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Age, Fluid Inclusion, and H–O–S–Pb Isotope Geochemistry of the Superlarge Huaaobaote Ag–Pb–Zn Deposit in the Southern Great Xing'an Range, NE China

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Abstract: The superlarge Huaaobaote Ag–Pb–Zn deposit is located on the western slope of the southern Great Xing'an Range (SGXR). The deposit includes four ore blocks, namely, ore blocks I, II, III, and V. Except for the no. I orebody of ore block I, which is hosted in the contact zone between the Carboniferous serpentinitized harzburgite and the Permian siltstone, the other orebodies all occur as veins controlled by faults. The mineralization process at the deposit can be divided into four stages: cassiterite–arsenopyrite–pyrite–quartz stage (stage I), cassiterite–chalcopyrite–pyrite–freibergite–arsenopyrite–pyrrhotite–quartz stage (stage II), sphalerite–galena–jamesonite–stibnite–freibergite–silver mineral–quartz–calcite–chlorite stage (stage III), and argentite–pyrargyrite–pyrite–quartz–calcite (stage IV). Cassiterite U–Pb dating of the Huaaobaote deposit yielded ages of 136.3–134.3 Ma, indicating that the deposit formed in the Early Cretaceous period. Two types of fluid inclusions (FIs), including liquid-rich and gas-rich FIs, have been distinguished in the quartz vein and sphalerite. The homogenization temperature during the four stages gradually decreases, with temperatures of 302–340 °C for stage I, 267–304 °C for stage II, 186–273 °C for stage III, and 166–199 °C for stage IV, respectively. The salinity (wt% NaCl eqv.) at stages I, II, III, and IV is 3.7–6.6, 0.2–4.5, 0.2–5.0, and 0.4–1.6, respectively, indicating that the ore-forming fluid is characterized by low salinity. The $\delta^{18}\text{O}_{\text{water}}$ and δD values of the ore-forming fluid range from -11.9‰ to 7.9‰ and -168‰ to -76‰ , respectively, indicating that the ore-forming fluid was dominantly derived from a mixture of magmatic and meteoric water. The calculated $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values range from -3.6‰ to 1.2‰ , indicating that the sulfur mainly came from granitic magma. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of sulfides are in the ranges of 18.195–18.317, 15.509–15.667, and 37.965–38.475, respectively, implying that the ore-forming material was mainly derived from felsic magma that may be formed by the partial melting of orogenic materials. Fluid mixing, cooling, and immiscibility were the three primary mechanisms for mineral precipitation in the Huaaobaote deposit.

Keywords: cassiterite U–Pb age; fluid inclusion; H–O–S–Pb isotopes; Huaaobaote Ag–Pb–Zn deposit; southern Great Xing'an Range

1. Introduction

The southern Great Xing'an Range (SGXR), located in the intersection of the Paleo-Asian and the circum-Pacific metallogenic megaprovinces (Figure 1a,b), is the most important Pb–Zn–Ag–Sn metallogenic belt in northern China [1–5]. To date, the range is known to host six superlarge, seven large, thirty-nine medium, and numerous small-sized Pb–Zn–Ag–polymetallic deposits (Figure 1c), with proven reserves of 8,130,000 tons Pb + Zn, 57,000 tons Ag, 850,000 tons Sn, 580,000 tons Cu, and 600,000 tons Li_2O [2,6–11].

The types of these Pb–Zn–Ag–polymetallic deposits in this area can be classified into an intrusion-related vein type, a subvolcanic-related vein type, and a skarn type. Some examples include the intrusion-related vein-type Baiyinchagandongshan Ag–Sn–Pb–Zn–Cu deposit [12] and Weilasituo Li–Sn–Pb–Zn–Cu deposit [13], the subvolcanic-related vein-type Huaaobaote Ag–Pb–Zn–Cu–Sn deposit [14] and Dajing Sn–Cu–Pb–Zn–Ag deposit [15], and the skarn-type Baiyinnuoer Pb–Zn deposit [16] and Haobugao Pb–Zn–Cu–Fe deposit [17]. The ore-forming element assemblage in these deposits is dominated by Ag–Pb–Zn, followed by Ag–Pb–Zn–Cu and Sn–Ag–Pb–Zn–Cu [2,13]. Numerous studies have revealed that the ages of mineralization and ore-related igneous rocks of these deposits are concentrated during the Late Jurassic–Early Cretaceous, especially in the Early Cretaceous [3,18–23].

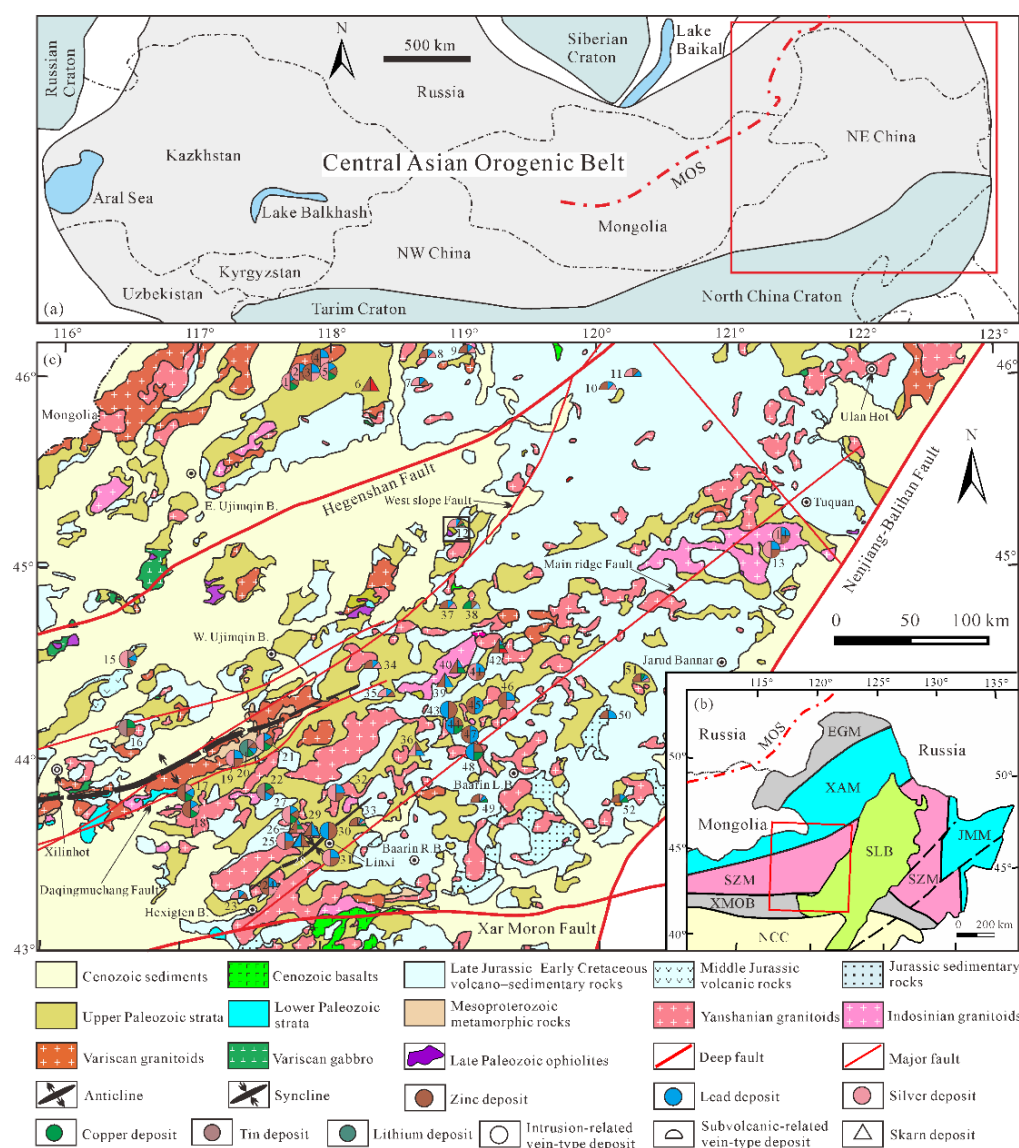


Figure 1. (a) Sketch geological map of the Central Asian Orogenic Belt (modified after [24]), showing the location of NE China; (b) simplified geotectonic division of NE China (after [25]); (c) geological map of the southern Great Xing'an Range and its neighboring areas, showing locations of major Pb–Zn–Ag–polymetallic deposits (geological base map modified after [9]; ore deposits modified after [13]). Notes: EGM = Ergun massif; JMM = Jiamusi massif; MOS = Mongol–Okhotsk suture zone; NCC = North China craton; SLB = Songliao basin; SZM = Songnen–Zhangguangcai Range massif;

XAM = Xing'an massif; XMOB = Xar Moron orogenic belt. Names of numbered Pb–Zn–Ag–polymetallic deposits: 1 = Hua'naote Ag–Pb–Zn–Cu deposit; 2 = Highland 1017 Ag–Pb–Zn deposit; 3 = Buyan'alin Pb–Zn–Ag deposit; 4 = Dugerlin Pb–Zn–Ag deposit; 5 = Jilinbaolige Ag–Pb–Zn–Cu deposit; 6 = Chagan'aobao Zn–Fe deposit; 7 = Wulantaolegaidong Ag–Pb–Zn deposit; 8 = Gunhudugengou Pb–Zn–Ag deposit; 9 = Lemageshan Pb–Zn–Ag deposit; 10 = Zhamuqin Pb–Zn–Ag deposit; 11 = Fuxingtun Ag–Pb–Zn deposit; 12 = Huaaobaote Ag–Pb–Zn–Cu–Sn deposit; 13 = Maohuduger Ag–Pb–Zn deposit; 14 = Meng'entaolegai Ag–Pb–Zn deposit; 15 = Baiyinchagandongshan Ag–Sn–Pb–Zn–Cu deposit; 16 = Maodeng–Xiaogushan Sn–Cu–Zn deposit; 17 = Aobaoshan Pb–Zn–Ag–Cu deposit; 18 = Harchulutu Pb–Zn–Ag–Cu deposit; 19 = Bayanwula Ag–Pb–Zn deposit; 20 = Weilasituo Li–Sn–Pb–Zn–Cu deposit; 21 = Bairendaba Ag–Pb–Zn–Cu deposit; 22 = Anle Sn–Cu–Pb–Zn deposit; 23 = Shidi Ag–Pb–Zn deposit; 24 = Dadi Ag–Pb–Zn deposit; 25 = Yonglong Ag–Pb–Zn deposit; 26 = Hadatu Pb–Zn–Cu–Ag deposit; 27 = Huangtuliang Ag–Pb–Zn–Cu deposit; 28 = Nasitai Pb–Zn deposit; 29 = Shalonggou Pb–Zn deposit; 30 = Erbadi Pb–Zn deposit; 31 = Bianjiadayuan Ag–Pb–Zn deposit; 32 = Xishijiangshan Ag–Pb–Zn deposit; 33 = Dajing Sn–Cu–Pb–Zn–Ag deposit; 34 = Wulanbaiqi Pb–Zn–Ag deposit; 35 = Chaowula Ag–Pb–Zn deposit; 36 = Daihuanggou Ag–Pb–Zn deposit; 37 = Bujinhei Pb–Zn–Ag deposit; 38 = Shabulengshan Cu–Zn–Mo deposit; 39 = Baiyinnuoer Pb–Zn deposit; 40 = Nailinba Pb–Zn–Cu deposit; 41 = Shuangjianzishan Ag–Pb–Zn deposit; 42 = Haobugao Pb–Zn–Cu–Fe deposit; 43 = Aguihundelun Pb–Zn deposit; 44 = Baiyinwula Pb–Zn–Cu deposit; 45 = Erdaoyingzi Pb–Zn deposit; 46 = Dongshan Pb–Zn–Ag deposit; 47 = Biliutaibei Pb–Zn deposit; 48 = Taipingdi Pb–Zn–Cu deposit; 49 = Hongguangmuchang Zn–Ag–Cu deposit; 50 = Aobaotu Pb–Zn deposit; 51 = Shuiquan Pb–Zn–Cu–Ag deposit; 52 = Panjiaduan Pb–Zn–Cu deposit.

The superlarge Huaaobaote Ag–Pb–Zn deposit accompanied by Cu, Sn, and Sb is located on the west slope of the SGXR. Previous studies have mainly focused on the characteristics of the Ag–Pb–Zn orebodies of the deposit [14,26,27] and the age of the igneous rocks in the ore district [28–30]. The mineralization of the Huaaobaote deposit is closely related to the subvolcanic rocks [14] and is distinguished from the Sn–Ag–polymetallic deposits in the SGXR, which are mainly related to Early Cretaceous highly fractionated granite [13]. Nevertheless, the lack of an accurate mineralization age and information on ore-forming fluids considerably constrains the understanding of genesis for the deposit. In this paper, we report cassiterite U–Pb age, fluid inclusions, and H–O–S–Pb isotopes of the Huaaobaote deposit, and discuss its possible ore-forming fluid source, metal source, and metallogenic mechanism. We intend to improve our understanding of the mineralization of Ag–Pb–Zn–polymetallic deposits related to subvolcanic magmatic activity in the SGXR.

2. Regional Geology

The SGXR, located in the central part of the Songnen–Zhangguangcai Range massif (Figure 1b), is bounded by the Hegenshan fault in the north, the Xar Moron fault in the south, the Nenjiang–Balihan fault in the east, and the East Ujimqin Banner–Xilinhot area in the west (Figure 1c). The tectonic evolution of the SGXR is dominated by the Paleo-Asian Ocean tectonic regime during the Paleozoic, and the Mongol–Okhotsk Ocean and Paleo-Pacific tectonic regimes in the Mesozoic [13,31,32].

The exposed strata in the SGXR include Mesoproterozoic, Paleozoic, Mesozoic, and Cenozoic (Figure 1c). The Mesoproterozoic (Xilin Gol complex), the oldest formation in the SGXR, being mainly composed of amphibole–plagioclase gneisses, biotite-bearing granitic gneiss, and mica schist, is mainly distributed in the southern part of Xilinhot and West Ujimqin Banner. The Lower Paleozoic primarily consists of marine volcanic rocks, carbonate rocks, and clastic rocks, which are only scattered in the southeast of Xilinhot and the southwest of Hexigten Banner. The Upper Paleozoic, including a set of marine clastic rocks, volcanic rocks, pyroclastic rocks, carbonates rocks assemblages, and continental clastic rocks, is widely distributed in the SGXR. The Mesozoic strata, including Jurassic–Cretaceous continental intermediate–felsic volcanic rocks and pyroclastic rocks, are widely distributed in a NE-trending belt, but the Triassic strata are absent due to the rapid uplifting

during this period [33]. The Cenozoic strata are composed of unconsolidated sediments and basalts [33]. Fold and fault structures are well-developed in the SGXR. Fold structures mainly formed in the late Variscan and are orientated in a NE or NEE direction, such as the Ganzhuermiao anticline and Linxi syncline (Figure 1c). Compared with the Variscan, the Yanshanian folds are fewer and exhibit broad anticline and syncline. The major faults include the NEE–NE-trending Hegenshan fault, approximate EW-trending Xar Moron fault, NE–NNE-trending Nenjiang–Balihan fault, and Great Xing’an Range main ridge fault (Figure 1c). The Ganzhuermiao anticline, Linxi syncline, Hegenshan fault, and Xar Moron fault formed in the Late Paleozoic due to the subduction, accretion, and closure of the Paleo-Asian Ocean, and established the basic tectonic framework in the SGXR [34,35]. The Great Xing’an Range main ridge and Nenjiang–Balihan faults formed during the Mesozoic, primarily in response to NW-dipping subduction of the Paleo-Pacific plate beneath the Eurasian continent and the subsequent subduction plate rollback [36,37]. The intrusive rocks in the SGXR can be subdivided into the Variscan, Indosinian, and Yanshanian [21,38,39]. The Variscan intrusive rocks, including hornblende gabbro, hornblende diorite, tonalite, granodiorite, and granite, with ages of 354–305 Ma, are scattered in southern Xilinhote and on both sides of the Hegenshan fault [40–45]. The Indosinian intrusive rocks with ages of 248–216 Ma, consisting of two-mica granite, biotite granodiorite, and granodiorite porphyry, are widely and sporadically distributed in the SGXR [16,46,47]. The Yanshanian intrusive rocks, being mainly composed of the Late Jurassic–Early Cretaceous granite and granite porphyry, as stock or batholith, are widely distributed along the NE–NNE-trending main ridge of the SGXR, and their zircon U–Pb ages range from 184 to 120 Ma, concentrated at 140–130 Ma [13,21,47–51]. Among them, the Late Jurassic–Early Cretaceous magmatism has a close genetic connection with the Ag–Pb–Zn–polymetallic mineralization of the SGXR [13].

3. Ore Geology

The superlarge Huaaobaote Ag–Pb–Zn deposit (No. 12 deposit in Figure 1c) is located 138 km northeast of West Ujimqin Banner, Inner Mongolia, with geographic coordinates of 118°56′30″–118°58′00″ longitude (east) and 45°15′00″–45°16′00″ latitude (north).

In the Huaaobaote area, the outcrop rocks are stratigraphically assigned to the Lower Permian Shoushangou Formation, Lower–Middle Permian Dashizhai Formation, Middle Jurassic Wanbao Formation, Upper Jurassic Manketouebo and Manitu formations, Lower Cretaceous Baiyin’gaolao Formation, Upper Neogene Baogedawula and Wuchagou formations, and Quaternary (Figure 2). The Shoushangou Formation consists of marine sandstone. The Dashizhai Formation is composed of marine intermediate–acidic volcanic rocks and pyroclastic rocks. The Wanbao Formation comprises continental clastic rocks. The Manketouebo consists of continental rhyolite, tuff, and pyroclastic rocks. The Manitu Formation is composed of continental intermediate–acidic lavas and pyroclastic rocks. The Baiyin’gaolao Formation comprises continental acidic lava and tuff. The Baogedawula Formation consists of sandy mudstone. The Wuchagou Formation is mainly composed of basalt, and the Quaternary comprises loose sediments. The Shoushangou and Dashizhai formations, the main host rock, are widely distributed in the northeastern part of the Huaaobaote area. The volcanic rocks and volcanoclastic rocks of the Jurassic–Cretaceous unconformably overlie the pre-Mesozoic strata.

The period of magmatism at Huaaobaote can be divided into the Variscan and Yanshanian. The former primarily consists of the Carboniferous serpentized harzburgite and a small volume of gabbro, as well as the Permian diorite porphyry (Figure 2). The latter is generally composed of the Cretaceous syenogranite and monzogranite, as well as hypabyssal rhyolite. The serpentized harzburgite and gabbro, with a zircon U–Pb age of 337.3 ± 3.2 Ma [29], are distributed along the Huaaobaote tectonic mélange belt that is part of the Meilaotewula ophiolite belt. The Permian diorite porphyry, with zircon U–Pb ages of 285.9 ± 4.1 Ma [29] and 294.8 ± 3.2 Ma [30], is scattered in the eastern part of the Huaaobaote area. The Early Cretaceous intrusions are mainly distributed in the southwestern part of the

Huaaobaote area, such as the Ganggantewula intrusion. Moreover, there are also quantities of the Early Cretaceous granite porphyry and hypabyssal rhyolite veins, with zircon U–Pb ages of 136–132.6 Ma [27,29,30], which are closely related to the spatial distribution of the orebodies.

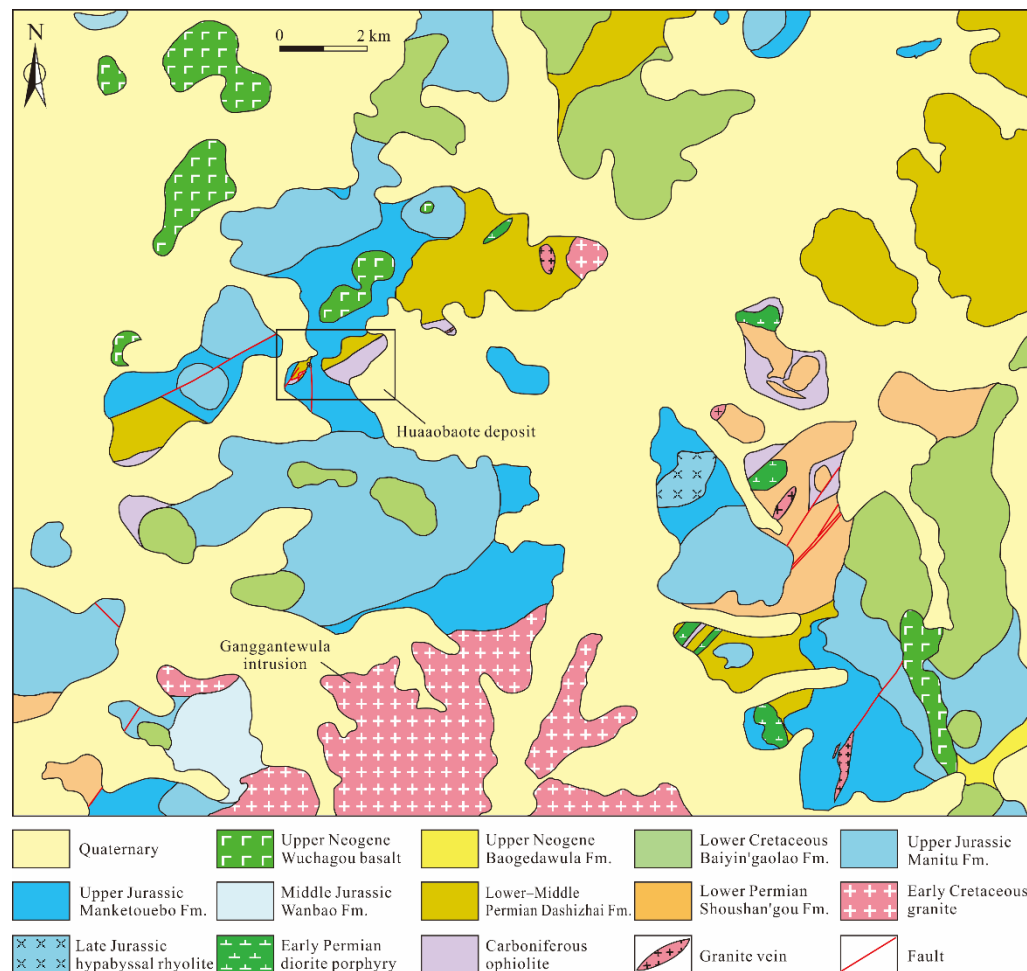


Figure 2. Simplified regional geological map of the Huaaobaote area (modified after [52]).

Structures in the Huaaobaote area are dominated by faults and folds. The NW-, NNE-, near N-trending faults, including the NEE-trending tectonic mélange belt, are the major ore-controlling structures in the Huaaobaote area, which may have originally formed during the accretion or closure stage of the Paleo-Asian Ocean and reactivated in the Yanshanian [14,33]. The NE-trending faults largely formed during the Yanshanian, with extensional features, which control the placement of the Early Cretaceous magmatic rocks [14,33]. Fold deformation mainly involves the Permian strata, while the Mesozoic strata are weakly deformed [52].

The Huaaobaote deposit, discovered by the Inner Mongolia Autonomous Region No. 10 Institute of Geological and Mineral Exploration and Development in 2001, contains proven reserves of 6369 tons Ag, 710,000 tons Pb, 920,000 tons Zn, 57,000 tons Cu, and 14,000 tons Sn, with average grades of 193 g/t Ag, 1.99% Pb, 2.37% Zn, 1.70% Cu, and 0.42% Sn, respectively, and is associated with 94,000 tons Sb [53].

According to the distribution of the orebodies, the deposit is divided into four ore blocks numbered I to IV (Figure 3). Ore block I, at the southern end of the deposit, is mainly composed of Ag–Pb–Zn–Sb orebodies and pyrite–pyrrhotite orebodies (Figures 3 and 4a). Of them, orebody I₁, with a length of 250 m and an extended depth of 273 m, is one of the typical Ag–Pb–Zn–Sb orebodies in the deposit. The orebody is mainly hosted in the contact

zone between the Carboniferous serpentized harzburgite and the Permian sandstone, which dips SSE at 45° – 60° . At the intersection of the NW-trending faults and the contact zone, orebody I₁ usually dilates as a cystic column or rhombic column (Figures 3 and 4a). Ore blocks II and III, located in the west and east of the deposit, respectively, consist of Pb–Zn–Ag–Sb orebodies. These orebodies are dominantly hosted in the Permian siltstone and are mainly controlled by the NW-trending faults, with some being controlled by near N- and NNE-trending faults (Figures 3 and 4b,c). Orebody II₂, with a length of 450 m, a thickness of 0.7–60.1 m, and an extended depth of 530 m, is the largest orebody in ore blocks II and III and dips to the NE at 45° – 70° . Ore block V, located in the central region of the deposit, is dominated by Ag–Cu–Sn orebodies, and these orebodies are controlled by NNE- and near N-trending faults with a large dip angle of 80° – 90° (Figures 3 and 4d). The Early Cretaceous hypabyssal rhyolite veins are mainly distributed along nearly N-trending faults with dip angles of 70° – 80° , in which a small amount of low-grade stockwork mineralization develops (Figure 3).

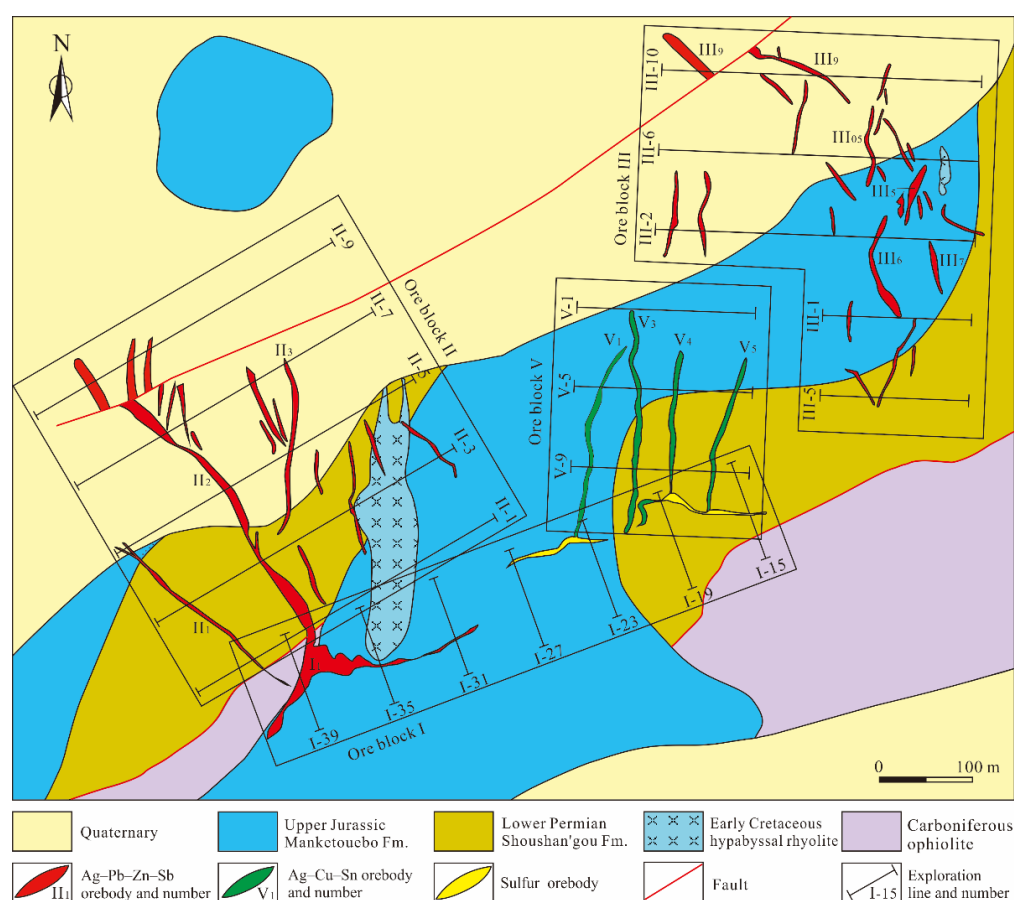


Figure 3. Geological map of the Huaaobaote deposit, showing the surface projection positions of the concealed orebodies at the 855-m level.

The ore minerals of the Sn orebodies in ore block V are mainly cassiterite, pyrite, and arsenopyrite, with gangue mineral of quartz (Figure 5a,i). The ore minerals of the Ag–Cu–Sn orebodies in ore block V are mainly chalcopyrite, cassiterite, arsenopyrite, pyrite, and freibergite, with gangue minerals of quartz, sericite, and chlorite (Figure 5b,c,j,k). The ore minerals of the Ag–Pb–Zn–Sb orebodies in the deposit are mainly galena, sphalerite, jamesonite, and freibergite, with gangue minerals of quartz and calcite (Figure 5d,e,l). The ore minerals of the Ag orebodies in ore block II are mainly argentite and pyrargyrite, with gangue minerals of quartz and calcite (Figure 5f). The ores' texture is anhedral granular, subhedral granular, radial, metasomatic dissolution, and exsolution (Figure 5a–f). The ore structure is mainly vein, massive, and densely disseminated structures, followed by

stockwork and breccia structures (Figure 6a–f). The wall-rock alteration is well-developed in all of these four ore blocks, and mainly includes silicification, sericitization, chloritization, carbonation, and pyritic phyllic alteration, with a small amount of pyrophyllization and kaolinization (Figure 5g–l).

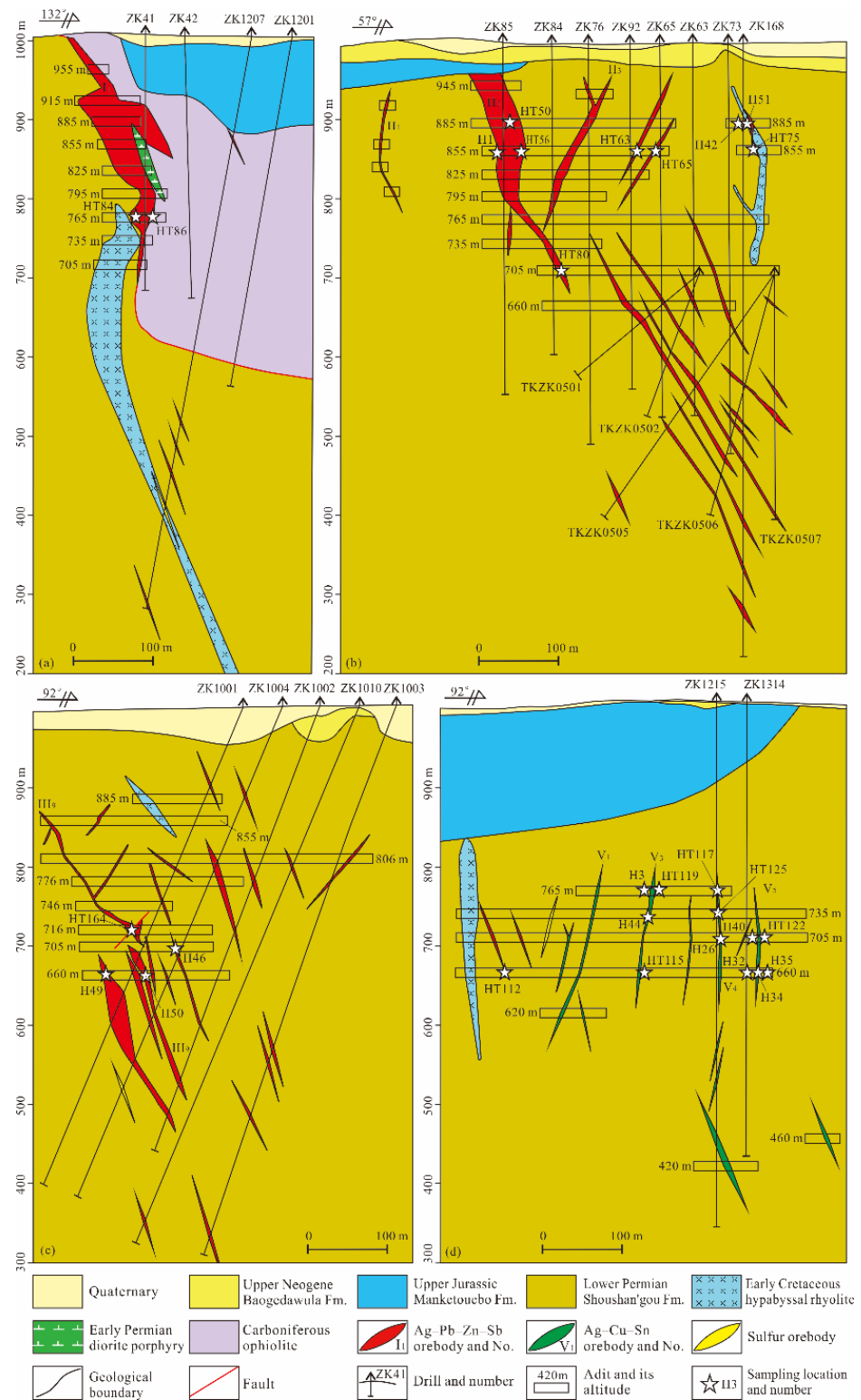


Figure 4. Simplified geological section along the exploration lines of I-39 (a), II-5 (b), III-10 (c), and V-9 (d) of the Huaobaote deposit.

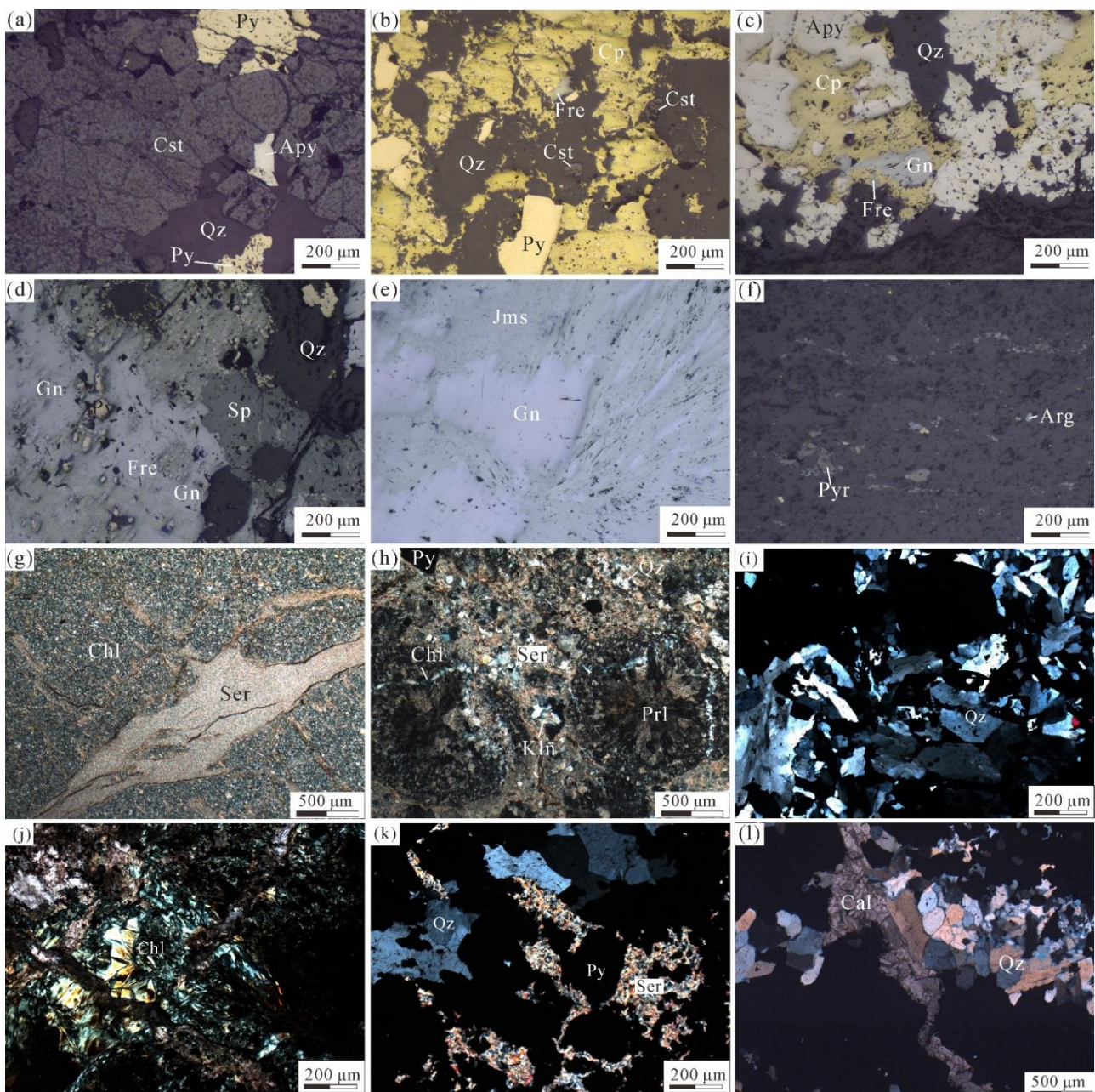


Figure 5. Representative photos of ores and major wall-rock alteration types in the Huaobaote deposit. (a) Coexisting cassiterite, pyrite, and arsenopyrite with silicification in Sn ore of stage I; (b) coexisting cassiterite, pyrite, chalcopyrite, and freibergite with silicification in Ag–Cu–Sn ore of stage II; (c) coexisting arsenopyrite, chalcopyrite, and freibergite with silicification in Ag–Cu ore of stage II, replaced by galena of stage III; (d) coexisting galena, sphalerite, and freibergite with silicification in Ag–Pb–Zn ore of stage III; (e) coexisting galena and jamesonite in Ag–Pb–Zn–Sb ore of stage III; (f) argentite and pyrrargyrite in Ag ore of stage IV; (g) strongly altered siltstone represented by chloritization and silicification; (h) sericitization, pyrophyllization, chloritization, kaolinization, silicification, and pyritization developed in the ore-hosting volcanoclastic rocks of the Dashizhai Formation; (i) silicification in stage I; (j) chloritization in stage II; (k) pyritic phyllic alteration in stage II; (l) silicification and carbonation developed in stage III. Abbreviations: Apy = arsenopyrite; Arg = argentite; Cal = calcite; Chl = chlorite; Ccp = chalcopyrite; Cst = cassiterite; Fre = freibergite; Gn = galena; Jms = jamesonite; Kln = kaolinite; Prl = pyrophyllite; Py = pyrite; Pyr = pyrrargyrite; Qz = quartz; Ser = sericite; Sp = sphalerite.

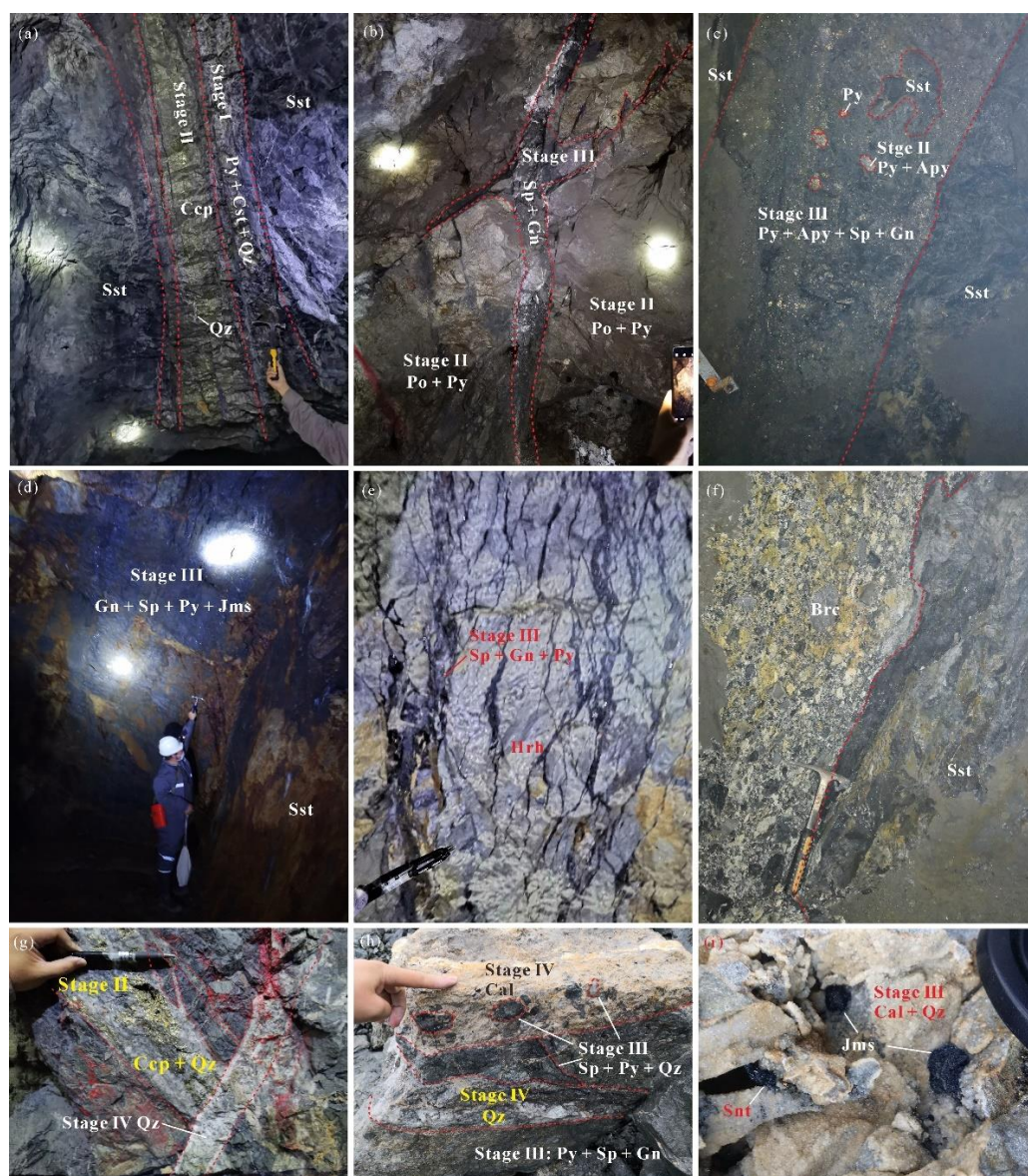


Figure 6. Representative photos of orebodies in the Huaaobaote deposit. (a) No. V₃ Ag–Cu–Sn orebody of stage II and Sn orebody of stage I, both occurring as steep veins; (b) Pb–Zn–Ag orebody of stage III cutting through sulfur orebody of stage II; (c) breccia ore in the Pb–Zn–Ag orebody of stage III, enclosing pyrite and arsenopyrite of stage II; (d) Pb–Zn–Ag–Sb orebody of stage III mainly composed of galena and sphalerite massive ores; (e) Pb–Zn–Ag orebody of stage III occurring in hypabyssal rhyolite, and sphalerite and galena distributing along the stockwork fractures within hypabyssal rhyolite; (f) cryptoexplosive breccia occurring within hypabyssal rhyolite near the contact zone of hypabyssal rhyolite and siltstone; (g) Ag-bearing quartz vein of stage IV cutting through Ag–Cu–Sn orebody of stage II; (h) Ag-bearing quartz and calcite veins of stage IV cutting through Pb–Zn–Ag orebody of stage III and wrapping ore breccia of stage III; (i) stibnite and jamesonite assemblages in quartz and calcite of stage III. Abbreviations: Apy = arsenopyrite; Brc = breccia; Cal = calcite; Ccp = chalcopryite; Gn = galena; Hrh = hypabyssal rhyolite; Jms = jamesonite; Po = pyrrhotite; Py = pyrite; Qz = quartz; Snt = Stibnite; Sp = sphalerite; Sst = siltstone.

Based on the crosscutting relationships of veins, ore fabrics, and mineral assemblages, four ore-forming stages are recognized (Figure 6): cassiterite–arsenopyrite–pyrite–quartz (stage I), cassiterite–chalcopryite–pyrite–freibergite–arsenopyrite–pyrrhotite–quartz (stage II), sphalerite–galena–jamesonite–stibnite–freibergite–silver mineral–quartz–calcite–chlorite (stage III), and argentite–pyrargyrite–pyrite–quartz–calcite (stage IV).

4. Sampling and Analytical Methods

4.1. Sampling

In this study, we selected 36 samples from different ore blocks, levels, and ore-forming stages of the Huaaobaote deposit for U–Pb dating, a fluid inclusion study, and H–O–S–Pb isotope analyses, and the details are listed in Table 1. Of these samples, two were selected for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) cassiterite U–Pb dating (Table 1, Figures 4d and 5a–c). Thirteen quartz and one sphalerite from four stages were collected for an FI study (Table 1, Figure 4). Twelve quartz samples from the four mineralization stages were collected for H–O isotope analysis (Table 1, Figure 4b–d). Nine sulfide samples from the first three mineralization stages were collected for S–Pb isotope analysis, including five pyrite, one arsenopyrite, one sphalerite, and two galena (Table 1, Figure 4b–d).

Table 1. List of analytical samples from the Huaaobaote deposit.

Sample	Orebody No.	Level (m)	Metal Assemblage	Stage	Mineral	Analysis
HT122	V ₅	705	Sn	I	Cassiterite	U–Pb dating
HT125	V ₄	735	Ag–Cu–Sn	II	Cassiterite	U–Pb dating
HT117	V ₄	765	Sn	I	Quartz	FIs study
HT119	V ₃	765	Sn	I	Quartz	FIs study
H44	V ₃	735	Ag–Cu–Sn	II	Quartz	FIs study
HT115	V ₃	660	Ag–Cu–Sn	II	Quartz	FIs study
HT50	II ₂	885	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT56	II ₂	855	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT80	II ₂	705	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT84	I ₁	765	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT86	I ₁	765	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT112	Ore block V	660	Ag–Pb–Zn–Sb	III	Quartz	FIs study
HT164	III ₉	716	Ag–Pb–Zn–Sb	III	Sphalerite	FIs study
HT63	Ore block II	855	Ag	IV	Quartz	FIs study
HT65	Ore block II	855	Ag	IV	Quartz	FIs study
HT75	Ore block II	855	Ag	IV	Quartz	FIs study
H32	V ₅	660	Sn	I	Quartz	H–O isotope analysis
H34	V ₅	660	Sn	I	Quartz	H–O isotope analysis
H40	V ₅	705	Sn	I	Quartz	H–O isotope analysis
H3-5	V ₃	765	Ag–Cu–Sn	II	Quartz	H–O isotope analysis
H3-7	V ₃	765	Ag–Cu–Sn	II	Quartz	H–O isotope analysis
H3-8	V ₃	765	Ag–Cu–Sn	II	Quartz	H–O isotope analysis
H3-9	V ₃	765	Ag–Cu–Sn	II	Quartz	H–O isotope analysis
H46	III ₉	705	Ag–Pb–Zn–Sb	III	Quartz	H–O isotope analysis
H49	III ₉	660	Ag–Pb–Zn–Sb	III	Quartz	H–O isotope analysis
H50	III ₉	660	Ag–Pb–Zn–Sb	III	Quartz	H–O isotope analysis
H42	Ore block II	885	Ag–Pb–Zn–Sb	IV	Quartz	H–O isotope analysis
H51	Ore block II	885	Ag–Pb–Zn–Sb	IV	Quartz	H–O isotope analysis
H32	V ₅	660	Sn	I	Pyrite	S–Pb isotope analysis
H34	V ₅	660	Sn	I	Pyrite	S–Pb isotope analysis
H35	V ₅	660	Sn	I	Pyrite	S–Pb isotope analysis
H3-1	V ₃	765	Ag–Cu–Sn	II	Arsenopyrite	S–Pb isotope analysis
H26	V ₃	765	Ag–Cu–Sn	II	Pyrite	S–Pb isotope analysis
H1-4	II ₂	855	Ag–Pb–Zn–Sb	III	Galena, Sphalerite	S–Pb isotope analysis
H1-5	II ₂	855	Ag–Pb–Zn–Sb	III	Galena	S–Pb isotope analysis
H46	III ₉	705	Ag–Pb–Zn–Sb	III	Pyrite	S–Pb isotope analysis

4.2. Cassiterite U–Pb Dating

The cassiterite grains were separated by conventional heavy liquid and magnetic techniques and purified by handpicking under a binocular microscope at the Tuoxuan Rock and Mineral Testing Service Co., Ltd., Langfang, Hebei Province, China (TRMTS).

The cassiterite target preparation, cathodoluminescence (CL) image photography, and LA-ICP-MS cassiterite U–Pb analysis were carried out at the Beijing Yandu Zhongshi Test Technology Co., Ltd., Beijing, China. The cassiterite U–Pb analysis was performed using an Analytik Jena Plasma Quant MC-ICP-MS with an NWR 193 nm Ar–F excimer laser system. The ^{118}Sn and SRM610 were used as the internal and external reference materials, respectively, and Yankee cassiterite was utilized for validation of the U–Pb isotope determinations (TIMS U–Pb age of 246.48 ± 0.51 Ma [54]). The test was performed by passing blank gas for 15 s, followed by 40 s of laser exfoliation analysis with a beam diameter of 35 μm , frequency of 8 Hz, and energy density of 4.0 J/cm². The test was performed by selecting particles with better crystal shape and fewer cleavages and inclusions to reduce the effect of common Pb. The raw data were corrected offline using ICPMSDataCal and Zskits, and the common Pb correction was performed using the ^{207}Pb -based correction mentioned in Chew et al. [55]. Isoplot 4.15 was used to calculate the U–Pb age and draw a Tera–Wasserburg diagram, and the lower intercept represents the age of cassiterite in the Tera–Wasserburg diagram [56].

4.3. Fluid Inclusion Microthermometry and Laser Raman Spectroscopy

Eighteen fluid plates of sixteen quartz and two sphalerite samples were double-polished at the TRMTS, with a thickness of 100–300 μm . The microthermometric measurements of the FIs were determined at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, China (IMRCAGS), using a LINKAM THMSG 600 programmable heating-freezing stage equipped with a German Zeiss microscope, which allowed a temperature range from -190 °C to 600 °C. Before each batch of microthermometry, the purified water and synthetic fluid inclusion standards, manufactured by Geofluid, Hong Kong, were used to calibrate the heating–freezing stage. The estimated accuracies were ± 0.1 °C from -100 °C to 25 °C, ± 1 °C from 25 °C to 400 °C, and ± 2 °C above 400 °C, respectively. The test heating rate was generally 0.2 to 5 °C/min, and the heating rate was reduced to 0.2 °C/min near the phase transition. The salinity of the gas–liquid two-phase aqueous solution inclusions was estimated by ice-melting temperatures [57], and the density of the fluid inclusions was calculated using Flincor software [58]. Volatile compositions of single fluid inclusion were identified using a Renishaw RM-2000 Raman probe at the IMRCAGS. The excitation wavelength was 514.53 nm argon laser line, and the measured spectrum time was 20 s. The counting rate was one per centimeter. The laser beam size was fixed at 1 μm with a spectral resolution of 1–2 cm^{-1} . The spectrum diagram was taken from the wavenumber of 1000–4000 cm^{-1} .

4.4. H–O–S–Pb Isotope Analyses

4.4.1. H–O Isotope Analyses

The samples were smashed, and the quartz grains were purified under binocular microscope to above 99% at the TRMTS. Then, the quartz H–O isotopes were accomplished with a MAT 251EM mass spectrometer at the IMRCAGS, with analytical accuracy better than $\pm 2\text{‰}$ for δD and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$. For analysis of the H isotopic compositions, water was first released from the fluid inclusions by a crushing method, then the water was reacted with zinc at 400 °C to produce H_2 [59], which was finally frozen in liquid nitrogen and collected in a sample bottle with activated carbon for testing. For the oxygen isotope, oxygen was liberated from quartz through a reaction with BrF_5 [60] and converted to CO_2 on a platinum-coated carbon rod. The CO_2 was then frozen, collected, and analyzed for the O isotope. The detailed operating conditions and analytical methods are discussed in [61]. The O isotope of the water in the quartz was calculated by the O isotope of the quartz using the fractionation equation: $1000 \ln \alpha_{\text{quartz-water}} = 3.38 \times 10^6/T^2 - 3.40$ [62], where T (in degrees Kelvin) is the mean value of the fluid inclusion homogeneous temperature corresponding to the stage of mineralization. The isotopic ratios were reported in per mil (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW).

4.4.2. S–Pb Isotope Analyses

The separation of a single sulfide was performed in the same way as described in Section 4.4.1. The S–Pb isotope compositions of the sulfides were measured at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, Beijing, China. The sulfur isotope analysis was first separated from the sulfides for SO₂ [63], and the test was performed using a Delta V mass spectrometer, and the experimental results were reported relative to the Vienna Canyon Diablo Troilite (V-CDT) with an analytical accuracy better than 0.2‰. The Pb isotope analysis was performed using an IsoProbe-T multi-receiver thermal ionization mass spectrometer. The measurement accuracy of the ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios was better than 0.005‰ (2σ). The isotopic ratios were reported with respect to the Pb standard reference NBS-981 values [64]: ²⁰⁶Pb/²⁰⁴Pb = 16.934 ± 0.007, ²⁰⁷Pb/²⁰⁴Pb = 15.486 ± 0.012, and ²⁰⁸Pb/²⁰⁴Pb = 36.673 ± 0.033, respectively.

5. Results

5.1. Cassiterite U–Pb Age

Most of the cassiterite grains from the Huaaobaote deposit are reddish-brown under an optical microscope, with lengths mostly between 50 and 110 μm. Cassiterite in the CL image presents as a black color with well-developed oscillatory zonation and a relatively homogeneous internal structure, most of which exhibit irregular shapes, most likely due to mechanical fragmentation during mineral selection (Figure 7). The cassiterite U–Pb isotopic data of two samples (HT122 and HT125) are listed in Table 2 and plotted on Tera–Wasserburg diagrams (Figure 8). The projection points of the two samples are both linearly aligned, indicating that their respective cassiterite grains have consistent U–Pb isotopic age, varying only in the content of common Pb.

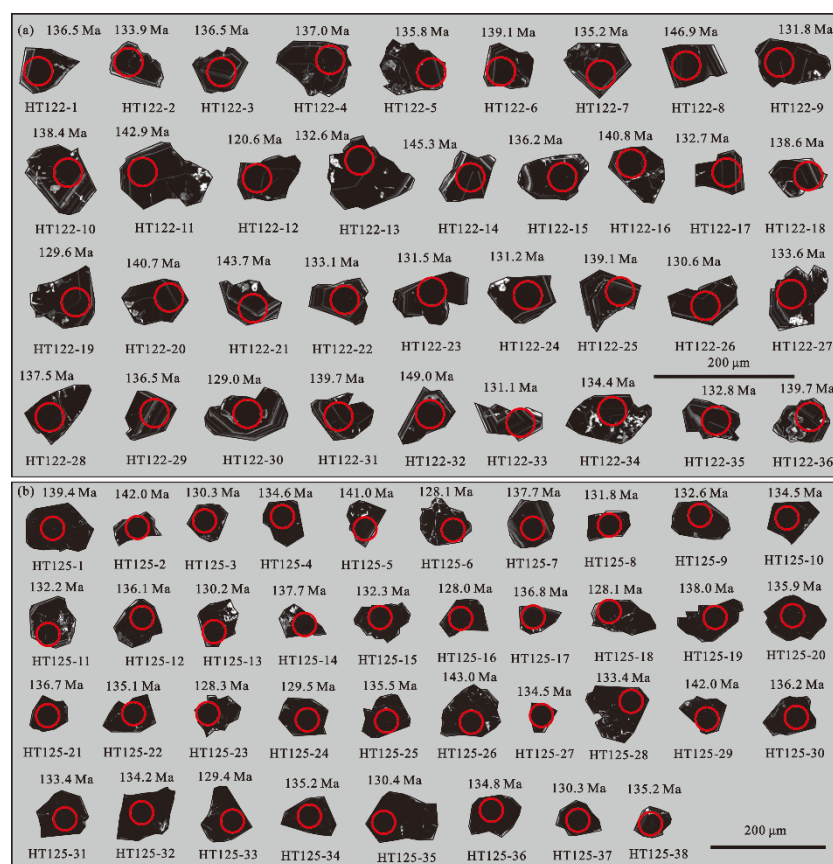


Figure 7. Representative cathodoluminescence (CL) images of cassiterite grains for samples HT122 (a) and HT125 (b) from the Huaaobaote deposit, showing U–Pb analytical spots and corresponding to ²⁰⁷Pb-corrected ²⁰⁶Pb/²³⁸U ages.

Table 2. LA-ICP-MS cassiterite U–Pb dating data for cassiterite samples HT122 and HT125 from of the Huaaobaote deposit.

Spot No.	Isotopic Ratios						Age (Ma)			
	$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	$^{238}\text{U}/^{206}\text{Pb}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
Sample HT122										
HT122-1	0.18218	0.01383	0.60982	0.04370	0.02556	0.00075	39.117	1.14860	136.5	4.8
HT122-2	0.30034	0.01448	1.17095	0.04923	0.03026	0.00069	33.052	0.75895	133.9	4.6
HT122-3	0.37176	0.02786	1.71566	0.11972	0.03528	0.00143	28.342	1.14960	136.5	9.4
HT122-4	0.20013	0.01145	0.70995	0.03903	0.02634	0.00054	37.967	0.77523	137.0	3.7
HT122-5	0.22319	0.01769	0.81919	0.06489	0.02703	0.00088	36.997	1.20590	135.8	5.8
HT122-6	0.27049	0.01844	1.06468	0.06628	0.02987	0.00116	33.482	1.30380	139.1	6.9
HT122-7	0.15183	0.01308	0.48058	0.03878	0.02424	0.00072	41.249	1.22980	135.2	4.7
HT122-8	0.33183	0.01858	1.54452	0.08127	0.03517	0.00090	28.436	0.72889	146.9	6.3
HT122-9	0.25919	0.01373	0.96060	0.04462	0.02778	0.00058	36.004	0.75039	131.8	4.1
HT122-10	0.38154	0.02464	1.98932	0.15360	0.03649	0.00131	27.407	0.98350	138.4	8.6
HT122-11	0.19588	0.01269	0.69459	0.03995	0.02731	0.00073	36.618	0.98444	142.9	4.7
HT122-12	0.40236	0.02763	1.80693	0.12910	0.03317	0.00100	30.148	0.90554	120.6	8.0
HT122-13	0.26315	0.03690	0.84534	0.08896	0.02812	0.00134	35.562	1.69210	132.6	10.2
HT122-14	0.22995	0.01729	0.88285	0.06680	0.02924	0.00092	34.199	1.07760	145.3	6.0
HT122-15	0.35397	0.02345	1.59832	0.10045	0.03399	0.00142	29.421	1.22970	136.2	8.4
HT122-16	0.24847	0.02076	0.95929	0.07770	0.02917	0.00132	34.278	1.55160	140.8	7.9
HT122-17	0.38626	0.02350	1.85798	0.13570	0.03530	0.00139	28.332	1.11580	132.7	8.3
HT122-18	0.25020	0.01460	0.95098	0.04669	0.02880	0.00066	34.727	0.79707	138.6	4.6
HT122-19	0.25124	0.02134	0.81666	0.05903	0.02696	0.00100	37.089	1.36970	129.6	6.5
HT122-20	0.52991	0.02117	3.88042	0.22128	0.05329	0.00200	18.764	0.70451	140.7	10.4
HT122-21	0.17166	0.01381	0.60705	0.04775	0.02651	0.00078	37.726	1.11050	143.7	5.1
HT122-22	0.31733	0.01468	1.32790	0.05656	0.03101	0.00075	32.248	0.78457	133.1	4.8
HT122-23	0.33752	0.01440	1.42328	0.05381	0.03179	0.00075	31.453	0.74608	131.5	4.8
HT122-24	0.32182	0.02448	1.26495	0.07958	0.03080	0.00121	32.470	1.27580	131.2	7.8
HT122-25	0.14340	0.01481	0.44976	0.04233	0.02466	0.00080	40.556	1.32290	139.1	5.3
HT122-26	0.35254	0.02453	1.45846	0.08065	0.03248	0.00111	30.791	1.05120	130.6	7.6
HT122-27	0.47591	0.02731	2.77106	0.16801	0.04363	0.00159	22.919	0.83258	133.6	10.5
HT122-28	0.22748	0.02325	0.81743	0.07506	0.02755	0.00108	36.295	1.42880	137.5	7.3
HT122-29	0.47537	0.01878	2.80595	0.09893	0.04453	0.00110	22.457	0.55362	136.5	7.5
HT122.30	0.36279	0.03071	1.55365	0.12622	0.03274	0.00115	30.541	1.06940	129.0	9.0
HT122-31	0.40657	0.02633	2.15246	0.16348	0.03881	0.00191	25.769	1.26830	139.7	10.5
HT122-32	0.53636	0.02193	4.22953	0.20672	0.05753	0.00189	17.383	0.57147	149.0	11.2
HT122-33	0.31196	0.02183	1.22766	0.07475	0.03023	0.00104	33.076	1.13850	131.1	6.8
HT122-34	0.27147	0.02640	1.05910	0.10508	0.02891	0.00145	34.589	1.73390	134.4	8.9
HT122-35	0.31703	0.03105	1.26983	0.10187	0.03091	0.00125	32.351	1.30510	132.8	9.2
HT122-36	0.46278	0.01903	2.86966	0.16269	0.04417	0.00152	22.641	0.77716	139.7	8.2
Sample HT125										
HT125-1	0.23209	0.01648	0.82036	0.04439	0.02815	0.00088	35.524	1.10990	139.4	5.6
HT125-2	0.12594	0.01146	0.41757	0.03330	0.02458	0.00075	40.681	1.24430	142.0	4.8
HT125-3	0.45501	0.01522	2.45790	0.07407	0.04040	0.00081	24.752	0.49765	130.3	5.4
HT125-4	0.12802	0.01112	0.38123	0.02755	0.02335	0.00064	42.821	1.17780	134.6	4.2
HT125-5	0.35582	0.01448	1.71781	0.06462	0.03531	0.00074	28.324	0.59438	141.0	4.9
HT125-6	0.47452	0.01936	2.59055	0.08873	0.04170	0.00109	23.979	0.62429	128.1	7.1
HT125-7	0.18274	0.01192	0.60364	0.03338	0.02579	0.00074	38.779	1.10750	137.7	4.6
HT125-8	0.42584	0.01803	2.11959	0.07174	0.03819	0.00089	26.188	0.60867	131.8	6.1
HT125-9	0.10556	0.01240	0.31141	0.03164	0.02233	0.00062	44.777	1.25130	132.6	4.2
HT125-10	0.25480	0.01468	0.93686	0.05344	0.02814	0.00088	35.531	1.10590	134.5	5.3
HT125-11	0.34228	0.01540	1.52473	0.07484	0.03224	0.00073	31.013	0.70531	132.2	4.9
HT125-12	0.34589	0.02015	1.51632	0.06840	0.03343	0.00080	29.912	0.71313	136.1	6.1
HT125-13	0.39094	0.01662	1.84290	0.08269	0.03497	0.00086	28.597	0.70575	130.2	5.5
HT125-14	0.35610	0.01571	1.63173	0.06322	0.03450	0.00087	28.986	0.73147	137.7	5.4
HT125-15	0.21478	0.01789	0.72135	0.05500	0.02599	0.00083	38.479	1.22450	132.3	5.5
HT125-16	0.29524	0.01245	1.15921	0.05036	0.02865	0.00064	34.898	0.77847	128.0	4.0
HT125-17	0.12691	0.01183	0.38632	0.03342	0.02371	0.00064	42.181	1.13200	136.8	4.3

Table 2. Cont.

Spot No.	Isotopic Ratios						Age (Ma)			
	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ	$^{238}\text{U}/^{206}\text{Pb}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ
HT125-18	0.51924	0.02029	3.26313	0.11403	0.04700	0.00122	21.275	0.55083	128.1	8.1
HT125-19	0.38652	0.02564	1.91581	0.14534	0.03675	0.00166	27.211	1.22990	138.0	9.5
HT125-20	0.34791	0.01688	1.56082	0.07380	0.03352	0.00080	29.831	0.71228	135.9	5.5
HT125-21	0.06820	0.00984	0.20369	0.03092	0.02195	0.00071	45.566	1.47830	136.7	4.7
HT125-22	0.26047	0.01596	0.96227	0.04704	0.02853	0.00068	35.048	0.82956	135.1	4.8
HT125-23	0.22954	0.01747	0.73737	0.05215	0.02579	0.00075	38.768	1.12700	128.3	5.1
HT125-24	0.19399	0.01821	0.59303	0.04814	0.02466	0.00080	40.551	1.31720	129.5	5.4
HT125-25	0.26297	0.01022	1.03694	0.04228	0.02873	0.00049	34.811	0.59889	135.5	3.3
HT125-26	0.41415	0.02364	2.29300	0.14495	0.04040	0.00132	24.754	0.81013	143.0	8.8
HT125-27	0.11492	0.01005	0.35371	0.02850	0.02294	0.00056	43.600	1.07270	134.5	3.7
HT125-28	0.32207	0.02154	1.31142	0.07402	0.03134	0.00093	31.909	0.94627	133.4	6.6
HT125-29	0.37509	0.01823	1.84603	0.08242	0.03695	0.00096	27.064	0.70453	142.0	6.5
HT125-30	0.34016	0.01459	1.52785	0.07061	0.03310	0.00084	30.212	0.76785	136.2	5.1
HT125-31	0.45724	0.01781	2.55851	0.09571	0.04161	0.00097	24.032	0.55766	133.4	6.7
HT125-32	0.46947	0.01560	2.67440	0.06923	0.04314	0.00096	23.180	0.51849	134.2	6.2
HT125-33	0.31778	0.02045	1.29124	0.08431	0.03015	0.00100	33.163	1.09710	129.4	6.4
HT125-34	0.41380	0.01523	2.11095	0.06994	0.03815	0.00085	26.210	0.58120	135.2	5.5
HT125-35	0.23452	0.01357	0.79918	0.03912	0.02641	0.00060	37.870	0.86509	130.4	4.1
HT125-36	0.24305	0.01643	0.90284	0.06345	0.02768	0.00084	36.131	1.10260	134.8	5.4
HT125-37	0.41542	0.01787	2.07215	0.09657	0.03688	0.00103	27.114	0.76006	130.3	6.4
HT125-38	0.36834	0.02640	1.66470	0.11191	0.03471	0.00106	28.812	0.88334	135.2	8.2

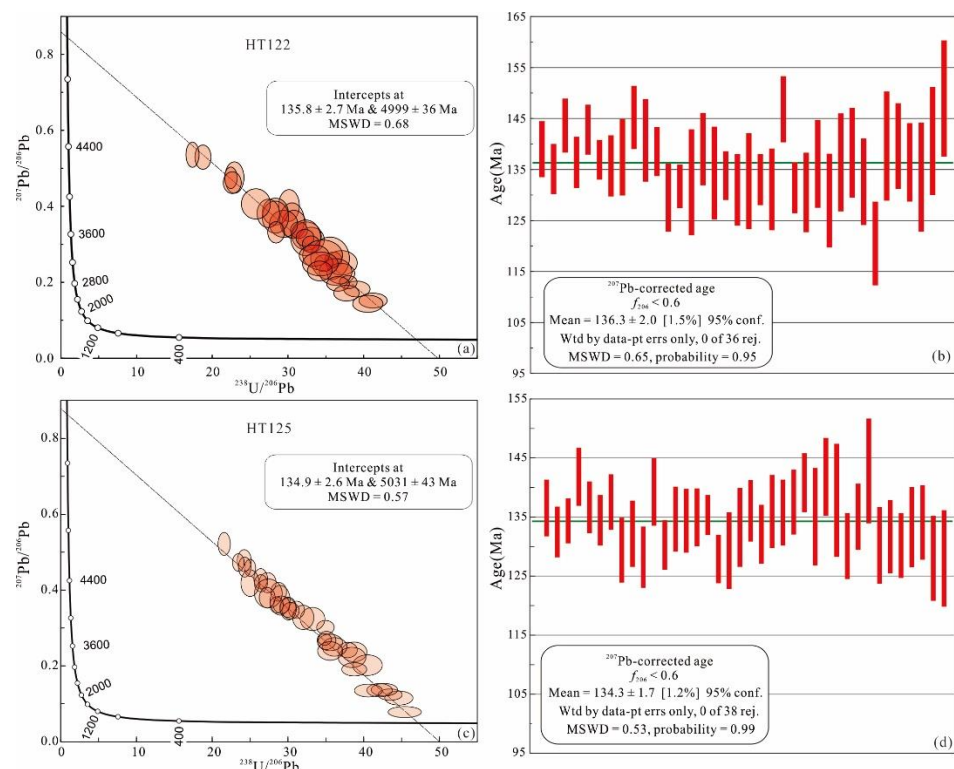


Figure 8. LA-ICP-MS cassiterite U-Pb Tera-Wasserburg concordia diagrams (a,c) and ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ age histograms (b,d) for samples HT122 and HT125 from the Huaobaote deposit.

Thirty-six spots on sample HT122 yielded a Tera-Wasserburg concordia lower intercept age of 135.8 ± 2.7 Ma (MSWD = 0.68; Figure 8a) and a weighted mean age of 136.3 ± 2.0 Ma (MSWD = 0.65; Figure 8b). Thirty-eight spots on sample HT125 yielded a Tera-Wasserburg concordia lower intercept age of 134.9 ± 2.6 Ma (MSWD = 0.57; Figure 8c)

and a weighted mean age of 134.3 ± 1.7 Ma (MSWD = 0.53; Figure 8d). All these age data are consistent within the limits of error; thus, the age of 136.3–134.3 Ma is interpreted to be the mineralization age of the Huaaobaote deposit.

5.2. Fluid Inclusion Study

5.2.1. Petrography

Based on the phase proportions at room temperature, the phase transitions during heating and cooling, and the results of laser Raman spectroscopy, FIs in the Huaaobaote deposit can be divided into the following four types:

- (1) Liquid-rich inclusions (WL type): These FIs are extensively hosted in the tested quartz of all the stages and sphalerite of stage III, accounting for approximately 88% of the total number of FIs. They are polygonal, elliptical, long columnar, and irregular in shape, with diameters of 5–20 μm . The bubbles account for 5%–40% of the total volume at room temperature (Figure 9a,c,d,g–i). These FIs were homogenized to liquid when heated. In addition, in this type of FIs, some FIs contain needle-like opaque minerals that did not dissolve when heated (Figure 9b,c,g), implying that they are not daughter minerals. According to the morphology of opaque minerals, we speculate that they may be stibnite and/or jamesonite.
- (2) Gas-rich inclusions (WG type): These are exclusively developed in the quartz veins of stages II and III, accounting for about 5% of the total number of FIs, with diameters of 5–40 μm . The WG-type FIs are mostly oval and negative crystal shapes, with bubbles accounting for 52%–85% of the total volume (Figure 9e,f). These FIs were homogenized to vapor when heated.
- (3) Pure liquid inclusions (L type): These inclusions are mostly found in stages III and IV, have an irregular or polygonal shape with a size of 4–9 μm , accounting for about 4% of the total number of FIs. They are in a liquid phase at room temperature; when heated, these L-type FIs have no phase change.
- (4) Pure gas inclusions (G type): These inclusions predominantly occur in stages II and III. They are 5–8 μm in size and irregular or round in shape, accounting for 3% of the total number of FIs. They are in a gas phase at room temperature and have no phase change when heated.

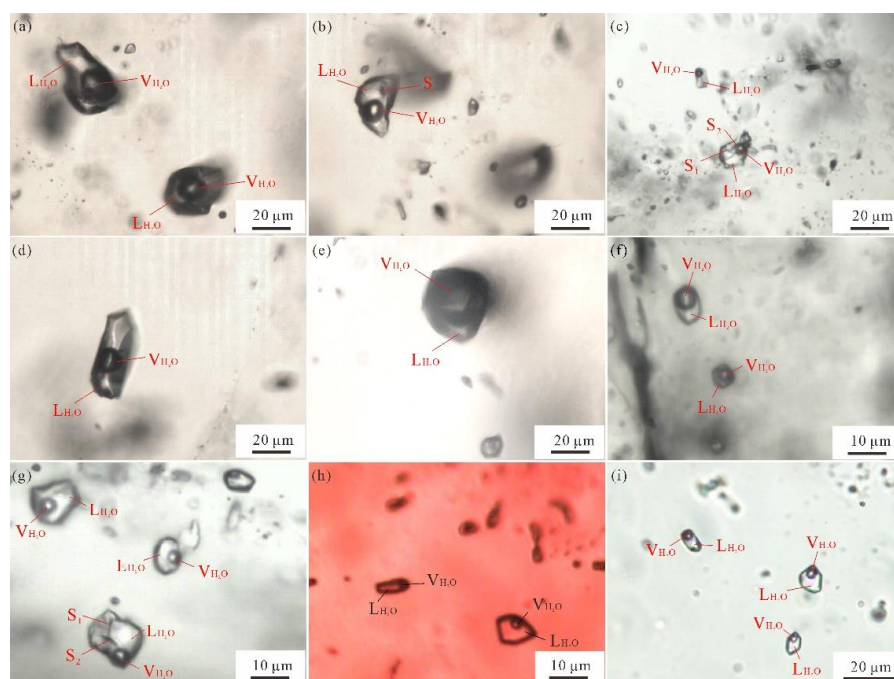


Figure 9. Representative microphotographs of fluid inclusions in quartz and sphalerite from the

Huaaobaote deposit. (a) WL-type FIs in the quartz of stage I; (b) WL-type FIs in the quartz of stage I, some of which contain solid sulfide; (c) WL-type FIs in the quartz of stage II, some of which contain one or more solid sulfide particles; (d) WL-type FIs in the quartz of stage II; (e) WG-type FIs in the quartz of stage II; (f) WL- and WG-type FIs in the quartz of stage III; (g) WL-type FIs in the quartz of stage III, some of which contain several solid sulfide particles; (h) WL-type FIs in the sphalerite of stage III; (i) WL-type FIs in the quartz of stage IV. L_{H_2O} = liquid phase H_2O ; S = solid sulfide particle; V_{H_2O} = vapor phase H_2O .

5.2.2. Microthermometry

The microthermometric results and fluid inclusion assemblage (FIA) parameters are shown in Table 3 and Figure 10.

Table 3. Microthermometry data and relative parameters of fluid inclusion assemblage (FIA) in the Huaaobaote deposit.

Type	Host Mineral	FIA No.	No.	Size (μm)	V (vol.%)	T _m (ice) (°C)		T _h (°C)		Salinity (wt% NaCl eqv.)		Density (g/cm ³)
						Range	Mean	Range	Mean	Range	Mean	
Stage I: cassiterite–arsenopyrite–pyrite–quartz stage (samples HT117 and HT119)												
WL	Quartz	1	7	6–22	20–35	−3.0 to −2.2	−2.7	315–340	327	3.7–5.0	4.5	0.69–0.72
WL	Quartz	2	13	7–28	20–35	−4.1 to −2.8	−3.3	323–339	332	4.6–6.6	5.4	0.70–0.72
WL	Quartz	3	5	8–15	15–20	−3.0 to −2.6	−2.8	302–306	304	4.3–5.0	4.7	0.74–0.76
Stage II: cassiterite–chalcopyrite–pyrite–freibergite–arsenopyrite–pyrrhotite–quartz stage (samples H44 and HT115)												
WL	Quartz	1	8	8–14	15–20	−2.7 to −2.3	−2.5	282–291	286	3.9–4.5	4.2	0.77–0.79
WL	Quartz	2	8	13–60	10–40	−2.4 to −1.9	−2.1	267–304	286	3.2–4.0	3.5	0.74–0.80
WG	Quartz	3	2	15–40	68–85	−2.1 to −1.9	−2.0	288–293	291	3.2–3.5	3.4	0.75–0.77
WL	Quartz	4	8	3–17	10–30	−1.3 to −0.1	−1.0	271–286	277	0.2–2.2	1.7	0.73–0.78
Stage III: sphalerite–galena–jamesonite–stibnite–freibergite–silver mineral–quartz–calcite–chlorite stage (samples HT50, HT56, HT80, HT84, HT86, HT112, and HT164)												
WL	Quartz	1	5	4–11	15–30	−0.4 to −0.1	−0.2	196–210	206	0.2–0.7	0.4	0.85–0.88
WL	Quartz	2	14	4–12	10–25	−3.0 to −0.9	−2.0	189–267	242	1.6–5.0	3.4	0.81–0.91
WL	Quartz	3	10	5–24	8–30	−2.3 to −2.0	−2.2	194–228	209	3.4–3.9	3.6	0.86–0.90
WL	Quartz	4	2	7–18	15–20	−2.1 to −0.1	−1.1	196–225	211	0.2–3.5	1.9	0.86–0.87
WL	Quartz	5	1	16	18	−0.7	−0.7	222	222	1.2	1.2	0.85
WL	Quartz	6	4	8–12	15–35	−0.5 to −0.1	−0.3	235–273	249	0.2–0.9	0.5	0.76–0.83
WG	Quartz	7	2	5–9	52–65	−0.3 to −0.2	−0.3	236–237	237	0.4–0.5	0.5	0.81–0.82
WL	Quartz	8	14	3–20	10–35	−2.7 to −0.4	−1.3	196–263	227	0.7–4.5	2.2	0.78–0.88
WG	Quartz	9	1	8	73	−0.8	−0.8	224	224	1.4	1.4	0.85
WL	Sphalerite	10	16	4–16	5–35	−2.9 to −0.4	−1.3	186–223	207	0.7–4.8	2.3	0.84–0.91
WL	Quartz	11	3	3–13	10–15	−0.9 to −0.8	−0.8	197–198	198	1.4–1.6	1.5	0.88
Stage IV: argentite–pyrrargyrite–pyrite–quartz–calcite stage (samples HT63, HT65, and HT75)												
WL	Quartz	1	5	4–13	5–10	−0.9 to −0.6	−0.8	188–199	193	1.1–1.6	1.4	0.88–0.89
WL	Quartz	2	4	4–9	10–15	−0.9 to −0.6	−0.8	187–194	190	1.1–1.6	1.4	0.88–0.89
WL	Quartz	3	24	5–10	10–20	−0.8 to −0.2	−0.5	166–192	180	0.4–1.4	0.9	0.88–0.91

Abbreviations: T_h = total homogenization temperature; T_m (ice) = final melting temperature of ice; V = volume fraction of gas phase in the total volume of inclusion.

FIs in the quartz of stage I: Three FIAs have been recognized. The homogenization temperature of these FIAs varies from 302 $^{\circ}\text{C}$ to 340 $^{\circ}\text{C}$; the final ice melting temperature is −4.1 $^{\circ}\text{C}$ to −2.2 $^{\circ}\text{C}$, corresponding to salinities of 3.7–6.6 wt% NaCl eqv.; and the density of the fluid is 0.69–0.76 g/cm^3 .

FIs in the quartz of stage II: Four FIAs have been recognized. The homogenization temperature of the WL-type FIAs varies from 267 $^{\circ}\text{C}$ to 304 $^{\circ}\text{C}$; the final ice melting temperature ranges from −2.7 $^{\circ}\text{C}$ to −0.1 $^{\circ}\text{C}$, corresponding to salinities of 0.2–4.5 wt% NaCl eqv.; and the fluid density is 0.73–0.80 g/cm^3 . The homogenization temperature of the WG-type FIAs varies from 288 $^{\circ}\text{C}$ to 293 $^{\circ}\text{C}$; the final ice melting temperature ranges from −2.1 $^{\circ}\text{C}$ to −1.9 $^{\circ}\text{C}$, corresponding to salinities of 3.2–3.5 wt% NaCl eqv.; and the density of the fluid is in the range of 0.75–0.77 g/cm^3 .

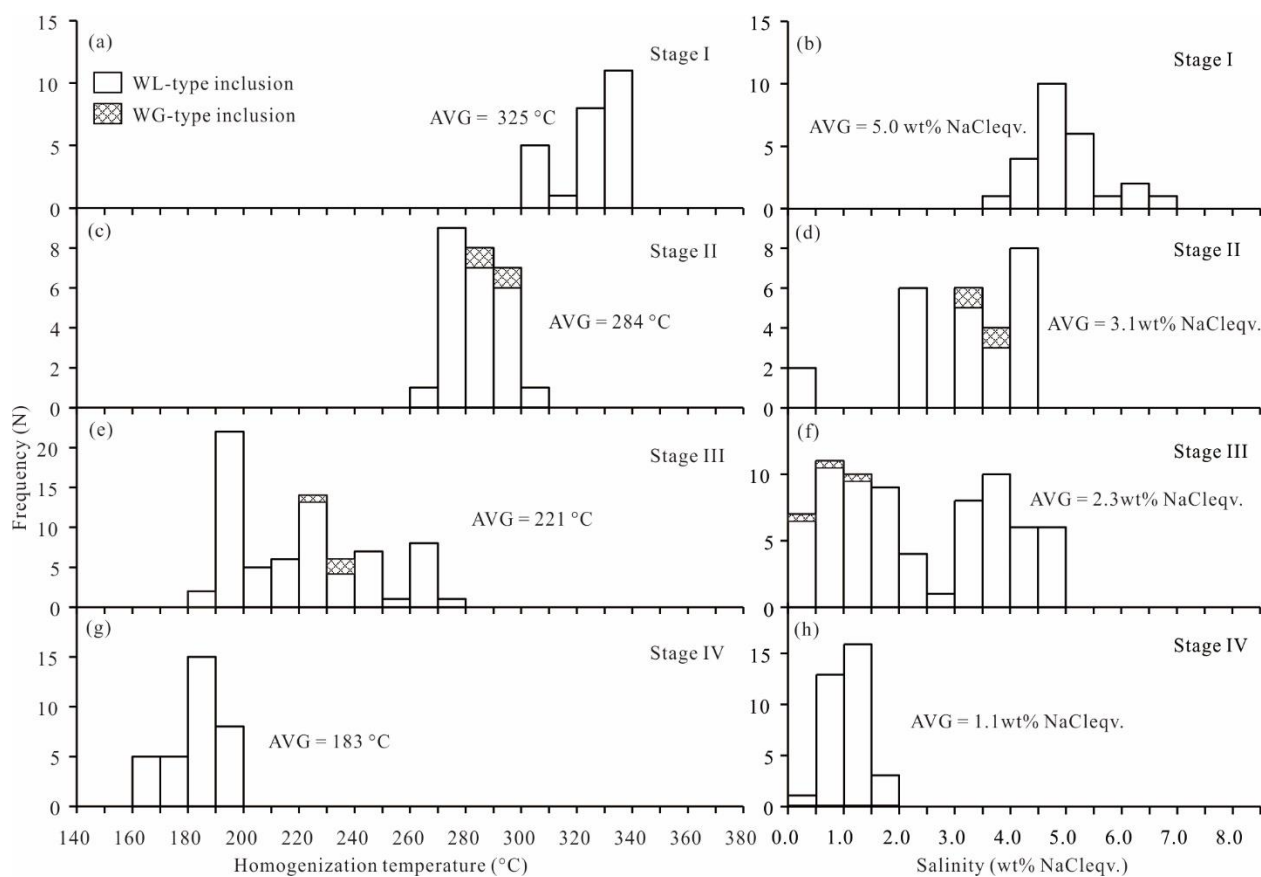


Figure 10. Histograms of homogenization temperature and salinity of fluid inclusions in the Huaoba deposit. (a) Homogenization temperature of stage I, (b) salinity of stage I, (c) homogenization temperature of stage II, (d) salinity of stage II, (e) homogenization temperature of stage III, (f) salinity of stage III, (g) homogenization temperature of stage IV, (h) salinity of stage IV.

FIs in the quartz and sphalerite of stage III: Eleven FIAs have been recognized. The homogenization temperature of the WL-type FIAs varies from 186 °C to 273 °C; the final ice melting temperature ranges from −3.0 °C to −0.1 °C, corresponding to salinities of 0.2–5.0 wt% NaCl eqv.; and the fluid density is 0.76–0.91 g/cm³. The homogenization temperature of the WG-type FIAs is 224–237 °C; the final ice melting temperature varies from −0.8 °C to −0.2 °C, corresponding to salinities 0.4–1.4 wt% NaCl eqv.; and the density of the fluid is 0.81–0.85 g/cm³.

FIs in the quartz of stage IV: Three FIAs have been recognized. The homogenization temperature of these FIAs varies from 166 °C to 199 °C; the final ice melting temperature ranges from −0.9 °C to −0.2 °C, corresponding to salinities of 0.4–1.6 wt% NaCl eqv.; and the fluid density is 0.88–0.91 g/cm³.

5.2.3. Laser Raman Spectra

The results of the representative laser Raman spectroscopic analyses of the individual FIAs from different stages are shown in Figure 11. The gas-phase components in stage I are dominated by H₂O and CH₄ (Figure 11a). The gas-phase components of stage II are characterized by H₂O and N₂ (Figure 11b). The gas-phase components for stages III and IV are mainly H₂O (Figure 11c,d). In general, it seems that the metallogenic fluid evolves gradually from the early-stage H₂O–NaCl–CH₄ system, through the middle-stage H₂O–NaCl–N₂ system, to the late-stage H₂O–NaCl system.

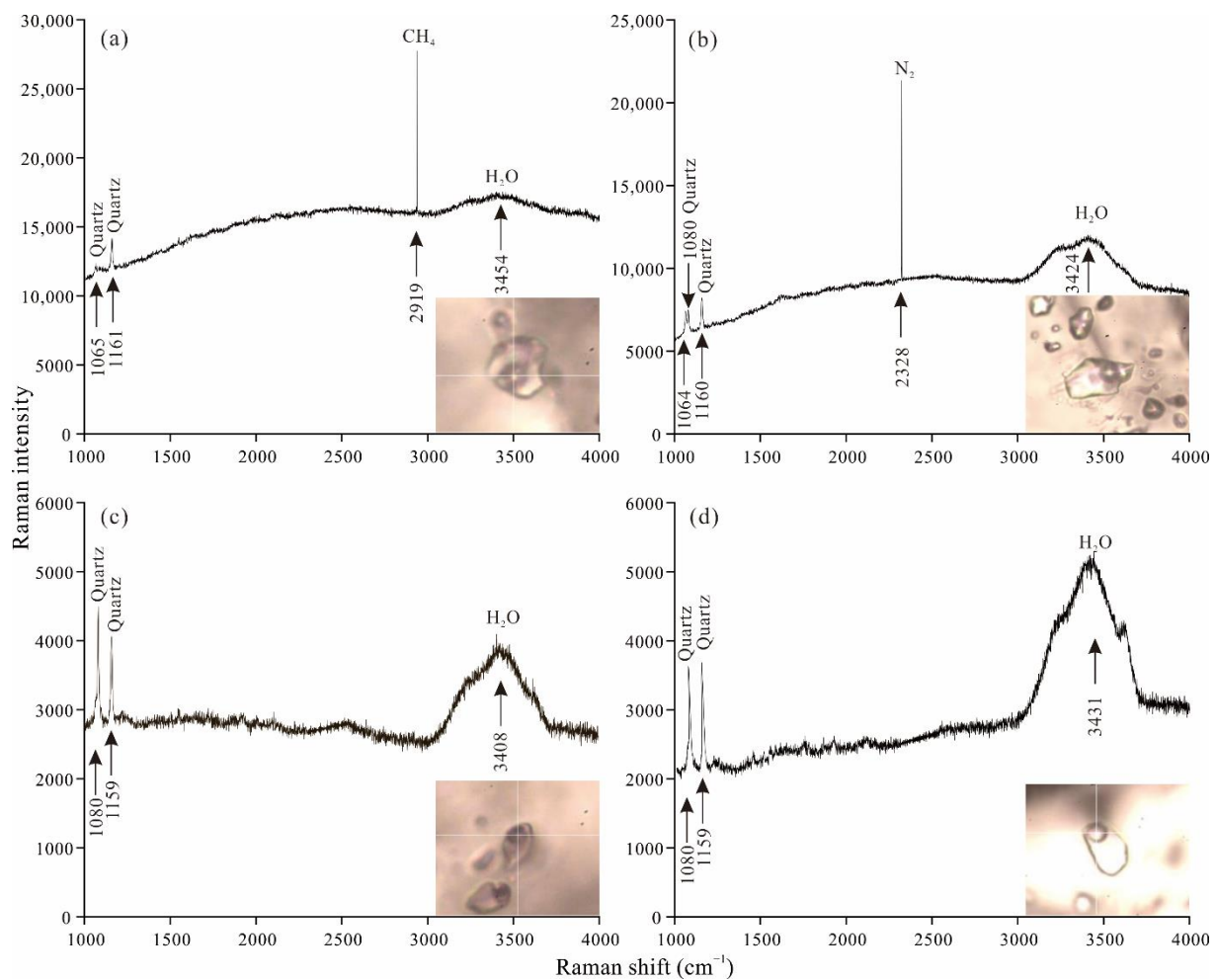


Figure 11. Laser Raman spectra for fluid inclusions in quartz from the Huaaobaote deposit. (a) WL-type FIs of stage I; (b) WL-type FIs of stage II; (c) WL-type FIs of stage III; and (d) WL-type FIs of stage IV.

5.3. Isotope Data

5.3.1. Hydrogen and Oxygen Isotopes

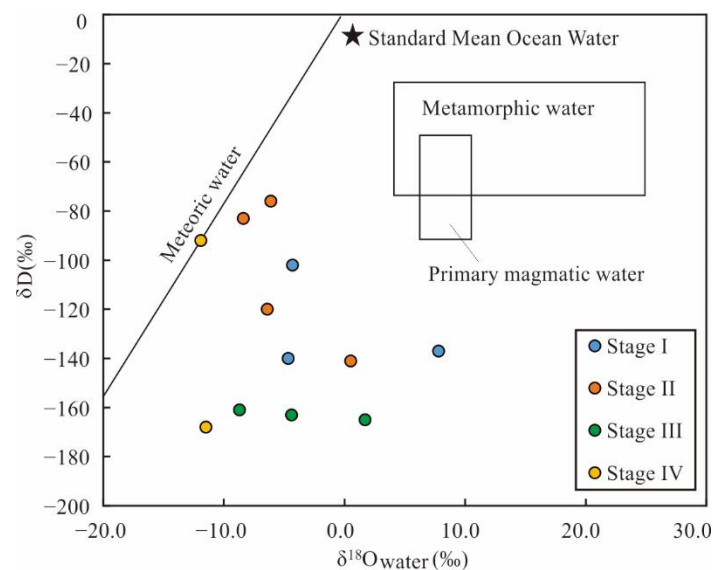
The analytical results for the oxygen isotopes of 12 quartz samples and hydrogen isotopes of fluid inclusions of the Huaaobaote deposit are listed in Table 4 and plotted in Figure 12. Three samples from stage I have δD values of -140‰ to -102‰ , $\delta^{18}O_{\text{quartz}}$ values of 1.4‰ – 13.9‰ , and $\delta^{18}O_{\text{water}}$ values of -4.6‰ to 7.9‰ , respectively. The δD , $\delta^{18}O_{\text{quartz}}$, and $\delta^{18}O_{\text{water}}$ values of four samples from stage II are -141‰ to -76‰ , -0.9‰ to 8.0‰ , and -8.4‰ to 0.5‰ , respectively. The δD , $\delta^{18}O_{\text{quartz}}$, and $\delta^{18}O_{\text{water}}$ values of three samples from stage III are -165‰ to -161‰ , 1.7‰ – 12.1‰ , and -8.7‰ to 1.7‰ , respectively. Two samples from stage IV have δD values of -168‰ and -92‰ , $\delta^{18}O_{\text{quartz}}$ values of 0.9‰ and 1.3‰ , and $\delta^{18}O_{\text{water}}$ values of -11.9‰ and -11.5‰ , respectively.

Table 4. Oxygen isotopic composition (‰) for quartz and hydrogen and oxygen compositions (‰) for fluid inclusions in quartz from the Huaaobaote deposit.

Sample No.	Stage	Mineral	T_h (°C)	$\delta^{18}O_{\text{quartz}}$ (V-SMOW)	$\delta^{18}O_{\text{water}}$ (V-SMOW)	$\delta D_{\text{V-SMOW}}$
H32	I	Quartz	325	1.5	−4.5	−102
H34	I	Quartz	325	1.4	−4.6	−140
H40	I	Quartz	325	13.9	7.9	−137

Table 4. Cont.

Sample No.	Stage	Mineral	T_h (°C)	$\delta^{18}\text{O}_{\text{quartz}}$ (V-SMOW)	$\delta^{18}\text{O}_{\text{water}}$ (V-SMOW)	$\delta\text{D}_{\text{V-SMOW}}$
H3-5	II	Quartz	284	1.4	−6.1	−76
H3-7	II	Quartz	284	8.0	0.5	−141
H3-8	II	Quartz	284	−0.9	−8.4	−83
H3-9	II	Quartz	284	1.1	−6.4	−120
H46	III	Quartz	221	12.1	1.7	−165
H49	III	Quartz	221	1.7	−8.7	−161
H50	III	Quartz	221	6.0	−4.4	−163
H42	IV	Quartz	183	1.3	−11.5	−168
H51	IV	Quartz	183	0.9	−11.9	−92

Figure 12. δD versus $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ diagram of the Huaaobaote deposit (base map from [65]).

5.3.2. Sulfur Isotope

The sulfur isotopic compositions of the five pyrite, one sphalerite, one arsenopyrite, and two galena samples are presented in Table 5 and Figure 13. The $\delta^{34}\text{S}$ (‰) values of three pyrite samples from stage I are between −0.2 and 0.3. The $\delta^{34}\text{S}$ (‰) values of one arsenopyrite sample and pyrite sample from stage II are 0.6 and 1.1, respectively. The $\delta^{34}\text{S}$ (‰) values of two galena samples, one pyrite sample, and one sphalerite sample from stage III are −3.4 to −0.9. In brief, the overall variation range of the $\delta^{34}\text{S}$ values is −3.4‰ to 1.1‰ (mean −0.5‰).

Table 5. Sulfur and lead isotopic compositions of sulfide samples from the Huaaobaote deposit.

Sample No.	Mineral	Stage	$\delta^{34}\text{S}_{\text{V-CDT}}$ (‰)	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (‰)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	t (Ma)	μ	ω	κ	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
H32	Pyrite	I	−0.2	−1.3	18.219	15.535	38.048	135	9.4	35.4	3.7	59.9	13.7	21.2
H34	Pyrite	I	0.3	−0.8	18.232	15.552	38.100	135	9.4	35.7	3.7	60.6	14.8	22.6
H35	Pyrite	I	0.1	−1.0	18.225	15.545	38.080	135	9.4	35.6	3.7	60.2	14.3	22.0
H3-1	Arsenopyrite	II	0.6	−0.7	18.225	15.546	38.084	135	9.4	35.6	3.7	60.2	14.4	22.1
H26	Pyrite	II	1.1	−0.2	18.237	15.565	38.137	135	9.4	35.9	3.7	60.9	15.6	23.6
H1-4	Galena	III	−3.4	−0.8	18.216	15.531	38.027	135	9.4	35.3	3.7	59.7	13.4	20.6
H1-4	Sphalerite	III	−0.9	−1.3	18.317	15.667	38.475	135	9.6	37.8	3.8	65.6	22.3	32.6
H1-5	Galena	III	−1.4	1.2	18.257	15.586	38.207	135	9.5	36.3	3.7	62.1	17.0	25.4
H46	Pyrite	III	−2.0	−3.6	18.195	15.509	37.965	135	9.3	34.9	3.6	58.5	12.0	18.9

Abbreviations: $\mu = ^{238}\text{U}/^{204}\text{Pb}$; $\omega = ^{232}\text{Th}/^{204}\text{Pb}$; $\kappa = \text{Th}/\text{U}$; $\Delta\alpha = [(^{206}\text{Pb}/^{204}\text{Pb})_{\text{d(t)}} / (^{206}\text{Pb}/^{204}\text{Pb})_{\text{m(t)}} - 1] \times 1000$; $\Delta\beta = [(^{207}\text{Pb}/^{204}\text{Pb})_{\text{d(t)}} / (^{207}\text{Pb}/^{204}\text{Pb})_{\text{m(t)}} - 1] \times 1000$; $\Delta\gamma = [(^{208}\text{Pb}/^{204}\text{Pb})_{\text{d(t)}} / (^{208}\text{Pb}/^{204}\text{Pb})_{\text{m(t)}} - 1] \times 1000$; d is the Pb of ore mineral; and m is mantle Pb calculated by the equation of Chen et al. [66].

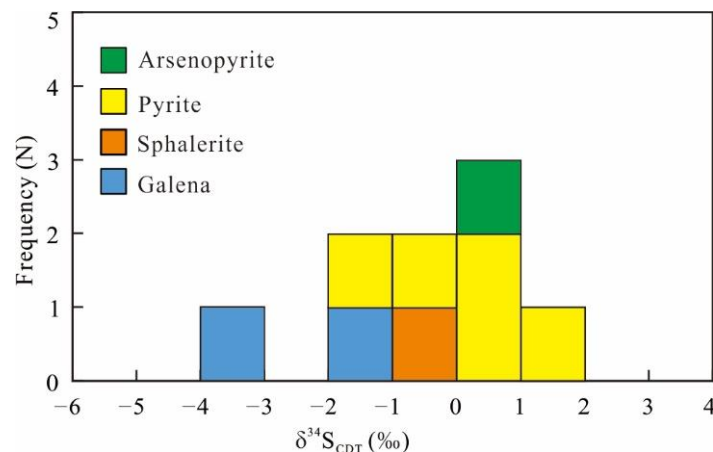


Figure 13. Sulfur isotope histogram of sulfides from the Huaaobaote deposit.

5.3.3. Lead Isotope

The lead isotopic data for nine sulfide samples are presented in Table 5 and Figure 14. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for three pyrite samples from stage I are between 18.219 and 18.232, 15.535 and 15.552, and 38.048 and 38.100, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for one arsenopyrite sample and one pyrite sample from stage II are 18.225 and 18.237, 15.546 and 15.565, and 38.084 and 38.137, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for two galena samples, one pyrite sample, and one sphalerite sample from stage III range from 18.195 to 18.317, 15.509 to 15.667, and 37.965 to 38.475, respectively.

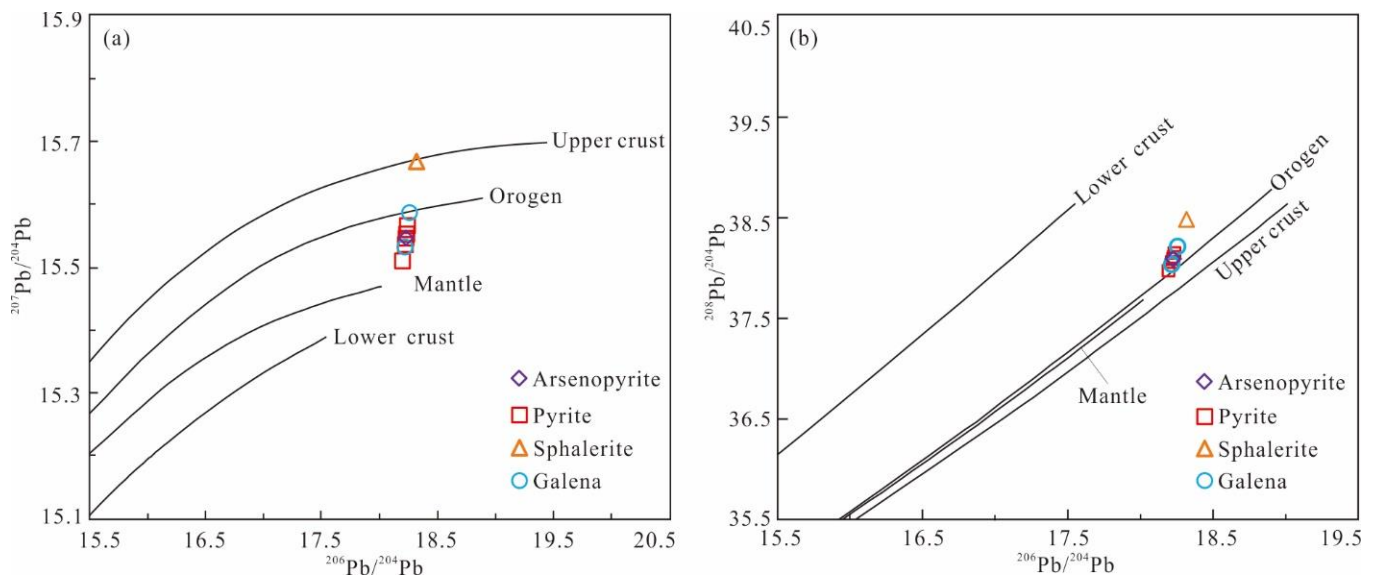


Figure 14. Diagrams of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ (a) and $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ (b) for sulfides from the Huaaobaote deposit (base map from [67]).

6. Discussion

6.1. Mineralization Age

Chen et al. [27] reported a zircon U–Pb age of 136 ± 0.8 Ma for the hypabyssal rhyolite in the Huaaobaote deposit. The Fujian Institute of Geological Survey [52] obtained zircon U–Pb ages of 132.6–127.0 Ma for the granite, monzogranite, and syenogranite of the Ganggantewula intrusion in the southern part of the Huaaobaote area. In addition, Zhou [29] and Shang et al. [30] obtained zircon U–Pb ages of 285.9 ± 4.1 Ma and 294.8 ± 3.2 Ma for the diorite porphyry, respectively, which is mainly distributed along the Huaaobaote

tectonic mélange belt and spatially accompanies the orebodies. However, a portion of the Ag–Pb–Zn–Sb mineralization in the Huaaobaote deposit crosscuts the hypabyssal rhyolite, suggesting the mineralization postdates the hypabyssal rhyolite crystallization, as well as the diorite porphyry. Some researchers have argued that the Early Cretaceous felsic-magmatism in the Huaaobaote area is related to the Ag–Pb–Zn–Cu–Sn–Sb mineralization [14,27,28,30], and infer that the mineralization is contemporaneous or slightly later than the granite and hypabyssal rhyolite (136–127 Ma) [27,30,52].

Cassiterite is the main ore mineral in the Ag–Cu–Sn orebodies of the Huaaobaote deposit. Petrographic observations revealed that the cassiterite is largely distributed in granular form within the quartz veins and coexisted with chalcopyrite, arsenopyrite, and pyrite. The U–Pb closure temperature of cassiterite ranges from 500 °C to 800 °C [68–70]. Therefore, the cassiterite U–Pb age can accurately define the mineralization time of the Huaaobaote deposit. In this study, we obtained cassiterite U–Pb ages of 136.3–134.3 Ma for the Sn and Ag–Cu–Sn ores, indicating that the mineralization of Sn and Ag–Cu–Sn in the Huaaobaote deposit occurred during the Early Cretaceous period. Our cassiterite U–Pb dating data indicate a clear temporal relationship between the Huaaobaote deposit and the Early Cretaceous hypabyssal rhyolite (136 ± 0.8 Ma), rather than the Permian diorite porphyry (285.9 ± 4.1 Ma and 294.8 ± 3.2 Ma) and the Early Cretaceous granite (132.6–127 Ma).

Previous studies have conducted extensive mineralization dating on representative deposits, including tin–polymetallic deposits, Ag–Pb–Zn deposits, and W–Mo deposits in the SGXR (Table 6). The dating results suggest that all the deposits formed during the Early Cretaceous (145–130 Ma).

Table 6. Mineralization ages of the major Ag–Pb–Zn–Sn–polymetallic deposits in the southern Great Xing’an Range.

Deposit	Metal Assemblage	Analytical Method	Mineralization Age (Ma)	References
Baiinchagandongshan	Ag–Sn–Pb–Zn–Cu	Cassiterite U–Pb	140–134	[23,51]
Daolundaba	Cu–Sn–W–Ag	Cassiterite U–Pb	136.8–134.7	[38]
Maodeng–Xiaogushan	Sn–Cu–Zn	Cassiterite U–Pb	135–133	[39,51]
Weilasituo	Li–Sn–Pb–Zn–Cu	Muscovite ^{40}Ar – ^{39}Ar	133.4	[71]
		Cassiterite U–Pb	136	[21]
Dajing	Sn–Cu–Pb–Zn–Ag	Cassiterite U–Pb	144	[15]
Huanggang	Fe–Sn–W	Molybdenite Re–Os	135	[48,72]
Bairendaba	Ag–Pb–Zn–Cu	Muscovite ^{40}Ar – ^{39}Ar	135	[73]
Bianjiadayuan	Ag–Pb–Zn	Molybdenite Re–Os	140	[74]
Haobugao	Pb–Zn–Cu–Fe	Molybdenite Re–Os	142	[17,75]
Chamuhan	W–Mo	Molybdenite Re–Os	139	[76,77]
Dongshanwan	Mo–W	Molybdenite Re–Os	140.5	[78]

The Huaaobaote deposit formed during the period of 136.3–134.3 Ma, which is contemporaneous with other deposits in the SGXR, indicating that the Early Cretaceous was the peak season for Ag–Pb–Zn–Sn–polymetallic mineralization in the SGXR.

6.2. Nature and Evolution of Ore-Forming Fluids

The results of the FIs petrography, microthermometry, and laser Raman spectroscopy indicate that ore-forming fluids of the Huaaobaote deposit have a fluid characteristic with multistage evolution from stage I to stage IV. The FIs in stage I are mainly WL-type, are characterized by moderate–high temperature (302–340 °C, mean 325 °C), low salinity (3.7–6.6 wt% NaCl eqv., mean 5.0 wt% NaCl eqv.), and low density (0.69–0.76g/cm³, mean 0.72g/cm³), and contain CH₄, indicating that it belongs to an H₂O–NaCl–CH₄ system. The FIs in stage II are dominantly WL-type, with a small amount of WG-type FIs. The ore-forming fluids are characterized by moderate temperature (267–304 °C, mean

284 °C), low salinity (0.2–4.5 wt% NaCl eqv., mean 3.1 wt% NaCl eqv.), and low density (0.73–0.80 g/cm³, mean 0.77 g/cm³), and contain N₂, indicating that it belongs to an H₂O–NaCl–N₂ system. For stage III, the FIs are mainly WL-type, with a small amount of WG-type FIs. The ore-forming fluids are characterized by moderate–low temperature (186–273 °C, mean 221 °C), low salinity (0.2–5.0 wt% NaCl eqv., mean 2.3 wt% NaCl eqv.), and low density (0.76–0.91 g/cm³, mean 0.85 g/cm³), and only contain H₂O, indicating that it belongs to an H₂O–NaCl system. This stage is essentially consistent with the data reported by Chen et al. [27] for FIs, i.e., the homogenization temperature ranges from 145 to 274 °C, the salinity is 0.5–8.5 wt% NaCl eqv., and the density is 0.79–0.94 g/cm³. With regard to stage IV, the ore-forming fluids are characterized by relatively low temperature (166–199 °C, mean 183 °C), low salinity (0.4–1.6 wt% NaCl eqv., mean 0.9 wt% NaCl eqv.), and low density (0.88–0.91 g/cm³, mean 0.89 g/cm³), and only contain H₂O, the same as stage III, and also belongs to an H₂O–NaCl system.

In general, both the temperature and salinity of the ore-forming fluid gradually decrease from stage I to stage IV (Figure 10), while the FIs' density slightly increases, with a mean density of 0.72 g/cm³ for stage I, 0.77 g/cm³ for stage II, 0.85 g/cm³ for stage III, and 0.89 g/cm³ for stage IV. The coexisting WL- and WG-type FIs were developed in stages II and III, while only WL-type FIs occurred in stages I and IV.

6.3. Sources of Ore-Forming Fluid and Materials

6.3.1. Origin of Ore-Forming Fluids

As shown in Table 4, the H–O isotope compositions of fluids in various stages of the Huaoabaote deposit have a significant range of variation. In the $\delta^{18}\text{O}_{\text{water}}\text{--}\delta\text{D}$ diagram (Figure 12), the H–O isotope compositions of the samples from each stage are projected between the primary magmatic water box and the meteoric water evolution line, indicating that the ore-forming fluids are dominantly originated from a mixture of magmatic and meteoric water. Previous studies also suggested that the ore-forming fluids of the deposit are characterized by the mixing of magmatic and meteoric water [27]. Overall, the ore-forming fluid of the Huaoabaote deposit is characterized by low H and O isotope composition, which is consistent with that of high-latitude meteoric water [79,80]. From early to late, the H–O isotope composition of the Huaoabaote deposit shows a gradual decreasing trend, although the projection points are relatively scattered, indicating that with the evolution of ore-forming fluids, the involvement of meteoric water gradually increases.

In summary, the ore-forming fluids of the deposit predominantly originate from a mixture of magmatic and meteoric water, and the involvement of meteoric water gradually increases with the evolution of ore-forming fluids.

6.3.2. Source of Ore-Forming Materials

As shown in Figure 13, the statistical histogram of the $\delta^{34}\text{S}$ values in the Huaoabaote deposit shows a tower-style distribution and varies within a narrow range (−3.4‰ to 1.1‰), which are in the same range as previously reported values (−3.6‰ to 1.2‰ [27]), indicating the sulfur source is isotopically uniform. In a hydrothermal system, the S isotopic composition of the sulfides is a function of the total S isotopic compositions ($\delta^{34}\text{S}_{\Sigma}$), oxygen fugacity ($f\text{O}_2$), pH, ionic strength, and temperature of the ore-forming solution [81]. This suggests that the S isotopic compositions of hydrothermal sulfides depend not only on the $\delta^{34}\text{S}$ value of the source materials, but also on the physical and chemical condition of the ore-forming fluids. However, when the hydrothermal fluids are dominated by H₂S with low oxygen fugacity, the relationship $\delta^{34}\text{S}_{\Sigma} \approx \delta^{34}\text{S}_{\text{H}_2\text{S}} \approx \delta^{34}\text{S}_{\text{fluid}} \approx \delta^{34}\text{S}_{\text{melt}}$ holds in the equilibrium state [82]. The absence of sulfate minerals in all the mineralization stages of the Huaoabaote deposit indicates that the metal minerals precipitated in a relatively reductive environment. The variation law of sulfur isotope composition in the Huaoabaote deposit is $\delta^{34}\text{S}_{\text{Py}} > \delta^{34}\text{S}_{\text{Sph}} > \delta^{34}\text{S}_{\text{Gn}}$ (Figure 13), which is consistent with the $\delta^{34}\text{S}$ enrichment condition of $\delta^{34}\text{S}_{\text{Py}} > \delta^{34}\text{S}_{\text{Sph}} > \delta^{34}\text{S}_{\text{Ccp}} > \delta^{34}\text{S}_{\text{Gn}}$ [82–85]. The mineral species and sulfur isotope characteristics indicate that the metal minerals of the Huaoabaote deposit precipitated in

an equilibrium state with a relatively reductive environment. Therefore, the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ value can represent the total S isotopic composition of the ore-forming fluids. The $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values were calculated using the equation $\delta^{34}\text{S}_{\text{H}_2\text{S}} = \delta^{34}\text{S}_i - A_i (10^6 \times T^{-2})$, where i stands for different sulfides; the A_i value is 0.4 for pyrite and arsenopyrite, 0.1 for sphalerite, and -0.63 for galena, respectively; and T is the temperature in Kelvin [86]. The average FIA homogenization temperatures for different mineralization stages were used to calculate the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values of respective stages.

As shown in Table 5, the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values range from -1.3‰ to -0.8‰ for stage I, -0.7‰ to -0.2‰ for stage II, and -3.6‰ to 1.2‰ for stage III. The sulfur isotope composition of the Huaoabaote deposit is consistent with that of the magmatic and meteorite, implying the ore-forming materials of the deposit predominantly originated from magma.

The Pb isotopic composition of the ore is mainly controlled by the initial Pb isotopic composition and formation time and is rarely fractionated in the processes of element migration and precipitation. Therefore, the Pb isotope serves as a useful geological tracer for tracing the source of ore-forming material [87–89]. The μ , ω , and κ values of the Pb isotope of sulfides from the Huaoabaote deposit are 9.3–9.6, 34.9–37.8, and 3.6–3.8, with average values of 9.4, 35.8, and 3.7, respectively (Table 5). Zartman and Doe [67] obtained μ values of 9.60 and 8.92, ω values of 36.84 and 31.84, and κ values of 5.85 and 3.45 for the crust and mantle, respectively. The Pb isotope μ , ω and, κ values of the Huaoabaote deposit are between the crust and mantle, implying that Pb was derived from a mixed source of the crust and mantle. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram (Figure 14a), except for one sample with a high $^{207}\text{Pb}/^{204}\text{Pb}$ ratio, all the remaining samples are plotted in the area between the mantle and orogenic belt evolution curves. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Figure 14b), all of the data points are located between the lower crust and orogenic belt evolution lines, and near the orogenic belt evolution line. In the $\Delta\beta$ versus $\Delta\gamma$ genetic classification diagram (Figure 15), all of the ore lead data of the Huaoabaote deposit are projected within a transition area of the mantle-derived lead and the subduction zone lead related to magmatism, implying that the Pb of the Huaoabaote deposit originated from a mixed source of the upper crust and mantle lead. In addition, all the data are arranged in a straight line with steep slope in Figure 14a, implying that it is not an isochronous line, but a mixed lead line of orogen and mantle. Furthermore, the data points are also close to the range of the orogenic belt lead, although they are projected within the ranges of the mantle-derived lead and subduction zone lead related to magmatism (Figure 15). Chen et al. [27] reported the Pb isotope composition of nine galena samples from the Huaoabaote deposit and believed that the ore Pb mainly originates from the upper mantle and has Pb isotopic characteristics of the subduction zone with crust–mantle mixing. Based on the lead isotopic compositions above, and with the knowledge that the Huaoabaote deposit is located in the eastern section of the Central Asian orogenic belt, meaning that the mineralization of this deposit is closely related to the Mesozoic granitic magmatic activity, we infer that the ore lead of the Huaoabaote deposit mainly originated from the partial melting of orogenic belt materials.

In summary, the ore-forming materials of the Huaoabaote deposit mainly came from the Early Cretaceous magma, which originated from a partial melting of orogenic materials, which were composed of a mixture of the crust and mantle.

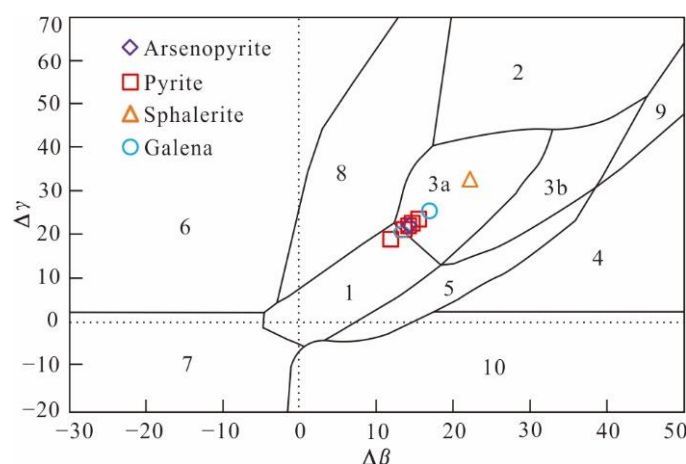


Figure 15. $\Delta\beta$ versus $\Delta\gamma$ genetic classification diagram for lead isotopes of ore minerals from the Huaaobaote deposit (base map after [90]). Numbered sections: 1 = mantle-derived lead; 2 = upper crust lead; 3 = subduction zone lead originated from the mixing of the upper crust and mantle lead (3a = lead related to magmatism; 3b = lead related to sedimentation); 4 = chemically deposited lead; 5 = submarine hydrothermal lead; 6 = medium–high grade metamorphism lead; 7 = lower crust lead of high-grade metamorphism; 8 = orogenic belt lead; 9 = upper crust lead in ancient shale; 10 = retrograde metamorphism lead.

6.4. Mechanism of Mineral Deposition

The capacity of hydrothermal fluids to transport metals in concentrations sufficient to form ore deposits is due in large part to the polar nature of the water molecule and the ability of metals to form strong aqueous complexes with a number of ligands [91]. Most hydrothermal liquids contain significant concentrations of solutes such as NaCl, CO₂, SO₂, H₂S, NH₃, HF, and H₃PO₄, and even some organic complexes, which interact with liquid water producing ligands that enable metal complexation [91–94]. Among them, the dominant ligands are Cl[−], HS[−], and OH[−] [92,94]. According to Pearson’s hard/soft acid/base (HSAB) principle [95], tin has a valence of 2⁺ or 4⁺ in hydrothermal fluids, and is a hard or borderline acid. In a reduced hydrothermal fluid, tin generally has a valence of 2⁺ [96,97], and Sn²⁺ as a borderline acid preferentially bonds with borderline bases, such as Cl[−] [91,95]. FI studies indicate that the tin mineralization stages are a relatively reduced environment, which is further supported by the symbiotic pyrrhotite in the same stages. Thus, we assume that tin is mainly composed of Sn²⁺ transported as chloride complexes. A possible reaction for the cassiterite precipitates is $\text{SnCl}_x^{2-x} + 2\text{H}_2\text{O} = \text{SnO}_2 + 2\text{H}^+ + x\text{Cl}^- + \text{H}_2$ [98]. Copper is a soft acid or intermediate acid, depending on whether it has a valence of 1⁺ or 2⁺, respectively [95]. Similarly, at low salinity and with a reduced hydrothermal fluids system, Cu⁺ is the dominant form of copper, a soft acid, and forms strong complexes with HS[−] [91]. Zinc is transported as chloride complexes in most physicochemical conditions, even Mississippi Valley-type (MVT) deposits, a fact that has been borne out by many solubility, spectroscopic, and thermodynamic studies [91,99]. However, the acidity of Pb²⁺ is softer than Zn²⁺ [95]; therefore, Pb²⁺ may bond with HS[−]. The thermodynamic modeling of Zhong et al. [99] revealed that Pb(HS)₂⁰ is the main Pb complex in a reduced hydrothermal fluid system under the conditions of low salinity (3.4 wt% NaCl eqv.), a temperature between 150 °C and 500 °C, and pressure greater than 1.0 kbar. Silver mainly exists in the form of Ag⁺ in hydrothermal fluids and preferentially bonds with soft ligands, such as HS[−] [95]. Indeed, in sulphide-containing solutions at temperatures between 25 °C and 400 °C, and a chloride concentration up to 0.5 mol kg^{−1}, silver (I) sulphide complexes are most important [91,100]. Sulfide ores, except for stage I, account for the majority of ore resources in the Huaaobaote deposit, in addition to a considerable amount of pyrite and pyrrhotite vein-bodies in the mine, indicating a high concentration of sulfur in the ore-forming fluid. Thus, we infer that silver was transported as a hydrosulfide complex. In summary, both Sn and Zn migrate in

the form of chloride complexes, while Cu, Pb, and Ag migrate in the form of hydrosulfide complexes in the Huaobaote deposit.

The precipitation of the dissolved constituents in hydrothermal fluid may be attributed to temperature variations, fluid immiscibility or boiling, reactions between wall rocks and solutions, and fluid mixing [93,94,101,102], which, in essence, affect the availability and stability of complexes of ligands. Figure 12 shows that the ore-forming fluid of the Huaobaote deposit is characterized by the mixing of magmatic and meteoric water; thus, fluid mixing is one of the main mechanisms for mineral precipitation in the deposit. From early to late periods, the temperature of the ore-forming fluid gradually decreased (Figure 16), indicating that fluid cooling is another one of the main mechanisms for mineral precipitation in the deposit. There are significant differences in the FIs type and fluid salinity at different stages, implying that the mineral precipitation mechanisms at each stage are not identical. For the first stage, the FIs are dominated by WL-type inclusions, with the highest homogenization temperature (302–340 °C) and salinity (3.7–6.6 wt% NaCl eqv.), suggesting that cooling was the main mechanism of cassiterite precipitation in the Huaobaote deposit. In stages II and III, WL- and WG-type inclusions coexist in the same quartz crystal. These different types of inclusions with different gas–liquid filling degrees have different homogenization patterns and contrasting salinities, but analogous homogenization temperatures (Figures 9 and 16), indicating that the fluids of the Ag–Cu–Sn and Ag–Pb–Zn–Sb mineralization stages are both immiscible. We believe that the phase separation caused by decompression induced fluid immiscibility, which is also demonstrated by the cryptoexplosive breccias developed in stage III. Therefore, fluid immiscibility is the main mechanism for the precipitation of the Ag–Cu–Sn of stage II and the Ag–Pb–Zn–Sb of stage III. Only WL-type FIs were observed in stage IV, and the ore-forming fluid is dominated by meteoric water with the lowest homogenization temperature (166–199 °C) and salinity (0.4–1.6 wt% NaCl eqv.), indicating that fluid cooling was the main mechanism of silver mineral precipitation in stage IV.

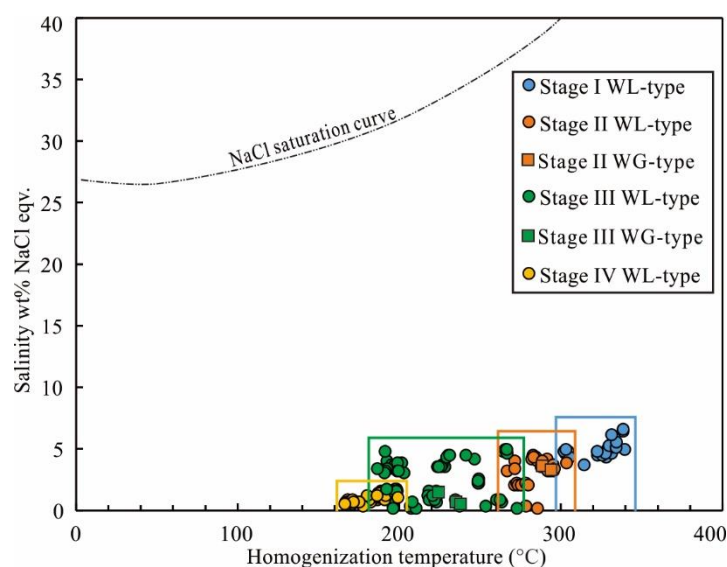


Figure 16. Diagram of homogenization temperature versus salinity of fluid inclusions in quartz and sphalerite from the Huaobaote deposit. NaCl saturation curve from [57].

In summary, fluid mixing, cooling, and immiscibility are the three main mechanisms for mineral precipitation in the Huaobaote deposit. Fluid mixing runs through the entire mineralization process. The cooling of the mixed fluid is the main mechanism for the Sn precipitation of stage I; fluid immiscibility is mainly responsible for the precipitation of the Ag–Cu–Sn of stage II and the Ag–Pb–Zn–Sb of stage III; and the Ag mineralization of stage IV is related to fluid cooling dominated by meteoric water.

7. Conclusions

- (1) Cassiterite U–Pb dating indicates that the Huaobaote deposit formed in the Early Cretaceous (136.3–134.3 Ma).
- (2) The ore-forming fluid is characterized by low salinity and has an affinity of $\text{H}_2\text{O}-\text{NaCl} \pm \text{CH}_4 \pm \text{N}_2$ in composition. From early to late periods, the ore-forming fluid underwent an evolution from the high temperature of stage I, through the medium temperature of stages II and III, to the low temperature of stage IV.
- (3) The ore-forming fluid of the Huaobaote deposit originated from a mixture of magmatic and meteoric water. With the evolution of ore-forming fluid, the amount of meteoric water increased gradually. The ore-forming materials were dominantly derived from the Early Cretaceous felsic magma.
- (4) Fluid mixing, cooling, and immiscibility were the three major mechanisms for the deposition of ore-forming materials. Of these, phase separation caused by fluid immiscibility was important for the precipitation of the Ag–Cu–Sn of stage II and the Ag–Pb–Zn–Sb of stage III, while fluid cooling was main mechanism for the Ag mineral precipitation of stage IV.

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