

Article

Mantle Volatiles and Heat Contributions to the Cu-Pb-Zn Mineralization in the Baoshan Deposit, South China: Constraints from He and Ar Isotopes

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Abstract: The Baoshan deposit is one of the important Cu-Pb-Zn deposits associated with granitic rocks in the Nanling Range, South China. Here, we present He and Ar isotope data for the Baoshan deposit to decipher the contributions of mantle-derived volatiles and heat to its Cu-Pb-Zn mineralization. The ore-forming fluids in sphalerite and pyrite exhibited $^3\text{He}/^4\text{He}$ ratios up to 1.51 Ra. A linear correlation between He and Ar isotopes suggests that the ore-forming fluids were a mixture of a predominantly mantle-derived fluid with a high $^3\text{He}/^4\text{He}$ ratio and a shallow crustal fluid, characterized by a low $^3\text{He}/^4\text{He}$ ratio. The $\delta^{34}\text{S}$ values of sulfides in the Baoshan deposit ranged from +2.30 to +5.21‰, consistent with the magma-derived sulfur. The calculated $^3\text{He}/\text{Q}$ ratios for the ore-forming fluid exceeded those of mid-oceanic ridge hydrothermal solutions by 10 to 50 times, indicating that the ore-forming fluids acquired both heat and volatiles in a convective hydrothermal regime rather than a conductive one. Therefore, there is a significant contribution of mantle-derived volatiles, heat, and possibly metals, to the Cu-Pb-Zn mineralization in the Baoshan deposit, and the continuous influx of mantle-derived fluids/melts probably plays a crucial role during the Cu-Pb-Zn mineralization related to granitic rocks.

Keywords: He-Ar isotopes; Cu-Pb-Zn mineralization; mantle-derived fluid; Baoshan deposit; South China



Citation: Huang, J.; Peng, J.; Xie, T. Mantle Volatiles and Heat Contributions to the Cu-Pb-Zn Mineralization in the Baoshan Deposit, South China: Constraints from He and Ar Isotopes. *Minerals* **2024**, *14*, 839. <https://doi.org/10.3390/min14080839>

Academic Editor: Ferenc Molnár

Received: 24 July 2024

Revised: 13 August 2024

Accepted: 18 August 2024

Published: 19 August 2024



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1. Introduction

Since the Mesozoic, South China has experienced significant tectonic activities and extensive magmatism [1–3], which contributed to the emplacement of substantial granites and the numerous related Cu-Pb-Zn, W-Sn, and Nb-Ta deposits [4–9]. Many aspects, including the metallogenic specialization, geochronology, tectonic setting, and mechanisms, have been topics of great interest among geologists for many years [5,7,10–14]. Traditionally, it is widely accepted that the Cu-Pb-Zn mineralization in South China preceded W-Sn mineralization, and these distinct types of hydrothermal mineralization formed during two independent metallogenic systems [11–19].

The Cu-Pb-Zn deposits in southern Hunan Province, situated in the central part of the Nanling Range, comprise the significant Cu-Pb-Zn ore districts in South China. In the last two decades, extensive studies have been carried out on the chronology and petrogenesis of the granodioritic rocks, along with associated ore deposits, and their corresponding geodynamic settings [16–22]. These investigations have provided compelling evidence that the Cu-Pb-Zn mineralization formed simultaneously with the large-scale W-Sn mineralization in the Nanling Range [6,20,23]. The complex relationship of these two mineralization types remains poorly understood.

Noble gas isotopes (He and Ar) are unique in tracing the contributions of mantle volatiles to the formation of ore deposits [24–32], due to the contrasting $^3\text{He}/^4\text{He}$ ratios between the upper mantle (6–9 Ra; where Ra is the atmospheric $^3\text{He}/^4\text{He}$ ratio, 1.39×10^{-6}) [33] and the crustal rocks (0.01–0.05 Ra) [25]. Consequently, it is of great significance to ascertain the He–Ar isotope signatures of the ore-forming fluid responsible for W–Sn deposits and Cu–Pb–Zn deposits, which can provide powerful information to better understand the relationship between both different metallogenic systems.

Numerous studies on He–Ar isotopes have been conducted on these W–Sn deposits in South China, and different proportions of mantle components were discovered to be involved in the formation of the W–Sn deposits [13,34–41], with the large-scale W–Sn mineralization in South China considered to result from the crust–mantle interaction [26,42]. In contrast, the Cu–Pb–Zn mineralization in this region has received less attention [43], and the constraint of He–Ar isotopes on the Cu–Pb–Zn mineralization is still unclear.

The Baoshan deposit, located in southern Hunan, is a significant porphyry- and skarn-type Cu–Pb–Zn deposit in the Qin–Hang belt [5,44]. It contains 238.7 kt Cu at a grade of 1.28%, 512.8 kt Zn at 4.34%, 470.7 kt Pb at 3.82%, and 11.7 kt Mo at 0.12% [45]. Previous studies have been carried out on the deposit, including the sources of the metallogenic materials [45–51], as well as the geochronology and petrogenesis of the related granitoids [17,18,52,53]. It is widely accepted that the Cu–Pb–Zn mineralization is spatially, temporally, and genetically associated with the granodiorite porphyry, which was believed to be formed by the crustal magma mixed with mantle-derived magma [18,45,46,48,53]. However, it is still unclear as to how, and to what extent, the mantle-derived magma initiated the felsic magmatism and drove the mineralizing fluid upwards.

In this study, we first present the He and Ar isotopic data for sulfides collected from the Baoshan deposit and aimed to assess the contributions of mantle-derived volatiles and heat during its ore formation; then, we elucidated its ore genesis, which can provide an important indicator for elucidating the relationship between the W–Sn mineralization and the Cu–Pb–Zn mineralization in South China.

2. Geological Settings

South China is composed of the Yangtze Block to the northwest and the Cathaysian Block to the southwest, separated by the Qin–Hang Neoproterozoic suture [54,55] (Figure 1). The basement comprises weakly metamorphosed Precambrian folded strata, unconformably covered by the folded strata from the Neoproterozoic (Sinian) to Mesozoic [56]. The granitic rocks and genetically associated W–Sn and Pb–Zn deposits are widespread throughout southern Hunan, South China [5,7,12,57–59] (Figure 1). Granite-related W–Sn deposits in the region mainly include the Yaogangxian W deposit [12,26,60], Shizhuyuan W–Sn deposit [35,61–63], Furong Sn deposit [13,64–66], and Xianghualing Sn deposit [32,67–69]. The Cu–Pb–Zn deposits in this region mainly include the Shuikoushan Pb–Zn–Au deposit [20,21,70], Baoshan Cu–Pb–Zn deposit [18,50,51,71,72], and Tongshanling Cu–Pb–Zn deposit [22,73].

The Baoshan deposit, situated in southern Hunan, comprises the central Cu–Mo–Bi ore block and Pb–Zn–Ag ore blocks, including the western block, northern Caishenmiao ore block, and eastern ore block (Figure 2). In this district, the stratigraphic sequence mainly consists of Carboniferous sandstone, limestone, and siltstone sedimentary rocks. The Devonian limestone is rare and found only locally occurs in the eastern part. Pb–Zn ores in the Baoshan deposit are primarily confined to the Carboniferous carbonate rocks (Figure 2) [48]. The deposit is characterized by a series of NE–NEE-trending reverse and synclinal folds, as well as NE–NEE- and NWW-trending faults.

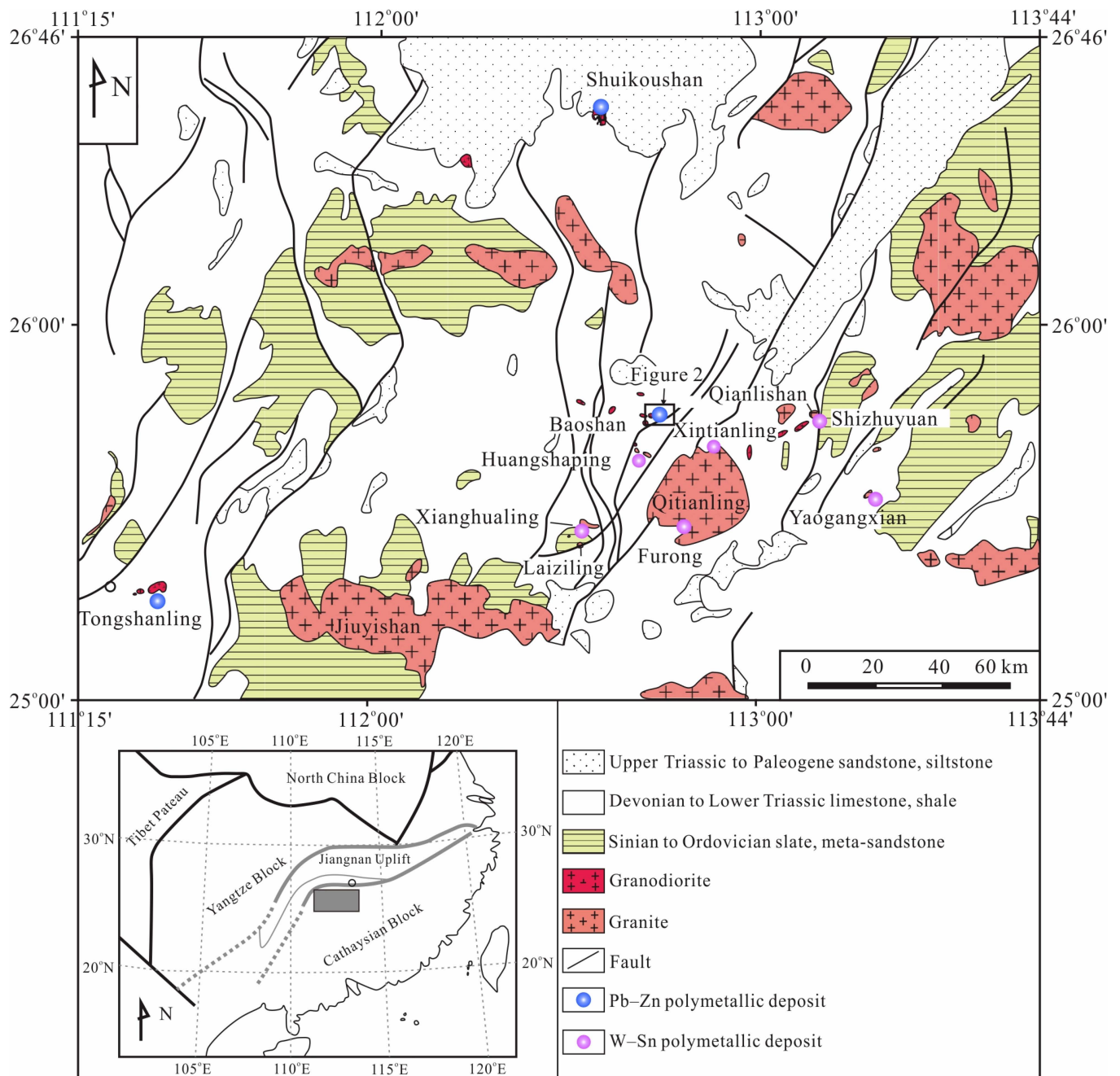


Figure 1. Distribution of some important Pb-Zn and W-Sn deposits in southern Hunan, South China. Modified after references [12,17].

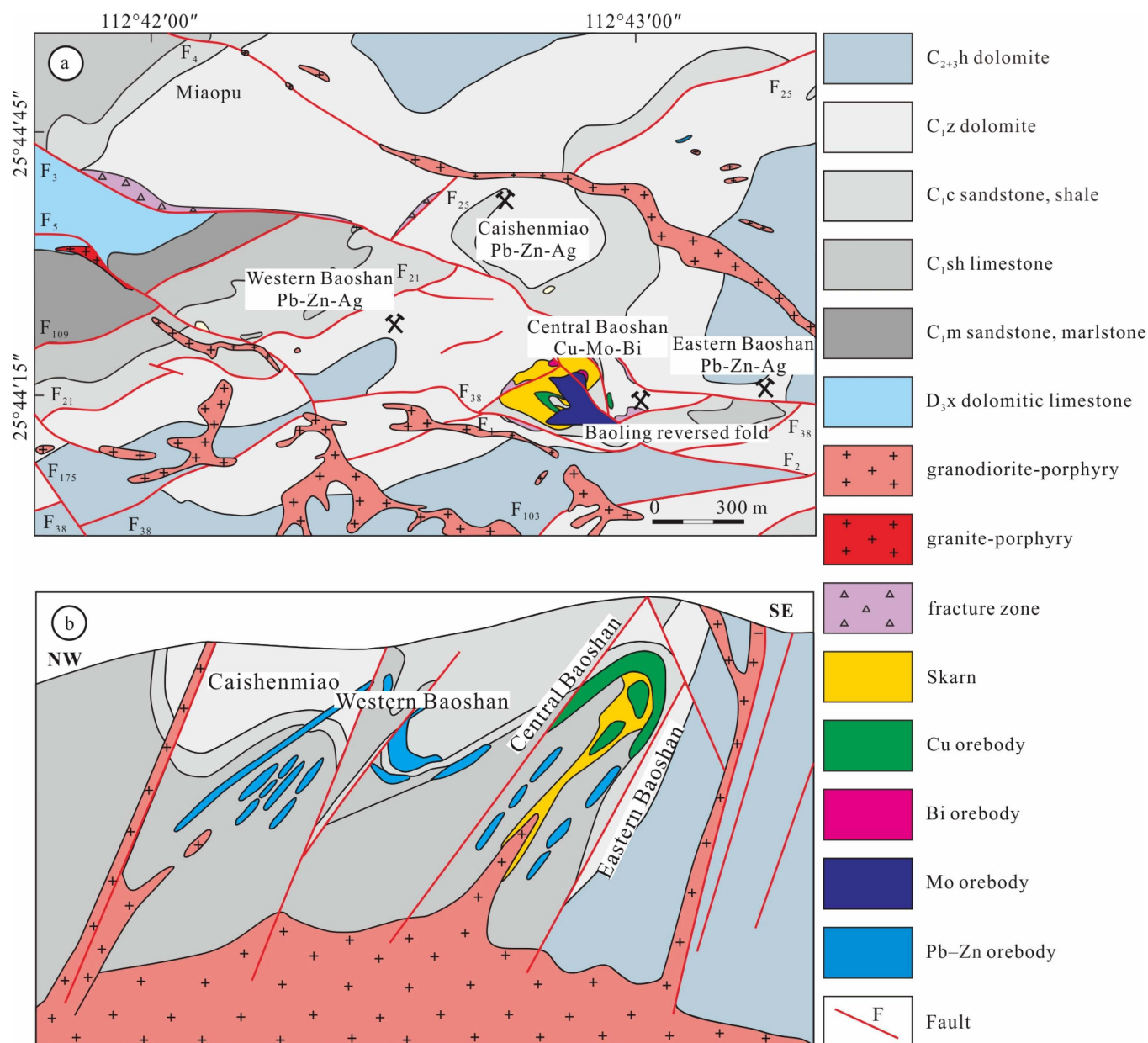


Figure 2. (a) Simplified geological map and (b) cross-section map for the Baoshan Cu–Pb–Zn deposit in southern Hunan, South China. Modified from references [48,74].

A total of 26 exposed intrusions, including granite-porphyry, granodiorite-porphyry [74], and lamprophyre [75], occur in the Baoshan deposit. Among these, granodiorite-porphyry is the most significant, characterized by some different-sized mafic microgranular enclaves (MMEs) [52]. These intrusions exhibit SiO_2 content in the range of 61.2–68.8 wt.%, K_2O 3.50–5.31 wt.%, and the A/CNK ratios ranging from 0.79 to 0.97 [52]. They were usually classified as I-type granite [17,52], with metaluminous to weak peraluminous, and high-K calc-alkaline series signatures [52]. Additionally, zircons from the MMEs yielded a U–Pb age of 155.2 ± 1.4 Ma, consistent with the emplacement time of the granodiorite porphyry within analytical errors (156–158 Ma) [18,52]. The molybdenite Re–Os dating on the Cu–Mo-bearing skarn in the central ore block indicates that the Cu–Mo mineralization in the deposit took place at 160 ± 2 Ma [18].

The orebodies at the Baoshan deposit are primarily governed by the Baoling reverse fold (Figure 2). Around the granodiorite-porphyry intrusions, distinct mineralization zones are observable. The sequence from the core outward includes hypothermal skarn Cu–Mo

mineralization, mesothermal Cu-Pb-Zn mineralization, meso- and epithermal Pb-Zn-Ag mineralization, and finally distal epithermal Ag-Mn mineralization (Figure 2a) [76,77]. The Cu-Mo-Bi ore blocks in the central Baoshan are outcropping and located at the top or in the two limbs near the top of the reversed fold [77]. In contrast, other ore blocks in the deposit are concealed, occurring within the two limbs of the Baoling fold (Figure 2). Cu-Mo ores include complex minerals and occur as stockwork and disseminated, while Pb-Zn-Ag ores occur as massive [76]. The deposit contains mainly sphalerite, galena, chalcopyrite, scheelite, bismuthinite, and molybdenite (Figure 3) [74]. Gangue minerals primarily include calcite, quartz, and fluorite, with minor garnet and tremolite [53]. Textures, crosscutting relationships, and mineral assemblages suggest that mineralization in the Baoshan deposit formed at four stages: an early skarn stage, a retrograde stage, a metal sulfides stage, and a late fluorite-calcite stage [49]. The metal sulfides stage is one of the most important stages in the Baoshan Cu-Pb-Zn deposit. The ore minerals mainly include pyrite, pyrrhotite, galena, and sphalerite, with minor quartz, fluorite, and calcite. Interestingly, pyrite is frequently associated with violet fluorite (Figure 3c,f), while galena and sphalerite are usually associated with green fluorite (Figure 3e).

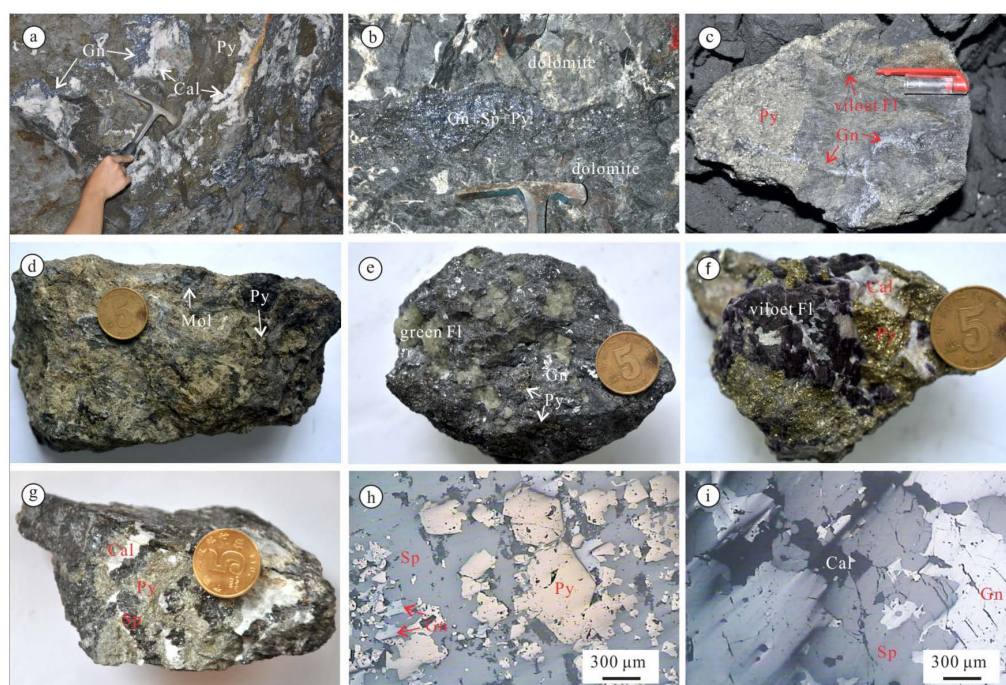


Figure 3. Field photographs, hand specimen photographs, and micrographs of ores from the Baoshan Cu-Pb-Zn deposit, South China. (a) Pyrite and galena occurring in C₁sh limestone; (b) sphalerite, galena, and pyrite vein occurring in dolomite; (c) pyrite coexisting with violet fluorite cut by galena; (d) coarse-grained pyrite associated with minor disseminated molybdenite in the skarn; (e) galena coexisting with green fluorite; (f) pyrite coexisting with violet fluorite; (g) pyrite and sphalerite coexisting with calcite; (h) subhedral pyrite coeval with sphalerite and galena replaced pyrite; (i) galena coeval with sphalerite and replaced by calcite. Abbreviations: Cal—calcite; Fl—fluorite; Gn—galena; Py—pyrite; Sp—sphalerite.

3. Sampling and Analytical Methods

Seven pyrite and sphalerite samples from three Pb-Zn ores and four pyrite ores of the metal sulfides stage were analyzed for He-Ar and S isotopes. The samples were collected from underground adits at different elevations (150 m and 190 m) in the Caishenmiao ore block. Using a binocular microscope, pure samples were selected from the crushed ores. Comprehensive details about these samples are provided in Table 1.

Table 1. A summary of the characteristics for the studied samples from the Baoshan Cu-Pb-Zn deposit.

Sample No.	Minerals	Sections	Sample Type	Mineralogical Characteristics
BS-7	Sp	−190 m	Pb-Zn ores	Massive structure, fine-grained pyrite accompanied by brownish sphalerite and calcite.
BS-11	Py	−190 m	Pyrite ores	Massive structure, abundant cubic pyrite accompanied by calcite and violet fluorite in the skarn.
BS-12	Sp	−190 m	Pb-Zn ores	Massive structure, abundant coarse-grained brownish sphalerite with minor galena and fine-grained pyrite.
BS-13	Py	−150 m	Pyrite ores	Massive structure, abundant coarse-grained and cubic pyrite with minor calcite.
BS-15	Py	−150 m	Pyrite ores	Massive structure, abundant coarse-grained and cubic pyrite with minor calcite.
BS-18	Py	−150 m	Pyrite ores	Massive structure, fine-grained pyrite accompanied by violet fluorite and calcite, also cut by veined calcite.
BS-25	Py	−150 m	Pb-Zn ores	Massive structure, fine-grained pyrite with fine-grained sphalerite.

He-Ar isotopic composition of sulfide separates was performed by a GV5400 mass spectrometer at the State Key Laboratory of Ore Deposit Geochemistry (SKLOGD), Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). Approximately 1.2–1.4 g coarse-grained (0.5–1.5 mm) sulfides were baked at about ~150 °C under ultra-high vacuum conditions for more than 24 h before analysis to eliminate adhered atmospheric gases. The volatiles in fluid inclusions were extracted through sequential crushing to eliminate secondary fluid inclusions, following the experimental procedures described by Hu et al. (2012) [26]. Procedural blanks with $<2 \times 10^{-10} \text{ cm}^3 \text{ STP } ^4\text{He}$ and $<4 \times 10^{-10} \text{ cm}^3 \text{ STP } ^{40}\text{Ar}$ were insignificant.

Sulfur isotopic composition was conducted using the MAT253 gas stable isotope ratio mass spectrometer at the State Key Laboratory of Ore Deposit Geochemistry, IGCAS. Detailed analytical procedures followed those described by Yang et al. (2021) [78]. All data were reported in $\delta^{34}\text{S}$ notation as per mil (‰) relative to Canyon Diablo Troilite (CDT). Samples were calibrated against external standard IAEA S1 ($\delta^{34}\text{S} = -0.3\text{‰}$), IAEA S2 ($\delta^{34}\text{S} = +22.62\text{‰}$), and IAEA S3 ($\delta^{34}\text{S} = -32.49\text{‰}$); the analytical uncertainties ($\pm 1\sigma$) for $\delta^{34}\text{S}$ were better than 0.2‰.

4. Results

He, Ar, and S isotopic data of pyrite and sphalerite separates in this study are listed in Table 2. Errors quoted at the 1σ confidence level. The concentrations of ^4He changed from 7.04×10^{-6} to $273 \times 10^{-6} \text{ cm}^3 \text{ STP g}^{-1}$, and the ^{40}Ar concentrations varied in the range of $(1.83\text{--}28.5) \times 10^{-7} \text{ cm}^3 \text{ STP g}^{-1}$. The large variations in noble gas concentrations likely reflect the He and Ar abundance variations within fluid inclusions in minerals. The $^3\text{He}/^4\text{He}$ ratios of the ore-forming fluid ranged from 0.04 to 1.51 Ra and its $^{40}\text{Ar}/^{36}\text{Ar}$ ratios varied in the range of 303–596. Additionally, the $\delta^{34}\text{S}$ values of sulfides in this study ranged from 2.30 to 5.21‰ (Table 2).

Table 2. He, Ar, and S isotopic results of sulfides collected from the Baoshan Cu-Pb-Zn deposit.

Sample	Mineral	Weight (g) ¹	⁴ He (10 ^{−7} cm ³ STP)	⁴⁰ Ar (10 ^{−7} cm ³ STP)	³ He/ ⁴ He (Ra)	⁴⁰ Ar/ ³⁶ Ar	³ He/ ³⁶ Ar (10 ^{−5})	⁴⁰ Ar*/ ⁴ He (10 ^{−3})	⁴ He (cm ³ STP g ^{−1})	⁴⁰ Ar (cm ³ STP g ^{−1})	F ⁴ He ²	⁴⁰ Ar* % ³	He _{mantle} (%)	³ He/Q (10 ^{−12} cm ³ STP J ^{−1}) ⁴	δ ³⁴ S (‰)
BS-7	Sp	0.24	2.04 ± 0.04	3.02 ± 0.05	0.65 ± 0.02	308 ± 7	18.71 ± 0.60	46.5 ± 0.68	8.61 × 10 ^{−6}	1.28 × 10 ^{−6}	1256	4.1	10.6	0.217	4.37
BS-11	Py	0.20	8.08 ± 0.17	0.37 ± 0.01	0.25 ± 0.01	596 ± 34	440.41 ± 26.9	23.0 ± 0.07	3.95 × 10 ^{−5}	1.83 × 10 ^{−7}	77910	50.4	3.9	5.10	5.02
BS-12	Sp	0.16	17.08 ± 0.36	4.55 ± 0.07	0.06 ± 0.01	303 ± 7	10.09 ± 0.38	3.6 ± 1.57	1.07 × 10 ^{−4}	2.85 × 10 ^{−6}	6861	2.4	0.9	0.117	2.30
BS-13	Py	0.22	59.20 ± 1.26	2.06 ± 0.03	0.04 ± 0.01	329 ± 7	52.79 ± 1.79	3.2 ± 0.23	2.73 × 10 ^{−4}	9.51 × 10 ^{−7}	56979	10.1	0.5	0.612	2.89
BS-15	Py	0.28	17.80 ± 0.38	2.55 ± 0.04	0.14 ± 0.01	326 ± 7	45.06 ± 1.44	11.9 ± 0.25	6.40 × 10 ^{−5}	9.18 × 10 ^{−7}	13712	9.3	2.2	0.522	2.56
BS-18	Py	0.21	4.51 ± 0.10	1.32 ± 0.02	1.51 ± 0.05	557 ± 14	398.89 ± 12.0	136.0 ± 0.05	2.19 × 10 ^{−5}	6.43 × 10 ^{−7}	11465	46.9	25.1	4.62	5.21
BS-25	Py	0.18	1.28 ± 0.03	3.87 ± 0.06	1.37 ± 0.04	312 ± 7	19.75 ± 0.57	128.2 ± 0.50	7.04 × 10 ^{−6}	2.12 × 10 ^{−6}	625	5.2	22.8	0.229	3.48

¹ Sample weights refer to the <100 µm fractions after crushing. ² F⁴He values reflect the enrichment of ⁴He in the fluid relative to air; F⁴He = (⁴He/³⁶Ar)_{sample}/(⁴He/³⁶Ar)_{atmosphere} where (⁴He/³⁶Ar)_{atmosphere} = 0.1655. Tables may have a footer. ³ ⁴⁰Ar* is non-atmospheric Ar, ⁴⁰Ar* = ⁴⁰Ar − [³⁶Ar × 298.6], ⁴⁰Ar*% = [(⁴⁰Ar/³⁶Ar)_{sample} − 298.6] × 100/[(⁴⁰Ar/³⁶Ar)_{samples}]. ⁴ ³He/Q = ³He/³⁶Ar × [³⁶Ar]MASW/(Cpθ), where [³⁶Ar]MASW refers to the ³⁶Ar concentration in MASW (7.65 × 10^{−7} cm³ STP g^{−1}), Cp denotes the specific heat of MASW (4.4 JK^{−1} g^{−1}), and θ is the temperature increase in the cold fluid (°C) [27,29,30]. The homogenization temperatures of 150.0 °C determined by Ding et al. (2016) [45] were used to calculate θ in this study.

5. Discussion

5.1. Post-Entrapment Modification of Fluid Inclusions

Some modifications after fluid inclusion trapping, such as He loss, in situ production of ^4He and ^{40}Ar , and contamination by atmospheric Ar and cosmogenic ^3He , probably affect the He and Ar isotopic compositions of the fluid inclusions [24,27,79].

It has been shown that the He loss caused by diffusion cannot lead to significant He isotope fractionation [24,26]. Additionally, the concentrations of U and Th in the ore-forming fluid are commonly low [26], and thus the in situ accumulation of radiogenic ^4He from the dissolved U in the fluid can be neglected. Cosmogenic He can also be excluded since all samples in this study were collected from the underground significantly below the Earth's surface [80]. The sulfides analyzed in this study are well-crystallized euhedral grains with no obvious subsequent deformation. In addition, the fluid inclusions in the sphalerite are mainly primary [49]. Adhered atmospheric gases and secondary fluid inclusions can also be eliminated by pre-baking at $\sim 150^\circ\text{C}$ prior to crushing [32]. Furthermore, potassium concentrations in pyrite and sphalerite are extremely low [81], indicating little radiogenic ^{40}Ar was released by in situ decay from the mineral lattice and can be negligible. Consequently, the measured isotopic values of noble gases in this study can be used to trace the source of the ore-forming fluid responsible for the Cu-Pb-Zn mineralization in the Baoshan deposit.

5.2. Sources of He, Ar, and S

He and Ar in the ore-forming fluids primarily originated from mantle-derived volatiles; radioactive decay of U, Th, and K in crustal rocks; and air-saturated water (ASW) [25,82]. The atmospheric He concentration is too low to significantly affect the analytical results; moreover, the contribution of atmospheric He can be further evaluated by the $F^4\text{He}$ value [28]. As listed in Table 2, the calculated $F^4\text{He}$ values for the sulfides in this study were significantly more than 1 (625–77,910), and thus the atmospheric He can be excluded. Consequently, it can be inferred that the He in the ore-forming fluids of the Baoshan deposit are mainly composed of mantle-derived He and crustal-radiogenic He, just like most hydrothermal deposits [82].

The measured $^3\text{He}/^4\text{He}$ ratios of the sulfides in this study (0.04–1.51 Ra; averaging 0.58 Ra; Table 2) were slightly above that of crustal radiogenic He (0.01–0.05 Ra) [25] but significantly less than the mantle value (6–9 Ra) [33]. The contributions of mantle-derived He for the ore-forming fluid can be estimated based on the crust–mantle dual model: $\text{He}_{\text{mantle}} (\%) = (R_S - R_C) / (R_M - R_C) \times 100\%$, where $R_M (=8)$, $R_C (=0.01)$, and R_S represent the $^3\text{He}/^4\text{He}$ ratios of the fluids in the upper mantle, crust, and the studied samples, respectively [28]. The calculated results of the $\text{He}_{\text{mantle}}$ values in this study ranged from 0.5% to 25.1%, with an average of 9.4%.

The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (303–596) of the studied sulfides were obviously higher than the value of ASW ($^{40}\text{Ar}/^{36}\text{Ar} = 298.6$), but significantly less than those of mantle-derived and crustal-derived radiogenic Ar. This indicates that not only Ar from ASW, but also the non-atmospheric ^{40}Ar ($^{40}\text{Ar}^*$) derived from the mantle- or crustal-radiogenic components were available. The proportions of $^{40}\text{Ar}^*$ can be calculated at 2.4% to 50.4%, while the contributions of the air-derived ^{40}Ar were estimated at 49.6% to 97.6%.

Therefore, He and Ar in the ore-forming fluid can be ascribed to the mixing of two end-member components, as indicated by the linear correlations in Figure 4, mantle-derived magmatic fluid characterized by high $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, and crust-derived fluid with low $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios.

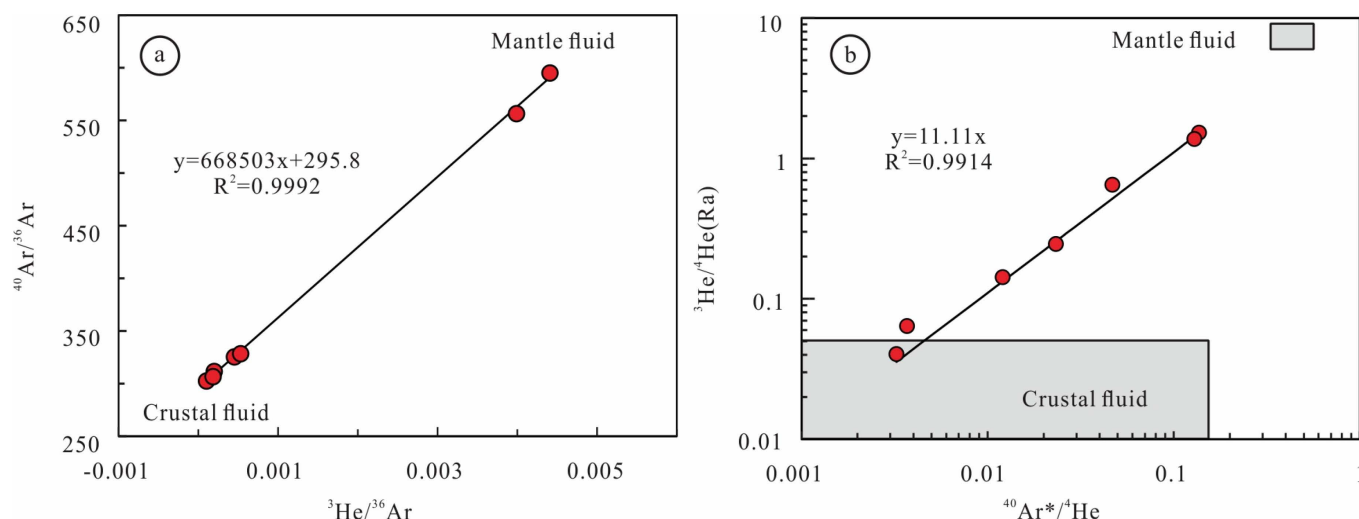


Figure 4. (a) $^3\text{He}/^{36}\text{Ar}$ vs. $^{40}\text{Ar}/^{36}\text{Ar}$ and (b) $^{40}\text{Ar}^*/^4\text{He}$ vs. $^3\text{He}/^4\text{He}$ (Ra) of sulfides from the Baoshan Cu-Pb-Zn deposit.

Given that both ^{36}Ar and ^3He are non-radiogenic, the $^3\text{He}/^{36}\text{Ar}$ value of ASW should be constant (5×10^{-8}). Therefore, extrapolating the trend line in Figure 4a to the $^3\text{He}/^{36}\text{Ar}$ value of ASW, the modified air-saturated water (MASW) component could be acquired with a $^{40}\text{Ar}/^{36}\text{Ar}$ value of 295.8. Obviously, this value is nearly identical to the atmospheric value of 298.6, and thus almost no radiogenic ^{40}Ar was available in the fluid. Additionally, extrapolating the mixing line in Figure 4b to a $^3\text{He}/^4\text{He}$ ratio of 0.04 Ra, the least value measured in this study, was able to obtain a $^{40}\text{Ar}^*/^4\text{He}$ ratio ($^{40}\text{Ar}^*$ is non-atmospheric Ar, i.e., $^{40}\text{Ar}^* = ^{40}\text{Ar} - [^{36}\text{Ar} \times 298.6]$) of 0.004. This ratio is significantly lower than the $^{40}\text{Ar}^*/^4\text{He}$ value produced in the crust (~ 0.2) [25], implying ^4He was preferentially acquired relative to ^{40}Ar from crustal rocks. Therefore, the crustal end-member probably consists of ASW but is modified by the crustal radiogenic ^4He . Furthermore, extrapolating this trend to a $^3\text{He}/^4\text{He}$ ratio of 1.51 Ra in Figure 4b, the highest value determined in this study, a magma $^{40}\text{Ar}^*/^4\text{He}$ ratio of 0.14 was obtained. Obviously, this value is slightly lower than mantle production ratios (0.24–0.63) [33]. In conclusion, the noble gases of the ore-forming fluids in the Baoshan deposit likely represent a mixture of two end-member components: mantle fluid (He and Ar from the mantle) and crustal fluid (Ar in ASW and radiogenic He produced by the crust).

The $\delta^{34}\text{S}$ values of sulfides determined in this study exhibited a restricted range (+2.30 to +5.21‰; Table 2, Figure 5), consistent with the previously reported values by Yao et al. (2006) [83] (−2.17‰~+5.29‰) and Bao et al. (2014) (+1.50‰~+4.50‰) [47], indicative of a magmatic origin [47,83]. Noticeably, the $\delta^{34}\text{S}$ values will generally increase with increasing $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $^3\text{He}/^{36}\text{Ar}$, and $^4\text{He}/^{40}\text{Ar}$ ratios, suggesting there is an identical source for the isotopically light S and radiogenic He [32]. However, the lack of a strict linear relationship between $\delta^{34}\text{S}$ and He-Ar isotopes (Figure 5) reveals that the S isotope systematic in the Baoshan deposit has not been disturbed by the fluid mixing revealed by the noble gases. This is likely attributed to the low S concentrations in the shallow, low-temperature fluid compared to the sulfur in the magmatic-hydrothermal fluid [32].

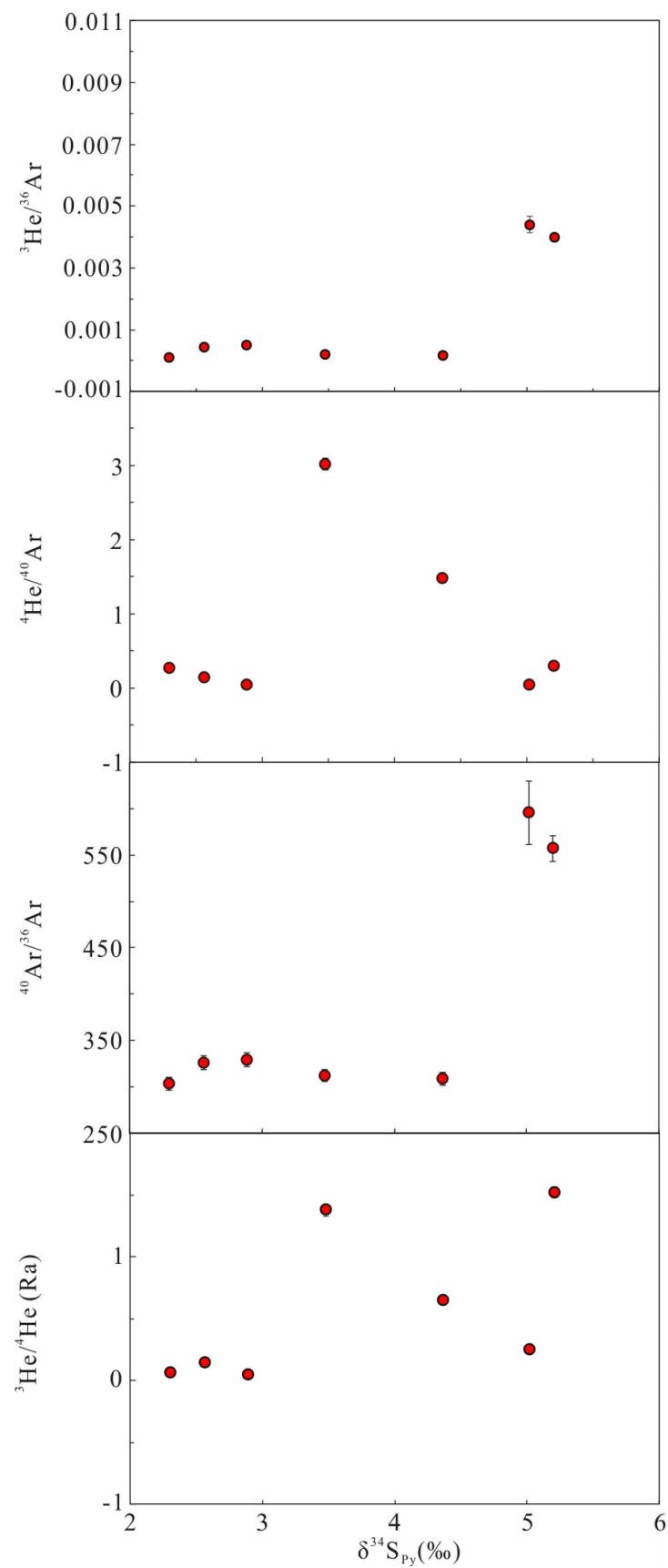


Figure 5. $^3\text{He}/^{36}\text{Ar}$ vs. $\delta^{34}\text{S}$, $^4\text{He}/^{40}\text{Ar}$ vs. $\delta^{34}\text{S}$, $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $\delta^{34}\text{S}$, and $^3\text{He}/^4\text{He}$ vs. $\delta^{34}\text{S}$ for sulfides from the Baoshan Cu-Pb-Zn deposit.

5.3. Helium and Heat

It is well known that the mantle-derived ^3He concentration varies systematically and varies with heat (Q) [30,84,85], and the $^3\text{He}/Q$ ratio of the fluids can provide insights into the hydrothermal regime, i.e., the convection regime and/or conductive regime [32]. The estimated $^3\text{He}/Q$ ratios for the ore-forming fluids associated with Cu-Pb-Zn mineralization in the Baoshan deposit varied in the range of $0.117\text{--}5.1 \times 10^{-12} \text{ cm}^3 \text{ STP J}^{-1}$ (Table 2, Figure 6). These values are about 10 to 50 times higher than those of hydrothermal solutions vented from mid-oceanic ridges ($0.1\text{--}0.2 \times 10^{-12} \text{ cm}^3 \text{ STP J}^{-1}$) [84,85], but similar to the values previously reported for the Zijinshan and Wuziqilong deposits [32] and the granite-related Panasqueira Sn-W mineralization [29]. Such a large variation range of $^3\text{He}/Q$ ratios reveals some notable variations in the ^3He concentrations and enthalpies of the fluids during trapping [27]. These high $^3\text{He}/Q$ ratios of the Baoshan deposit indicate that the deep fluids acquired heat and volatiles through convection across the magma/hydrothermal interface in the deep crust, rather than in a conductive regime (Figure 6). These extensive deep faults in the deposit control the distribution of various intrusions and Cu-Pb-Zn ores, likely acting as the high-permeability channels for the transport of heat and volatiles [52].

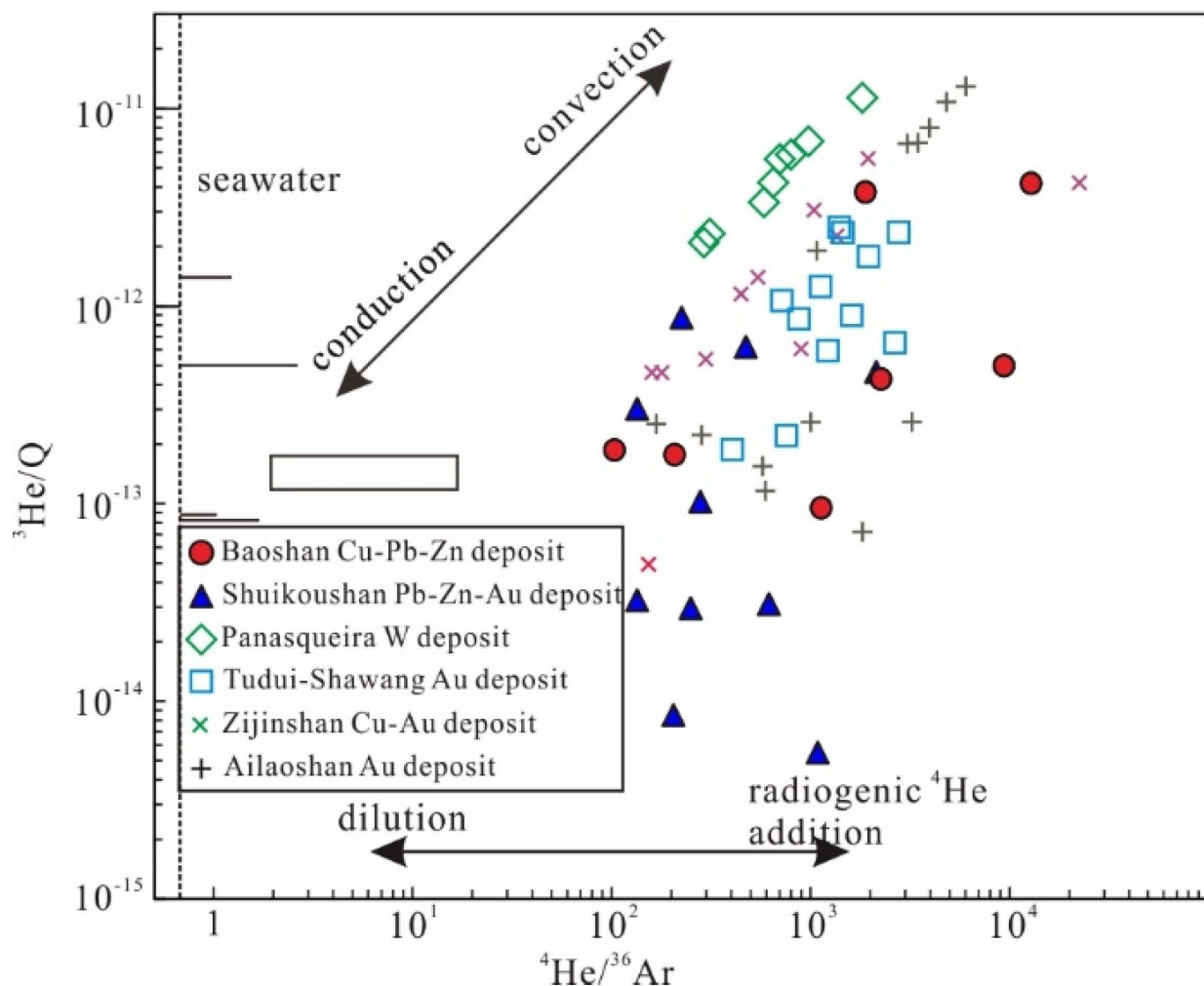


Figure 6. $^3\text{He}/Q$ vs. $^4\text{He}/^{36}\text{Ar}$ for sulfides from the Baoshan Cu-Pb-Zn deposit. Solid horizontal lines = range in $^4\text{He}/^{36}\text{Ar}$ of EPR vent fluids and plumes [29]; Box = Lucky Strike vent fluids [86]. Data of the Panasqueira W deposit from Burnard and Polya (2004) [32]; Tudui-Shawang Au deposit from Liu et al. (2021) [87]; Zijinshan Cu-Au deposit from Wu et al. (2017) [32]; Ailaoshan Au deposits from Hu et al. (1999) [88]; Shuikoushan Pb-Zn-Au deposit from Huang et al. (2024) [43].

5.4. Implications for the Cu-Pb-Zn Mineralization

The Baoshan Cu-Pb-Zn deposits and the Shuikoushan Pb-Zn-Au in southern Hunan exhibited similar $^3\text{He}/^4\text{He}$ ratios (0.01–2.93 Ra; Table 3, Figure 7), while most granite-associated W-Sn deposits in the Nanling Range had higher $^3\text{He}/^4\text{He}$ ratios of 0.06–4.43 Ra (Table 3). In most cases, these remarkably high $^3\text{He}/^4\text{He}$ ratios (up to 5 Ra), such as the Zijinshan Cu-Au deposit (up to 5.67 Ra) and the Panasqueira W-Sn deposit, indicate a direct input of mantle-derived He into the ore-forming fluid [29]. However, these $^3\text{He}/^4\text{He}$ ratios of below 3 Ra usually reveal that there are predominantly crustal contributions with insignificant mantle-derived He during the hydrothermal mineralization, independent of the granite types spatially and temporally associated with the deposits (Figure 7).

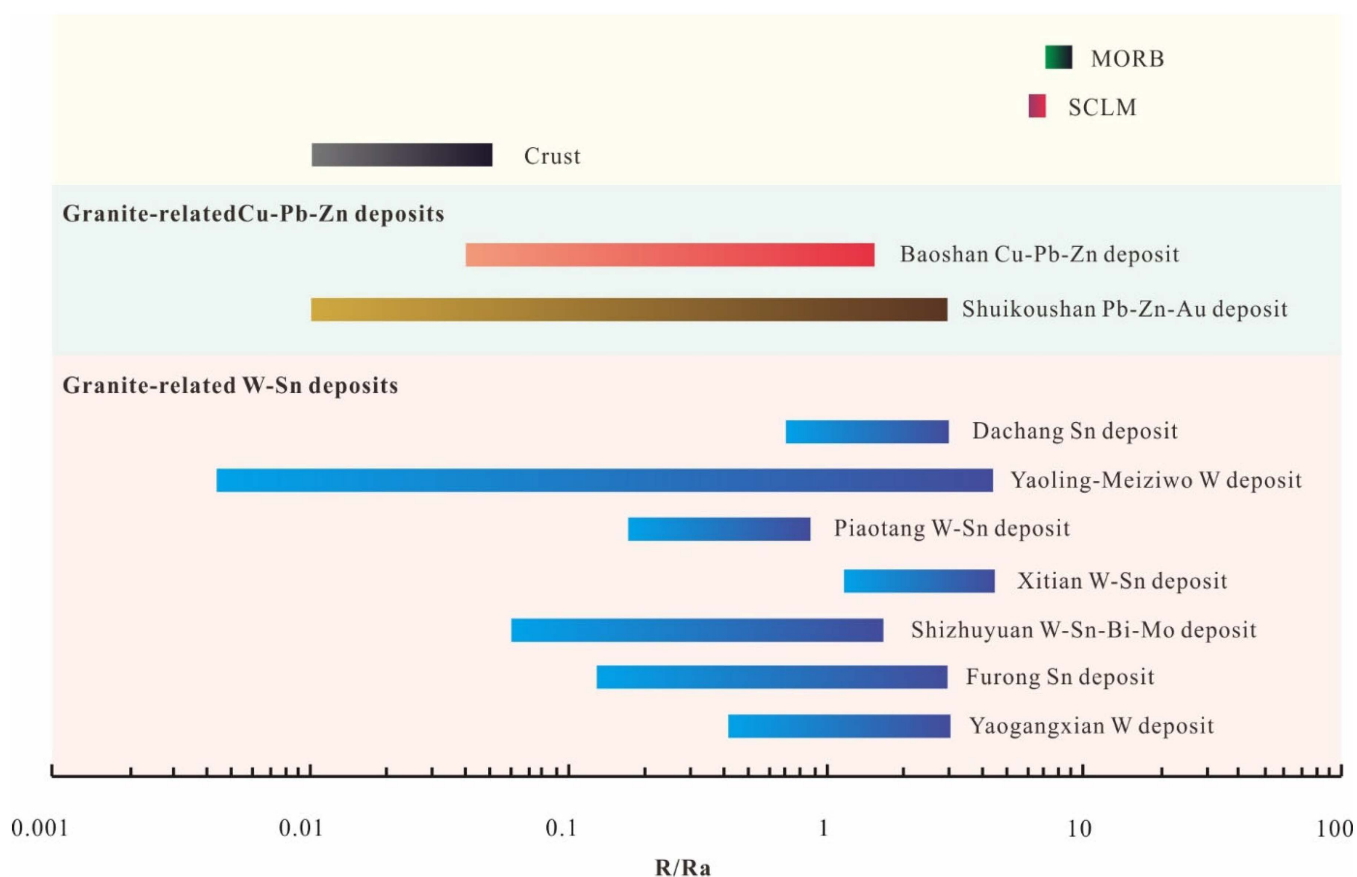


Figure 7. He-Ar isotopic compositions of granite-related W-Sn deposits and Cu-Pb-Zn deposits in South China.

Hu et al. (2012) concluded that the ore-forming fluids in the Yaogangxian W deposit resulted from the mixing of a crustal fluid with another fluid derived from the W-associated granitic magma. This granitic magma was generated by crustal melting triggered by the mantle-derived magma [26]. Zhai et al. (2012) also proposed that the introduction of extensive basaltic magma through underplating or intrusion, resulting from partial melting of the upper mantle, supplied the requisite heat for the crustal melting and the subsequent formation of abundant S-type granitic magma [36]. This process involved the release and mingling of magmatic fluids from the crust and mantle, characterized by high $^3\text{He}/^4\text{He}$ ratios, with circulating, modified air-saturated water, and ultimately led to the formation of the tungsten deposit.

Recent studies indicated that the Shuikoushan Pb-Zn-Au deposit exhibits $^3\text{He}/^4\text{He}$ values of 0.01–2.93 Ra (Table 3), which reveal that it was derived from a mixture of crustal radiogenic end-member and mantle-derived components [43]. As discussed above, the

Baoshan Cu-Pb-Zn deposit exhibited similar $^3\text{He}/^4\text{He}$ ratios (0.04 to 1.51 Ra), also suggesting that a mixture of crustal-derived and mantle-derived fluids was involved in the mineralization. Additionally, the characteristics of the Hf isotope and trace element also indicate that the granitic rocks in the Baoshan deposit resulted from the partial melting of Paleoproterozoic crustal components, with considerable input from mantle sources [53]. This interpretation is supported by the presence of abundant mantle-derived mafic microgranular enclaves in the mining district [89].

Interestingly, recent studies of the He-Ar isotope in Jiaodong Au deposits, North China [90], and the SGXR Sn deposits in Northeast China [91], revealed a positive correlation between the $^3\text{He}/^4\text{He}$ ratios and metal reserves. The Baoshan deposit contains approximately 470.7 kt of Pb and 512.8 kt of Zn [45], while the Shuikoushan Pb-Zn-Au deposit has about 874.6 kt of Pb and 1110.8 kt of Zn [20]. Coincidentally, although involving only two deposits, our latest He-Ar isotope data (Table 3) revealed a similar trend that the larger granite-associated Pb-Zn deposits in South China generally exhibit higher contribution from mantle-derived fluid. This further indicates that the ore-forming fluid carries both volatiles and metals in the extensional tectonic settings [90].

Table 3. He-Ar isotopic compositions of some W-Sn deposits and Cu-Pb-Zn deposits in South China.

Deposit	$^3\text{He}/^4\text{He}$ (Ra)	$^{40}\text{Ar}/^{36}\text{Ar}$	References
<i>Granite-related W-Sn deposits</i>			
Yaogangxian W deposit	0.41–3.03	328–1191	[26]
Furong Sn deposit	0.13–2.95		[13]
Xintianling W deposit	4.08	342	[37]
Shizhuyuan W-Sn-Bi-Mo deposit	0.06–1.66	293–1072	[35]
Xitian W-Sn deposit	1.15–4.43	288–325	[92]
Xianghualing Sn deposit	1.84	326	[92]
Piaotang W-Sn deposit	0.17–0.86	355–591	[93]
Yaoling-Meiziwo W deposit	0.0043–4.36	330–2953	[36]
Dachang Sn deposit	0.7–2.9	310–446	[94,95]
<i>Granite-related Cu-Pb-Zn deposits</i>			
Baoshan Cu-Pb-Zn deposit	0.04–1.51	303–596	This study
Shuikoushan Pb-Zn-Au deposit	0.01–2.93	298–382	[43]

As mentioned in the Introduction, the Cu-Pb-Zn mineralization in South China is traditionally considered to precede the W-Sn mineralization, and both of them formed in two distinct systems [9–11,15]. However, recent chronological studies indicate that Cu-Pb-Zn and W-Sn deposits in the Nanling Range formed nearly simultaneously [20,23]. Moreover, noble gas isotope analyses suggest that mantle-derived volatiles contributed to both types of mineralization. Therefore, we propose that the granite-related W-Sn and the Cu-Pb-Zn deposits in South China likely formed under the same tectonic setting. Similar to other Cu-Pb-Zn and W-Sn deposits in South China, the Baoshan deposit appears to be related to the westward subduction of the Paleo-Pacific Oceanic Plate beneath the Eurasian continent, followed by an extensional tectonic regime [5,15]. A large-scale extensional window occurred in the Nanling Range and led to the upwelling of asthenospheric materials, which likely mixed with the upper crust, resulting in the emplacement of the granitic intrusions and the related Cu-Pb-Zn mineralization in the Baoshan deposit.

6. Conclusions

The ore-forming fluid in the Baoshan deposit originated from a mixture of shallow crustal fluid, which contains crustal ^4He and near-atmospheric Ar, as well as a magmatic fluid with a significant proportion of gases and materials from the mantle. Approximately 25% of the He in the ore-forming fluid is estimated to originate from the mantle. Additionally, the elevated $^3\text{He}/\text{Q}$ values in the Baoshan deposit suggest that the ore-forming fluid acquired heat, volatiles, and metals from magma through convection rather than conduction. The sulfur in the deposit predominantly originates from magma, with a negligible

contribution from crustal fluid. Therefore, the mantle-derived component played a role in both granite-related W-Sn and Cu-Pb-Zn mineralization in South China, indicating a common geological event.

Author Contributions: Conceptualization, J.H. and J.P.; methodology, J.H.; investigation, J.H., J.P. and T.X.; data curation, J.H.; writing—original draft preparation, J.H.; writing—review and editing, J.P. and T.X.; visualization, J.H.; supervision, J.H. and J.P.; funding acquisition, J.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 42102079; the Natural Science Foundation of Sichuan Province, grant number 2023NSFSC0762; the State Key Laboratory of Ore Deposit Geochemistry Key Laboratory Open Project Fund, grant number 201804; and the Southwest University of Science and Technology Doctoral Fund, grant number 16zx7132 and 21zx7159.

Data Availability Statement: The data presented in this study are available in this paper.

Acknowledgments: We thank the geologists of the Baoshan Nonferrous-metal Corporation for their help during our field investigations. We acknowledge two anonymous reviewers of their constructive reviews and valuable suggestions that led to great improvement in the presentation of the paper, and we extend our thanks to the editor of Minerals for their insightful comments.

Conflicts of Interest: The authors declare no conflicts of interest.

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