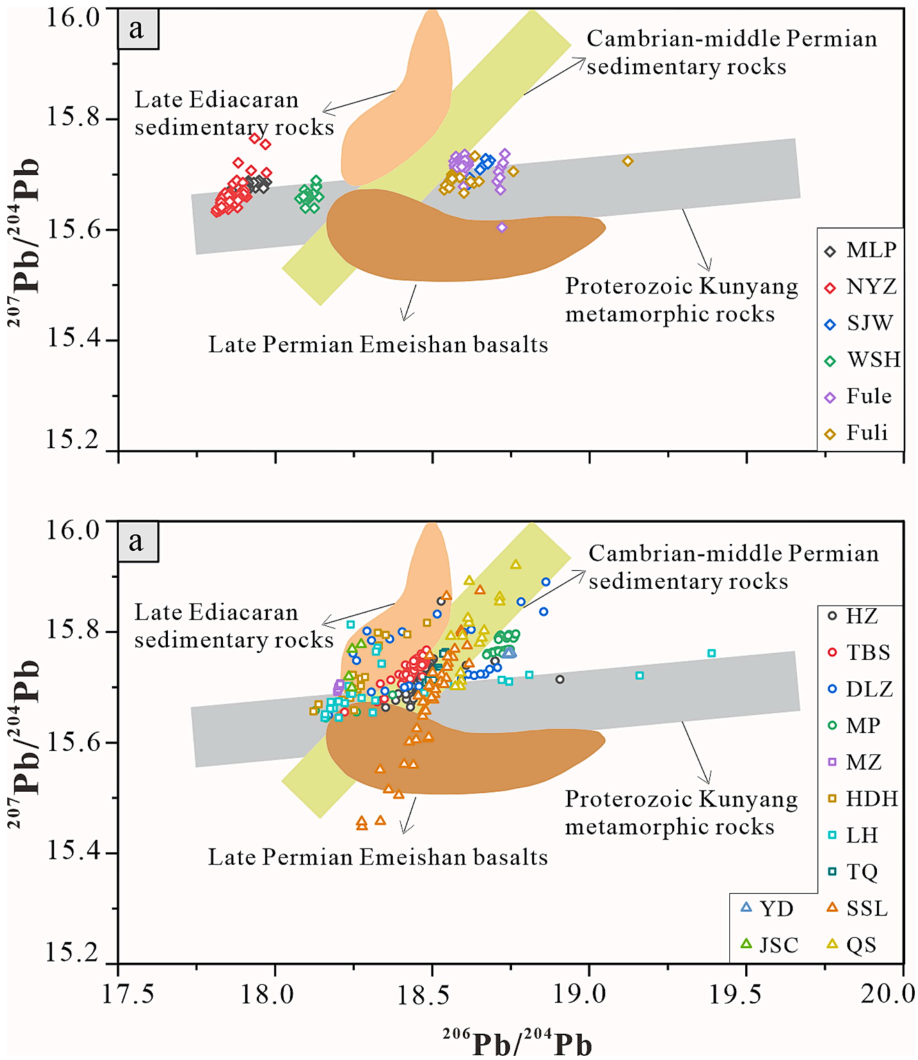

Fig. 8. Plots of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ of sulfides from Zn-Pb deposits in the SYG region showing the deposits with predominant sources of basement rocks (a) and deposits with a mixed source (b). The fields of late Permian Emeishan basalts, late Ediacaran sedimentary rocks, Cambrian-middle Permian sedimentary rocks, and Proterozoic metamorphic rocks are referred to Zhou et al., (2018a).Data sources: Maliping (Luo et al., 2019); Nayongzhi (Zhou et al., 2018b; Wei et al., 2023); Shaojiwan (Zhou et al., 2013b); Wusihe (Luo et al., 2020); Fule (Zhou et al., 2018a); Fuli (Liang et al., 2023); Huize (Zhang et al., 2023); Tianbaoshan (Tan et al., 2019b); Daliangzi (Wang et al., 2018a); Maoping (Tan et al., 2019a; Wu et al., 2021); Maozu (Wang et al., 2018b); Huodehong (Jin et al., 2016; Wu et al., 2016); Lehong (Zhao et al., 2021); Tianqiao (Zhou et al., 2014b); Shanshulin (Zhou et al., 2014a); Qingshan (Zhou et al., 2013c); Yadu (He et al., 2021); Jinshachang (Zhou et al., 2015).

which is also easily observed in the external crystal morphology (Belissont et al., 2014). A study on the Saint-Martin-la-Sauvete District deposit by (Johan, 1988) revealed preferential concentration of In in sphalerite within the (1 1 1) growth zone. Studies have demonstrated that the (1 1 0) crystal plane of sphalerite has the lowest surface energy and stability. However, for Zn-poor surface stoichiometries, the (1 1 1) surface becomes the most stable, indicating that the change in Zn content may cause the conversion between the two crystal planes (Wright et al., 1998). At present, there is a lack of research on the crystal structure of sulfides in the SYG region. The above research progress provide ideas for the future study of crystal orientation effect on the enrichment of Ge, Ga, and In in the SYG region.

5.2. Mineral textures

5.2.1. Colloform textures

Colloform textures are commonly observed in early sphalerite and have been extensively studied in Ireland-type deposits. These textures are often associated with fluid supersaturation and primarily result from the mixing of hydrothermal fluids rich in metal and bacterial sulfur. Colloform sphalerite displays a complex growth history characterized by fluctuations in color and particle size, trace element and isotope composition caused by multiple pulses of fluids (Barrie et al., 2009; Gagnevin et al., 2012; Gagnevin et al., 2014).

Some studies have shown that colloform sphalerite promotes the enrichment of Ge. For example, colloform sphalerite from the Bleiberg deposit in Austria has higher average Ge content (1500 ppm) than sphalerite with normal texture (160–550 ppm) (Möller and Dulski, 1993). Similarly, colloform sphalerite from the Cave de predil Zn-Pb deposit in Italy contains 500 ppm Ge, whereas normal sphalerite has Ge content below 200 ppm (Möller and Dulski, 1993). Likewise, colloform sphalerite from the Huodehong and Nayongzhi deposits has higher Ge content than normal sphalerite (Fig. 6a). A similar pattern is observed in the Zhulingou deposit in eastern Guizhou and the Jinding Pb-Zn deposit in the Sanjiang region (Fig. 6a). However, there is no similar trends of Ga contents between sphalerite with colloform and normal textures. The colloform sphalerite has similar (e.g., Huodenghong), higher (e.g., Zhulingou), or lower (e.g., Jinding) Ga contents

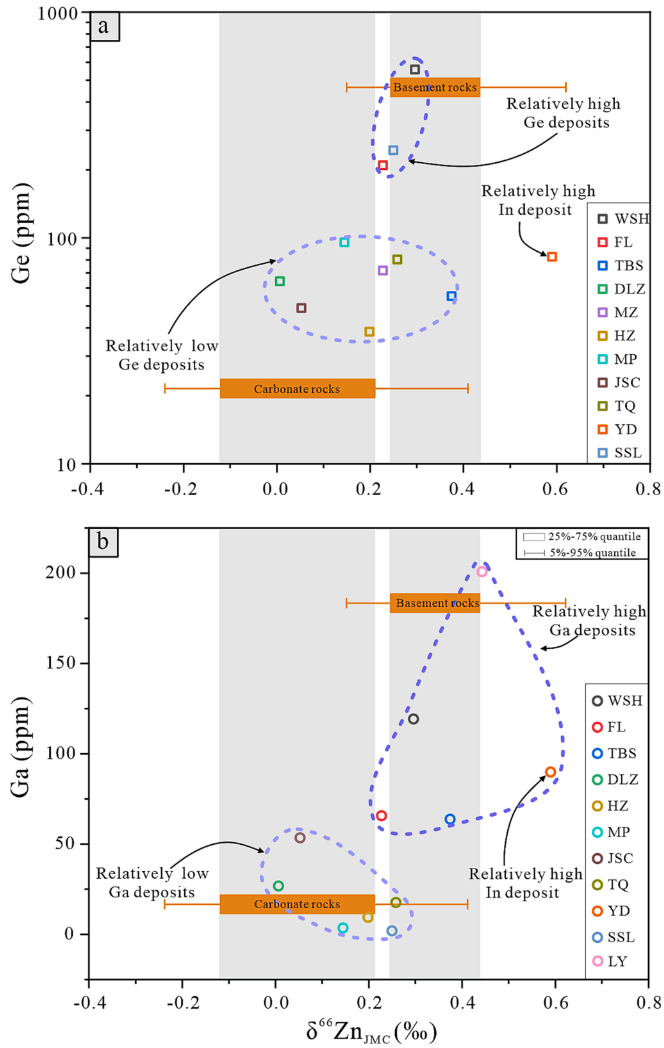

Fig. 9. The plots of average Ge and Ga contents in sphalerite versus Zn isotopic composition. Data sources of Zn isotopes: Wusihe (WSH) (Zhang et al., 2019a); Jinshachang (JSC), Maozu (MZ), Daliangzi (DLZ) and Fule (FL); Tianbaoshan (TBS) (He et al., 2016; Xu et al., 2020; Zhang et al., 2019b); Huize (Zhang et al., 2022); Maoping (Wu et al., 2021); Tianqiao (TQ) (Zhou et al., 2014b); Yadu (YD) (He et al., 2021); Shanshulin (SSL) (Zhou et al., 2014a); Liangyan (Wu et al., 2023).

than sphalerite with normal texture (Fig. 6b).

5.2.2. Zoned textures

The zoned textures can be divided into rhythmic banding and normal zoned textures. Rhythmic banding were found in Saint-Salvy deposit (Belissont et al., 2014). Normal zoned textures have been observed in Zn-Pb deposits in the SYG region, including the Wusihe, Huize, Lehong, Nayongzhi, and Tianqiao deposits (Wei et al., 2019, 2021b; Liu et al., 2022a; Yang et al., 2022b). Although rhythmic banding and normal zoned textures exhibit similar morphology, they differ in terms of color, element partition, and geochemical behaviors (Belissont et al., 2014; Wei et al., 2019, 2021b; Liu et al., 2022a; Fougerouse et al., 2023).

Rhythmic bands are usually associated with sector zoning. In the Saint-Salvy deposit, elements Cu, Ag, Ge, and Ga are preferentially enriched in the sector zoning, whereas Fe, In, and Sn are enriched in the rhythmic banding (Belissont et al., 2014). Sector zoning exhibits more pronounced variations in color and element contents compared to rhythmic banding. However, there is negligible element partition observed in the rhythmic banding, suggesting that there are no Ge, Ga, and In partitions in the rhythmic banding (Belissont et al., 2014). In normal zoned textures, brown domain of zoned sphalerite from the Nayongzhi deposit has higher Ge and lower Ga and In contents than the light domain (Wei et al., 2021c). This trend is similar to the observation of the Wusihe deposit (Luo et al., 2021). Germanium is more enriched in dark domain than light domain of sphalerite from the Huize deposit (Liu et al., 2022a). Germanium is also relatively enriched in Fe-rich zone (dark sphalerite) in the Tres Marias MVT Zn deposit in Mexico (Cook et al., 2015). Therefore, Ge is predominantly enriched in the dark sphalerite compared to light sphalerite in normal zoned textures. The two textures correspond to the influence of internal (Holten et al., 1997; Di Benedetto et al., 2005) and external (Wei et al., 2021c) mechanisms, so there is no change in Ge, Ga and In in the rhythmic banding, whereas the change in the normal zoned textures is obvious.

5.3. Source of ore-forming materials

5.3.1. Background of Ge, Ga, and in

The Ge, Ga, and In contents of sedimentary strata (Mesozoic, Cambrian, Devonian, Paleozoic and Permian) and underlying basement rocks in the SYG region are illustrated in Fig. 7. The basement rocks have higher Ge and In contents than sedimentary strata in all ages (Fig. 7a, c). It is likely that the basement rocks represent an important source of Ge and In. However, the basement rocks have similar Ga contents to the Cambrian, Devonian and Permian carbonate strata (Fig. 7b). Therefore, both basement rocks and carbonate strata can serve as potential sources for Ga.

5.3.2. Various degree of involvement of basement rocks

Lead and Zn isotopes are crucial tools to constrain the source of ore-forming materials in Zn-Pb deposits (Leach et al., 2010; Xiong et al., 2022). Based on published Pb isotope data, four possible sources of ore-forming materials are defined (Zhou et al., 2010, 2012, 2013c): 1) the Proterozoic Kunyang metamorphic rocks representing basement rocks endmember, 2) Late Ediacaran and 3) Cambrian-middle Permian sedimentary rocks representing carbonate strata endmember, and 4) Late Permian Emeishan basalts representing main magmatic rocks endmember (Fig. 8). Sulfides from the Maliping, Nayongzhi, Shaojiwan, Wusihe, Fule, and Fuli deposits have Pb isotope compositions similar to the Proterozoic Kunyang metamorphic basement rocks (Fig. 8a), whereas sulfides from other deposits plot in the overlapping field between carbonate strata and basement rocks (Fig. 8b). Sphalerite from the Nayongzhi, Shaojiwan, Wusihe, Fule, and Fuli deposits have a basement source and higher average Ge, and Ga contents of 111.15–556.73 ppm, and 22.35–120.76 ppm, respectively (Fig. 2a). The Maliping Zn-Pb deposit is the most In-rich deposit in the SYG region (Fig. 2a), with Pb isotope compositions indicating a basement source. This indicates that basement rocks have played important role in the enrichment of Pb and associated Ge, Ga and In.

In addition to Pb isotopes, Zn isotopes of sulfides of basement rocks and carbonate rock strata can also be distinguished in terms of main compositional ranges (Fig. 9). It was shown that sulfides from deposits with relatively low Ge content (<~100 ppm) have Zn isotope composition between those of basement rocks and carbonate rock strata (Fig. 9a). Sulfides from those Zn-Pb deposits with relatively high Ge content (>~100 ppm) have Zn isotope composition similar to those of basement rocks (Fig. 9a). This indicates that involvement of basement rocks in the ore formation is beneficial for the enrichment of Ge. This conclusion is similar to the result of Pb isotopes. The same observation is for Ga (Fig. 9b). In addition, sulfides with high In content of Yadu deposit are commonly have Zn isotope composition similar to basement rocks (Fig. 9a, b). Therefore, Zn isotope composition indicates that basement rocks play important role in the enrichment of Zn and associated Ge, Ga, and In.

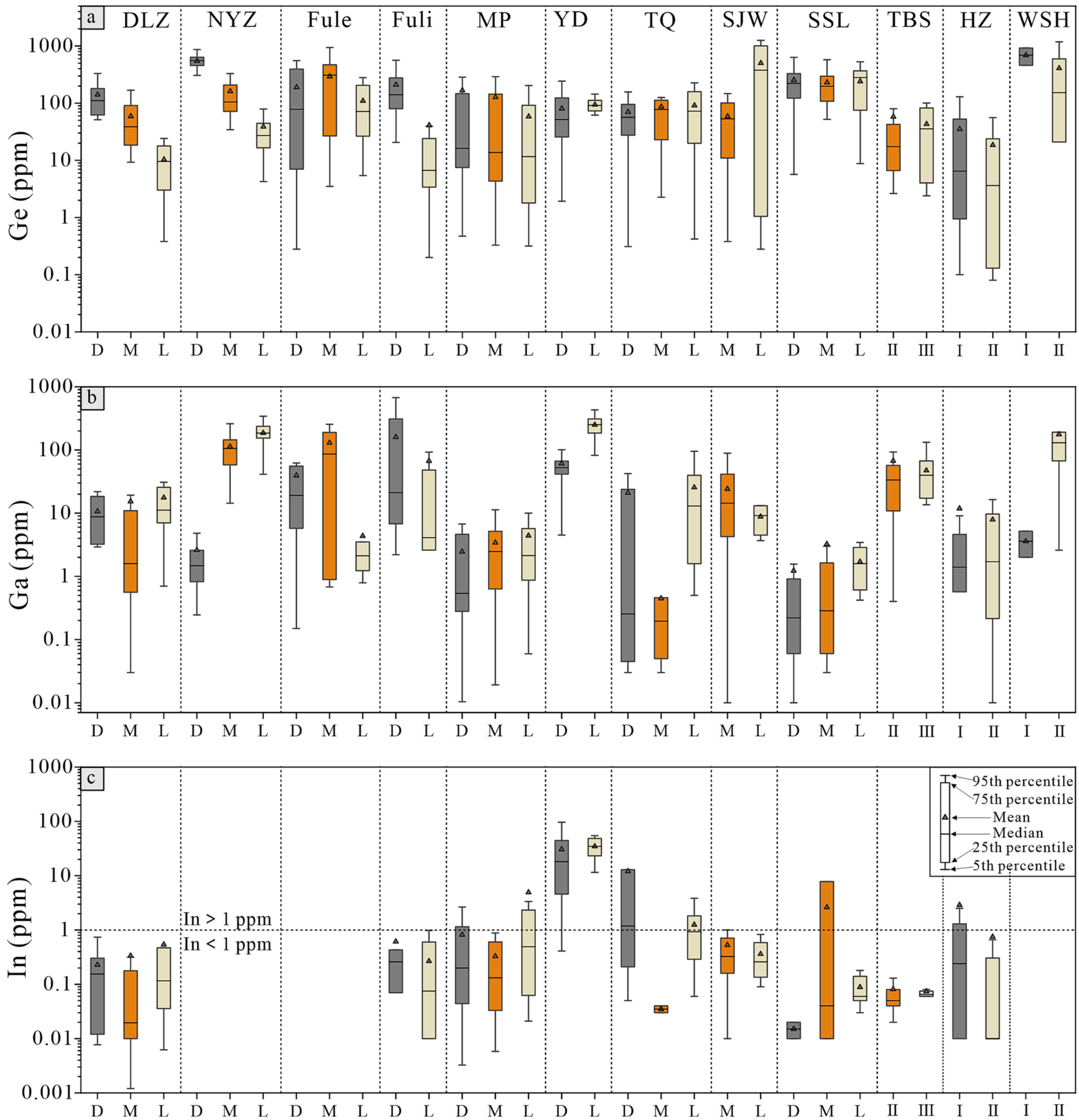

Fig. 10. The contents of Ge (a), Ga (b) and In (c) in sphalerite of different colors or stages in Zn-Pb deposits in SYG region. D, M and L represent dark, middle and light sphalerite, whereas I-III represent three stages of sphalerite. Data sources: Daliangzi (DLZ) (Li et al., 2022b); Nayongzhi (NYZ) (Wei et al., 2021c); Fule (Ren et al., 2019); Fuli (Liang et al., 2023); Maoping (MP) (Wang et al., 2023a); Yadu (YD), Tianqiao (TQ), Shaojiwan (SJW), Shanshulin (SSL) (Yang et al., 2022b); Tianbaoshan (TBS) (Yu et al., 2022); Huize (HZ) (Oyebamiji et al., 2020).

5.4. Ore-forming process

The contents of Ge, Ga, and In in sphalerite formed in different stages and with different colors are affected by the physical and chemical condition of ore-forming fluids (Barrie et al., 2009; Belissont et al., 2014; Wei et al., 2021c), and crystal self-organization processes (Di Benedetto et al., 2005; Belissont et al., 2014). Numerous studies of Zn-Pb deposits in the SYG region have considered that dark sphalerite corresponds to the early stage of mineralization, whereas light sphalerite corresponds to the late stage of mineralization (Zhou et al., 2014b; Wei et al., 2019; Li et al., 2022b; Luo et al., 2022b; Yu et al., 2022). The temperature of GGIMFis also supports the interpretation that the transition from dark to light sphalerite corresponds to a cooling process (Appendix A Table 4). There is a correlation between the color and stages of sphalerite and the contents of Ge. For most deposits such as the Daliangzi, Tianbaoshan, Huize, Nayongzhi, Fule, Fuli, Wusihe, and Maoping deposits, the early or dark sphalerite has higher Ge content than the late or light sphalerite (Fig. 10a). The variation patterns of Ga and Ge with sphalerite color or stage in the Daliangzi, Nayongzhi, Maoping, Shaojiwan, and Wusihe Zn-Pb deposits are opposite (Fig. 10a-b). This indicates that the controlling factors for the distribution of Ge and Ga may be different. There is no obvious correlation between the content of In and color or stage due to the relatively low content in sphalerite (Fig. 10c).

In the process of fluid precipitation, the physical and chemical conditions changes. Some studies suggest that Ge and Ga are conducive to enrichment in low-temperature Pb-Zn deposits, and In tends to be enriched in high-temperature Pb-Zn deposits (Cook et al., 2009; Ye et al., 2011). Germanium and Ga in the sphalerite of the Freiberg district also tend to be enriched in low-temperature fluids, whereas In tends to be enriched in high-temperature fluids (Bauer et al., 2019). Because the contents of Ge and Ga are related with the colors and stages of sphalerite, the precipitation of these two elements may be related to temperature to some degree during Zn-Pb mineralization. However, there is no correlation between In content and different colors and stages of sphalerite, which may be attributed to a In-depleted source of fluids as the first-order of control on metal enrichment.

6. Conclusion

Nearly twenty Zn-Pb deposits in the SYG region rich in critical metals such as Ge, Ga, and In are investigated for the deposit geology, trace element and isotope compositions of sulfide minerals. The data set are used to discuss the distribution, occurrence, and the enrichment mechanism of Ge, Ga, and In. The conclusions are summarized as follows. Sphalerite is the main host mineral of Ge, Ga, and In in the SYG region, locally pyrite is also rich in Ge. Germanium, Ga, and In mainly appear in the form of isomorphism in sphalerite, and independent mineral of Ge, ruizhongite, is only found in the Wusihe Zn-Pb deposit. Copper is the main coupling ions for substitution of Ge, Ga, and In in sphalerite. The substitution mechanisms vary both on deposit and mineral grain scales. Compared to sphalerite with normal texture, colloform sphalerite is beneficial for the enrichment of Ge. For zoned sphalerite, dark domain is more enriched in Ge and Ga than light domain. The involvement of basement rocks may have a significant effect on the budget of Ge, Ga, and In in the ore-forming fluids. During the Zn-Pb mineralization, Ge is usually richer in dark or early sphalerite, which may be related to variation in temperature. No correlation between Ga or In and the color or stage of sphalerite indicates that these two elements behave differently from Ge.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.oregeorev.2023.105853.

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