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# Genesis of Metal Sulfides and Its Significance on Graphite Mineralization in the Huangyangshan Graphite Deposit, East Junggar, Xinjiang Province, China

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Abstract: The Huangyangshan super-large graphite deposit is located in the Qitai area of East Junggar in Xinjiang Province, China. This deposit is well known for its distinguishing properties, including the alkaline granite complex that hosts the graphite ore, the dominantly orbicular structure developed in the graphite ore, and the association of graphite with metal sulfides in the orbicular ore. This study aims to determine the genetic relationship between graphite and metal sulfides in order to better understand the graphite mineralization process of the Huangyangshan deposit. The methods applied in the study include X-ray micro-CT scanning and scanning electron microscopy (SEM) analyses of the orbicular graphite ore and in situ inductive laser ablation-coupled plasma mass spectrometry (LA-ICP-MS) trace element analyses of the pyrrhotite and chalcopyrite associated with the graphite. The analytical results show that the graphite ore is composed of crystalline graphite, K-feldspar, albite, quartz, biotite, amphibole, and metal sulfides. The metal sulfides in the orbicular ore include pyrite, pyrrhotite, pentlandite, and chalcopyrite. According to the color, crystalline shape, texture, and occurrence, pyrrhotite can be classified into four types (I, II, III, and IV), and chalcopyrite into two types (I and II), of which types I, II, and III pyrrhotite and type I chalcopyrite have a close genetic relationship with graphite. The granular types (I, II, and III) of pyrrhotite are enriched in Co, Ni, Se, Ge, and Te and are depleted in As, Sb, Ag, and Au; they also have a high value of Co/Ni, indicating that these types of pyrrhotite have a magmatic origin. Low values of Co/Ni suggest that type IV pyrrhotite has a hydrothermal origin. The similar contents of Co and Ni and the values of Co/Ni compared with the chalcopyrite from the magmatic Co-Ni sulfide deposits imply that type I chalcopyrite has a magmatic origin. In summary, the metal sulfides of the Huangyangshan deposit are genetically related to graphite mineralization and formed predominantly by magmatic processes.

**Keywords:** in situ LA–ICP–MS trace element analysis; CT and SEM scanning; magmatic origin; orbicular graphite ore; Huangyangshan graphite deposit; East Junggar

# 1. Introduction

The Huangyangshan graphite deposit was discovered in the early 21st century in the Karamaili area of East Junggar, Xinjiang Province. This deposit is the first nonmetamorphic super-large crystallized graphite deposit to be discovered in China and contains probable graphite resources of >70 Mt. As a result, the deposit has attracted extensive research and prospecting attention from geologists [1,2]. The Huangyangshan deposit, together with the adjacent Sujiquan graphite deposit discovered in the 1960s, has some distinguishing characteristics. For instance, it occurs within the Huangyangshan alkaline granite complex, is characterized by an orbicular ore structure, and contains metal sulfides associated with graphite in the ore. In recent years, more and more geochronological and petrogeochemical



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). data for the ore-hosting Huangyangshan granite complex have shown that it is an A-type granite that was emplaced during the late Carboniferous period [2–4]. In order to determine the genesis of the Huangyangshan deposit and the original source of the carbon, studies of the graphite using X-ray powder diffraction (XRD), laser Raman spectroscopy, and carbon isotope analysis have led to the common view that the graphite mineralization in this area was sourced from the organic carbon in sedimentary strata at the periphery of the Huangyangshan pluton [5,6]. In contrast to the consensus regarding the carbon source, the genetic type and graphite mineralization mechanism of the Huangyangshan and adjacent Sujiquan graphite deposits remains uncertain. Two main hypotheses have been proposed: (1) graphite in the Huangyangshan and Sujiquan deposits crystallized during the magmatic period and are, therefore, of a magmatic origin [1,7–9]; (2) the graphite is of postmagmatic hydrothermal origin [2,5,10,11].

Available petrographic and ore microscopy data have shown that metal sulfides in the Huangyangshan graphite ore have a close spatial relationship with graphite, implying that the investigation of the metal sulfides should help to determine the mechanism of graphite mineralization. Aside from the S and Pb isotope data for the pyrrhotite samples, which indicate that the ore-forming material was derived from the mantle, as reported by Ai et al. [12] and Sun et al. [6], the nature and origin of the metal sulfides, including their occurrence and temporal and intergrowth relationships with the graphite and mineralization mechanism remain unclear. In this study, micro-CT scanning and scanning electron microscope (SEM) analyses were conducted on the graphite ore, and in situ trace element analysis using inductive laser-ablation coupled plasma mass spectrometry (LA–ICP–MS) was performed on the chalcopyrite and pyrrhotite. Integrating the results of these analyses, together with information on the ore-forming geological conditions and deposit geology, allow the genetic type and mineralization mechanism of the metal sulfides, as well as their genetic relationship with graphite mineralization in the Huangyangshan deposit, to be established.

## 2. Geological Background and Deposit Geology

## 2.1. Regional Geology

The East Junggar Orogenic Belt (EJOB) is located in the northeastern Junggar basin and comprises the Dulate arc, Armantai ophiolite belt, Yemaquan arc, Karamaili ophiolite belt, and the Halic-Dananhu arc from north to south [13–16]. The available data have suggested that the formation and evolution of the EJOB are related to the closure of the Junggar Ocean between the Junggar and Altai plates during the Paleozoic [17–19]. Geochronological data indicate that the Junggar Ocean formed during the early Ordovician and closed during the late Paleozoic, which caused the EJOB to evolve into a postcollision orogenic regime [17–21]. The Karamaili area, located in the southern EJOB, is a well-known tectonic-magmaticmetallogenic belt controlled by the deep NWW-trending Karamaili fault (Figure 1). Besides the scattered Silurian and Permian volcanic rocks and small amounts Mesozoic and Cenozoic sedimentary rocks, voluminous Devonian and Carboniferous volcanic sedimentary strata dominate the geology of the Karamaili area. The sedimentary rocks in this area were derived from active continental margin sediments that were deposited in a fore-arc basin setting, with the deposition also being influenced by various regional faults, including the Beitashan, Kubusu, Qingshui-Sujiquan, and Karamaili faults [22-24]. Alkaline granite complexes that were identified in the Karamaili area included the Laoyaquan, Beilekuduke, Yemaquan, Huangyangshan, and Yebushan complexes and were formed by postcollision alkaline magmatic activity during the Carboniferous [3,16,25,26]. Some of the gold, copper, tin, and graphite deposits in this area are considered to be products of these Carboniferous alkaline magmatic events [27-30].



Figure 1. Simplified geological map of the Kalamaili area, Eastern Junggar (modified after [4]).

## 2.2. Huangyangshan Complex

The Huangyangshan graphite deposit is located in the northern segment of the Karamaili fault and within the Huangyangshan alkaline granite complex. The graphite-hosting Huangyangshan pluton is part of the Karamaili alkaline graphite belt, which extends NW– SE. In accordance with and owing to the multiple injections of magma, the Huangyangshan complex is characterized by a series of concentric rings (Figure 2a). According to mineral grain sizes and dark-colored mineral types, the Huangyangshan granite complex can be classified into five petrographic facies (five periods), from the north (early) to south (late), medium-grained arfvedsonite granite, medium-fine-grained arfvedsonite granite, mediumfine-grained hornblende granite, medium-grained biotite granite, and fine-grained biotite granite. All of the discovered graphite ore bodies have a close temporal–spatial relationship with the medium–fine-grained hornblende granite, medium-grained biotite granite, and fine-grained biotite granite (Figure 2a).



**Figure 2.** (a) Geological map of the Huangyangshan pluton; (b) simplified map of the No. 1 and 2 ore bodies of the Huangyangshan graphite deposit (after [2]); (c) cross-section along line 7–7' in (b) (modified after [6]).

## 2.3. Characteristics of Graphite Mineralization

According to the graphite mineral reserves, three of the eight graphite ore bodies (i.e., No. 1, 2, and 4) are large-scale. Ore bodies No. 1 and 2 occur at the contact between the medium–fine-grained amphibole granite and fine-grained biotite granite, and the No. 4 ore body occurs within the fine-grained biotite granite (Figure 2a,b). The concealed No. 1 ore body, which is hosted by the graphite-bearing medium–fine-grained amphibole granite, is of lentiform appearance, extends N–S, and occurs as a small, gently dipping rock bed (Figure 2b,c). The No. 2 opencast ore body extends E–W and is almost entirely mineralized. This ore body displays a saddle shape at the surface (Figure 2b) and is steep-standing in the deep, showing that the No. 2 ore body is nearly upright and has a semiclosed cylindrical form (Figure 2c). The semiconcealed No. 4 ore body is located in the southwestern part of the Huangyangshan complex, where it extends nearly E–W and shows a spindle-shaped form, being thick in the north and thin in the south (Figure 2a).

The Huangyangshan deposit contains primary graphite ores, some of which are weathered. In the weathered ores, the graphite retains its original shape and is associated with malachite (Figure 3a). The primary graphite ores collected from the drill holes and prospecting trenches show an orbicular structure characterized by an inner core and an outer circle. The inner core is composed of felsic minerals and dark minerals, whereas the outer circle is composed of graphite and graphite-associated metal sulfides (Figure 3b).



**Figure 3.** Characteristics and intergrowth of the graphite and metal sulfides in the orbicular graphite ore; (**a**) spherical graphite associated with malachitization on the surface; (**b**) metal sulfides surrounded by spherical and irregular graphite in drill holes; (**c**) nodular pyrrhotite containing chalcopyrite and pentlandite in the graphite (reflected light); (**d**) coarse-grained pyrrhotite coexisted with euhedral biotite (reflected light); (**e**) flake graphite growing along the edge of granular pyrrhotite (reflected light); (**g**) fine-grained xenomorphic granular light yellow and brown pyrrhotite (reflected light); (**g**) metal sufficient orbicular ore (reflected light); (**h**) metal somatic structure of pyrrhotite and sphalerite (reflected light); (**i**) copper yellow and brown chalcopyrite in graphite orbicular ore (reflected light). Gr—graphite, Po—pyrrhotite, Ccp—chalcopyrite, Pn—pentlandite, Bt—biotite Sp—sphalerite.

## 3. Samples and Analytical Methods

## 3.1. Sample Descriptions

The orbicular ore samples analyzed in this study were collected from the No. 704 drill holes of the No. 1 ore body (Figure 2c). These samples are composed mainly of graphite, metal sulfides, and felsic minerals, such as quartz and plagioclase. Samples for X-ray micro-CT scanning and SEM analysis were taken from a small drill core measuring ~16 mm in diameter, drilled from an 8 cm  $\times$  20 cm section of the drill core from the No.704 drill hole. Sulfide-rich ores were selected and produced 7 polished probe thin sections for the in situ LA–ICP–MS trace element analysis of the sulfides.

## 3.2. Analytical Methods

X-ray micro-CT scanning analysis, SEM rock mineral quantitative analysis (quantitative evaluation of minerals by SEM, referred to as "Qemscan"), and micro-scanning imagestitching analysis (Modular Automated Processing System, referred to as "MAPS") were conducted at the Beijing Institute of Digital China, Ltd., using a NanoVoxel-3502E X-ray three-dimensional microscope (Sanying precision instrument Co. Ltd., Tianjin, China), and a Quanta FEG 450 SEM and QEMSCAN 650F mineral quantitative analyzer (FEI, Hillsboro, OR, USA). The operating conditions for micro-CT scanning included an electric current of 20 mA, a voltage of 150 kV, and a scan duration of 90-120 min. After scanning, the obtained slice image data were imported into the 3D space using 3D reconstruction software. Each coordinate point was filled with data recorded from the X-ray CT scan, with reference to a scan resolution of 7.1999 µm. The CT images were denoised by median filtering method, and the 3D digital drill core images (Figure 4) were obtained by image enhancement and filtering. The scanned drill core portions were cut from the middle part and polished into thin sections (~5 mm thick). The thin-sections were mechanically polished, argon-ion polished, and surface carbon sprayed after being sealed with epoxy resin for QEMSCAN analysis. The principle of QEMSCAN analysis is to judge the element type of the scanning point material through the unique X-ray energy generated on the sample surface and calculate the mineral distribution information according to the mineral and element composition database so as to obtain the mineral distribution characteristics on the sample surface. Analyses were performed at an accelerating voltage of 20 kV, an emission current of 10  $\mu$ A, and a working distance of 15 mm. The resolution for quantitative mineral analysis varied from 1 to 50  $\mu$ m. In images obtained from the QEMSCAN analysis (Figure 5a), the elemental species and composition are determined mainly by X-ray energy, and different mineral types are represented by different colors. The area fraction can be obtained from the statistics of the number of pixel points of each mineral component in the image. Then, combined with the density of the different minerals, their mass fraction can be calculated. MAPS analysis was performed with a resolution of 250 nm and a field of view of 16 mm  $\times$  16 mm. The MAPS images were spliced from 1300 high-precision back-scattering electron microscope images.

In-situ LA–ICP–MS trace element analyses were conducted at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guizhou Province, China. Laser sampling was performed using an ASI RESOLution-LR-S155 laser microprobe equipped with a Coherent Compex-Pro 193 nm ArF excimer laser. An Agilent 7700x ICP–MS instrument was used to acquire ion-signal intensities. Helium was used as a carrier gas at a flux of 350 mL/min. Before exiting the cell, the ablated aerosol was mixed with Ar (900 mL/min) as a transport gas. Each analysis involved a background acquisition of ~30 s (gas blank) followed by 60 s of data acquisition from the sample. Ablation was performed using a uniform spot diameter of 26  $\mu$ m pit size, 5 Hz laser pulse frequency, and 3 J/cm<sup>2</sup> energy fluence. The contents of S and Fe were calibrated using pure pyrite as an internal standard. The USGS reference glasses GSE-1G and GSD-1G were used to calibrate the elemental contents. STDGL3 was used to determine the elemental compositions of chalcophile and siderophile. Sulfide standard MASS-1 was analyzed as an unknown sample to check the accuracy of analyses.



**Figure 4.** 3D sketch images of the drill core from the Huangyangshan graphite deposit; (**a**) grayscale image; (**b**) color rendering image; (**c**) distribution of medium density minerals; (**d**) distribution of high density minerals.



**Figure 5.** (a) Scan results of QEMSCAN and MAPS test; (b) the flake graphite was mainly distributed as bundled and banded aggregates, cutting through and metasomatizing sulfides; (c) the quartz, mainly occurring as xenomorphic granular metasomatized sulfides and contained a small amount of fine-grained disseminated graphite; (d) the sulfide aggregates cut and metasomatized by quartz contained fine-grained graphite bands.

## 4. Analytical Results

## 4.1. Metal Sulfides in Orbicular Ores

The metal sulfides associated with graphite in the orbicular ore (Figure 3b) include subhedral-xenomorphic pyrrhotite and xenomorphic chalcopyrite and minor pyrite, pentlandite, and sphalerite. These sulfides are largely enclosed or cut by the graphite, meaning that they were crystallized before the graphite. Of these metal sulfides, pyrrhotite has the highest content and the most extensive distribution in the Huangyangshan deposit, hosting mostly chalcopyrite and pentlandite and occurring in nodular aggregates composed of subhedral coarse-grained crystals (Figure 3c). The phenomenon whereby both the pyrrhotite and flake graphite are intruded by the biotite indicates they both formed earlier than the biotite (Figure 3d). In general, the pyrrhotite content has a positive relationship with the graphite content, and the flake graphite is commonly distributed along the edges of granular pyrrhotite (Figure 3e). The chalcopyrite and pentlandite are enclosed within the pyrrhotite. The contact boundaries of chalcopyrite and pentlandite with pyrrhotite are straight, suggesting that they are associated with pyrrhotite. (Figure 3c). The particle size of the pentlandite is small, mostly <0.1 mm (Figure 3e). The sulfides and graphite cut through the biotite that crystallized during the late magmatic stage (Figure 3d). Type IV pyrrhotite and type II chalcopyrite occur in silicate mineral cores lacking graphite, or replaced types I–III pyrrhotite and type I chalcopyrite (Figure 3h,i)

According to its color, crystalline shape, texture, and occurrence, the pyrrhotite associated with graphite in the Huangyangshan deposit can be grouped into four types. Type I pyrrhotite comprises coarse xenomorphic (Figure 3c) or medium–fine-grained xenomorphic granular grains that are included in the graphite (Figure 3e,f) and are cream-yellow in color, which encloses the associated chalcopyrite and pentlandite. Type II pyrrhotite consists of xenomorphic granular and light-yellow and brown grains (Figure 3f), which accompanies the type I pyrrhotite and encloses no other metal sulfides. Type III pyrrhotite is composed of fine-grained xenomorphic grains occurring in the core of the orbicular graphite (Figure 3g), which enclose small amounts of the chalcopyrite grains and is associated with fine-grained disseminated graphite. Type IV pyrrhotite comprises grains that are distributed within the granite intrusion and metasomatized along the edges of felsic mineral grains (Figure 3h).

The chalcopyrite in the orbicular graphite ore of the Huangyangshan deposit can be classified into two types: Type I chalcopyrite is composed of xenomorphic–granular grains and is enclosed within the pyrrhotite with a metasomatic texture (Figure 3c,i). Type II chalcopyrite consists of brown grains and is enclosed within the type I chalcopyrite (Figure 3i).

Type IV pyrrhotite and type II chalcopyrite occur in silicate mineral cores lacking graphite or replace types I–III pyrrhotite and type I chalcopyrite (Figure 3h,i).

#### 4.2. X-ray Micro-CT Scanning and SEM Analysis

The 3D digital drill core image obtained by image enhancement and filtering is shown in Figure 4a. According to its density variation, the white high-density sulfides, gray medium-density dark minerals (and graphite), and black low-density quartz and feldspar can be clearly distinguished. Figure 4b was obtained after color rendering, in which the blue, yellow, and red represent low-, medium-, (Figure 4c), and high-density (Figure 4d) material areas, respectively.

The calculated percentages of various mineral contents for the studied section are given in Table 1. The MAPS images of the three representative horizons (graphite vein, quartz, and sulfide) of the section are shown in Figure 5b–d. The plagioclase content in the ore is highest (31.03%), followed by K-feldspar (13.39%) and dark minerals (14.26%), with a quartz content of only 12.02%, which is largely lower than that of the ore-bearing granite (>50% [3])

Minerals	Area Fraction (%)	Mass Fraction (%)
Albite	19.53	21.62
K-feldspar	12.29	13.39
Graphite	11.82	8.55
Dark minerals (mainly biotite)	11.09	14.26
Quartz	10.78	12.02
Sulfide	6.47	12.67
Oligoclase, andesine	7.98	9.41
Altered and unidentified minerals	14.58	8.07

Table 1. Contents of the main minerals in the orbicular graphite ore analyzed by QEMSCAN testing.

#### 4.3. In Situ LA-ICP-MS Trace Element of Sulfides

The results of LA–ICP–MS trace element analysis for 40 analytical spots in the four types of pyrrhotite and 13 analytical spots in the two types of chalcopyrite are given in Tables 2 and 3 respectively. A comparison of the element compositions is presented in Figure 6.



**Figure 6.** Comparison of the trace element compositions of pyrrhotite and chalcopyrite in the Huangyangshan deposit; (**a**) the trace element compositions of four types pyrrhotite; (**b**) the trace element compositions of two types chalcopyrite.

In type I pyrrhotite: element contents are Cr = 0.19 to 173.15 ppm (mean of 21.77 ppm), Mn = 0.03 to 11.18 ppm (mean of 1.24 ppm), Co = 123 to 357 ppm (mean of 251 ppm), Ni = 1998 to 3466 ppm (mean of 2769 ppm), Cu 0.11 to 16.94 ppm (mean of 1.82 ppm), Zn = 0.30 to 11.21 ppm (mean of 1.98 ppm), Ga = 0.01 to 0.09 ppm (mean of 0.07 ppm), Ge = 1.57 to 4.99 ppm (mean of 3.0 ppm), As = 0.04 to 2.17 ppm (mean of 0.78 ppm), Se = 66.44 to 129.47 ppm (mean of 99.52 ppm), Ag = 0.03 to 21.57 ppm (mean of 1.4 ppm), Cd = 0.01 to 0.64 ppm (mean of 0.30 ppm), Sn = 0.03 to 0.32 ppm (mean of 0.11 ppm), Sb = 0.03 to 1.09 ppm (mean of 0.32 ppm), Te = 0.06 to 20.60 ppm (mean of 0.43 ppm) (Table 2).

In type II pyrrhotite: element contents are Cr = 0.35 to 23.07 ppm (mean of 7.82 ppm), Mn = 0.06 to 24.70 ppm (mean of 4.30 ppm), Co = 225 to 362 ppm (mean of 275 ppm), Ni = 2595 to 3233 ppm (mean of 2884 ppm), Cu = 0.08 to 2.23 ppm (mean of 0.94 ppm), Zn = 0.09 to 1.93 ppm (mean of 0.91 ppm), Ga = 0.03 to 0.06 ppm (mean of 0.03 ppm), Ge = 2.65 to 3.71 ppm (mean of 2.95 ppm), As = 0.37 to 1.33 ppm (mean of 0.96 ppm), Se = 74.03 to 102.85 ppm (mean of 89.09 ppm), Ag = 0.27 to 2.04 ppm (mean of 0.07 ppm), Cd = 0.03 to 0.65 ppm (mean of 0.13 ppm), Te = 0.45 to 2.37 ppm (mean of 1.25 ppm), Pb = 0.37 to 24.45 ppm (mean of 6.23 ppm), and Bi = 0.05 to 2.90 ppm (mean of 0.77 ppm) (Table 2).

 Table 2. Trace element analysis results of pyrrhotite in Huangyangshan deposit (ppm).

Number	Туре	Cr	Mn	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Ag	Cd	Sn	Sb	Te	Pb	Bi
422Po-1		2.14	1.31	357	3109	/	0.69	/	4.36	/	117.02	0.5	/	0.07	/	1.81	1.72	0.29
412Po-2		2.02	0.15	336	2764	0.34	0.83	/	3.24	0.68	86.13	0.66	0.09	0.16	0.03	/	3.1	1.15
433Po-2		3.23	1.25	232	2482	0.27	1.64	0.03	2.64	0.04	100.04	0.57	0.01	0.12	0.14	1.07	0.81	0.19
423Po-2		1.78	0.34	227	3178	0.11	/	0.03	2.07	/	92.68	/	0.5	0.04	0.11	1.81	1.45	0.13
423Po-10		7.76	0.46	243	3172	0.3	1.07	0	2.23	0.41	80.59	0.3	0.54	/	/	0.5	1.72	0.19
423Po-13		75.07	0.76	238	3216	1.85	2.96	/	1.59	0.27	97.3	0.63	0.14	/	/	1.33	1.71	0.46
411Po-3		154.43	1.21	292	2534	0.85	2.07	/	3.76	/	122.89	0.42	0.26	0.07	0.61	0.25	0.36	0.06
411Po-13		0.99	0.41	256	2835	0.77	0.44	0.04	4.99	/	101.23	0.2	/	/	/	0.59	1.83	0.16
421Po-1		2.86	0.68	261	3466	0.5	0.44	0.03	3.96	0.41	100.24	0.42	/	/	/	/	0.85	/
421Po-7		173.15	0.46	224	2987	4.5	1.21	/	3.25	0.81	106.22	0.03	/	0.11	/	2.21	1.26	0.11
423Po-1		3.75	0.03	197	2885	0.11	/	/	2.53	/	95.01	0.09	/	0.23	0.02	0.06	2.2	0.4
ZK43Po-1	type I	0.19	0.37	249	2398	0.71	3.57	/	3.77	0.73	94.34	1.77	/	0.05	/	4.46	4.81	0.71
411Po-4	yellow	1.53	0.21	276	2356	0.31	1.69	0.04	2.99	/	101.06	0.2	0.42	/	/	1	0.6	0.34
411Po-11	pyrrhotite	70.53	4.9	281	3065	16.94	/	0.01	4.47	1.76	66.44	2.09	/	/	/	/	1.72	0.22
422Po-3		0.39	0.83	288	2962	0.25	/	0.07	2.23	0.26	108.56	0.3	0.09	/	/	0.31	0.78	/
421Po-2		2.49	0.47	302	3448	0.6	1.04	0	2.7	0.04	109.55	0.23	/	/	/	0.68	0.79	0.25
421Po-8		71.84	/	285	2910	0.15	3.5	/	2.95	0.99	83.3	/	0.25	0.03	/	/	0.86	0.14
433Po-1		4.31	0.83	239	2562	1.12	0.3	/	2.93	0.17	103.54	0.07	0.21	/	0.13	1.18	0.09	0.08
423Po-3		0.8	0.81	257	2964	0.8	0.5	0.04	1.57	0.51	129.47	/	0.1	0.04	0.15	/	0.97	0.08
ZK43Po-2		4.42	0.84	298	2883	2.37	/	/	3.05	/	100.09	2.34	/	/	/	10.03	11.59	0.76
ZK45Po-1		12.37	/	155	2117	/	/	0.02	3.39	1.45	89.63	0.12	0.12	0.13	0.25	2.15	0.91	0.38
ZK45Po-2		1.57	2.06	123	2240	1.24	/	/	2.88	1.72	81.89	1.03	0.64	0.32		5.77	3.77	0.53
423Po-4		1.28	0.9	247	3014	0.55	/	0.09	2.16	/	105.27	0.21	/	0.09	0.02	/	1.79	0.15
ZK41Po-2		4.69	0.4	195	2241	1.54	0.96	/	2.89	2.17	102.89	0.15	0.46	0.03	/	2.66	1.22	0.36
411Po-7		0.29	0.23	338	2779	2.52	/	0.09	2.28	/	89.7	1.47	/	/	/	10.17	10.93	1
C51Po-1		1.89	0.27	191	2215	2.9	/	0	3.61	/	100.88	21.57	0.56	0.17	0.02	20.6	7.91	0.5
C51Po-2	type I	13.66	11.18	153	1998	6.6	11.21	0.25		/	100.6	0.36	0.33	0.04	1.09	2.1	4.9	0.64
411Po-9	yellow	11.2	2.19	265	2707	0.89	/	0.38	2.93	/	112.86	0.12	0.46	0.25	/	/	1.21	0.39
421Po-3	pyrrhotite	0.74	0.03	262	2807	0.11	1.5	0.05	2.67	/	106.63	0.67	/	0.03	0.31	15.6	22.91	2.05
average		21.77	1.24	251	2769	1.82	1.98	0.07	3	0.78	99.52	1.4	0.3	0.11	0.24	3.92	3.27	0.43
411Po-8		14.09	0.08	298	2595	0.73	1.2	0.06	3.71	/	83.71	0.27	/	0.02	/	/	0.79	0.33
412Po-5	type II	0.35	0.06	362	2662	/	0.58	/	2.7	/	101.11	0.49	0.03	/	0.07	0.7	0.37	0.14
422Po-2	brown	23.07	/	348	2852	0.96	0.73	0.03	3.2	1.33	98.18	/	0.37	0.02	0.05	2.37	0.53	0.05
423Po-7	pyrrhotite	3.08	0.24	237	2991	0.68	1.93	/	2.66	0.98	102.85	0.43	/	0.12	0.05	0.45	4.08	0.54
423Po-8		6.34	24.7	225	2944	/	/	/	3.11	0.37	85.22	0.35	0.1	0.12	/	/	15.02	1.45

Table 2. C	ont.
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Number	Туре	Cr	Mn	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Ag	Cd	Sn	Sb	Te	Pb	Bi
423Po-9		4.2	0.31	227	2946	2.23	0.95	/	2.81	1.21	79.99	2.04	/	0.12	0.34	1.62	24.45	2.9
423Po-11		3.6	3.87	240	3233	0.08	0.09	/	2.65	/	87.59	/	/	0.04	0.2	/	1.23	0.26
423Po-12		/	0.87	267	2852	/	/	0	2.77	0.89	74.03	0.85	0.65	/	0.04	1.12	3.39	0.51
average		7.82	4.3	275	2884	0.94	0.91	0.03	2.95	0.96	89.09	0.74	0.29	0.07	0.13	1.25	6.23	0.77
422Po-4	type III	6.67	17.94	181	4173	1.03	2.52	0.85	4.03	/	130	0.13	/	0.06	/	0.78	4.33	0.6
422Po-5	Pyrrhotitein	25.04	4.48	166	2691	0.37	/	/	3.16	/	124	0.65	/	/	0.03	6.8	2.33	1.15
average	fine-grained core	15.85	11.21	174	3432	0.7	2.52	0.85	3.6	/	127	0.39	/	0.06	0.03	3.79	3.33	0.87
412Po-1	type IV	1.61	1.52	480	283	0.25	/	0.02	2.66	0.25	47.58	0.64	0.3	0.22	0.04	0.15	5.49	0.81

**Table 3.** Trace element analysis results of chalcopyrite in Huangyangshan deposit (ppm).

Number	Туре	Cr	Mn	Со	Ni	Zn	Ga	Ge	As	Se	Ag	Cd	In	Sn	Sb	Te	Pb	Bi
411Ccp-1	29 60 33 type I copper yellow talaananita	29.08	/	1.73	32.92	323	0.13	2.58	1.41	133.85	2.77	6.71	12.61	115.79	/	3.93	1.01	0.12
422Ccp-1		60.68	0.07	1.74	8.66	363	0.08	1.24	/	95.69	3.23	6.48	4.96	7.82	/	/	1.16	0.03
421Ccp-1		336.9	/	0.81	6.46	680	0.01	2.15	0.22	78.79	15.46	10.03	5.59	2.58	/	15.82	15.77	0.75
423Ccp-1		7.49	0.34	3.63	14.93	559	/	1.19	/	95	8.39	9.46	5.04	25.26	0.02	37.66	48.72	0.82
423Ccp-2		5.48	/	1.4	9.14	528	0.04	2.31	/	108.36	8.81	10.5	5.93	8.68	0.2	7.58	3.63	0.22
423Ccp-4		5	0.15	1.8	22.12	725	/	1.66	/	133.34	3.95	13.93	5.76	6.06	/	7.19	27.99	0.23
ZK46Ccp-1		13.87	9.36	1.63	13.5	445	0.09	1.81	/	93.15	6.84	9.71	7.43	36.2	0.38	36.2	8.67	1.98
ZK46Ccp-1	chalcopyfile	13.72	0.44	6	69.66	581	0.05	2.21	/	133.24	11.17	17.34	7.71	46.54	0.17	58.19	13.63	2.05
C51Ccp-1		0.53	0.21	1.85	43.26	546	0.07	2.34	/	124.52	7.79	10.31	5.85	87.3	/	54.98	11.72	1.03
411Ccp-2		27.87	0.34	1.74	35.8	453	0.03	0.93	0.53	75.63	6.53	8.44	6.5	117.85	/	29.24	25.51	1.45
average		50.06	1.56	2.23	25.64	520	0.06	1.84	0.72	107.16	7.49	10.29	6.74	45.41	0.19	27.87	15.78	0.87
422Ccp-4	turno II	50.43	0.56	4881	1098	435	0.08	0.87	10,784	83	266	7.99	4.74	17	7.05	203	24.06	31.47
422Ccp-5	brown chalcopyrite	57.89	/	4352	1138	465	0.05	2.51	12,572	116	244	9.37	5.1	18.91	6.1	213	22.96	29.11
412Ccp-1		51.02	1.68	4084	923	355	0.12	1.63	11,490	121	217	8.24	5.94	17.1	5.63	210	23.65	26.12
average		53.11	1.12	4439	1053	419	0.08	1.67	11,615	107	242	8.53	5.26	17.67	6.26	209	23.56	28.9

Detection limit (10<sup>-6</sup>): Cr 0.34, Mn 0.39, Fe 24.13, Co 0.03, Ni 0.07, Cu 0.35, Zn 1.57, Ga 0.01, Ge 0.71, As 0.11, Se 0.91, Ag 0.13, Cd 0.04, In 0.01, Sn 0.08, Sb 0.26, Te 0.14, Pb 0.04, Bi 0.02.

In type III pyrrhotite: element contents are Cr = 6.67 to 25.04 ppm (mean of 15.85 ppm), Mn = 4.48 to 17.94 ppm (mean of 11.21 ppm), Co = 166 to 181 ppm (mean of 174 ppm), Ni = 2691 to 4173 ppm (mean of 3432 ppm), Cu = 0.37 to 1.03 ppm (mean of 0.7 ppm), Zn = 2.52 ppm, Ga = 0.85 ppm, Ge = 3.16 to 4.03 ppm (mean of 3.6 ppm), As = below detection limit (b.d.l.), Se = 124 to 130 ppm (mean of 127 ppm), Ag = 0.13 to 0.65 ppm (mean of 0.39 ppm), Cd = b.d.l., Sn = 0.60 ppm, Sb = 0.03 ppm, Te = 0.78 to 6.80 ppm (mean of 3.79 ppm), Pb = 2.33 to 4.33 ppm (mean of 3.33 ppm), and Bi = 0.6 to 1.15 ppm (mean of 0.87 ppm) (Table 2).

In type IV pyrrhotite: element contents are Cr = 1.61 ppm, Mn = 1.52 ppm, Co = 283 ppm, Ni = 480 ppm, Cu = 0.25 ppm, Zn = b.d.l., Ga = 0.02 ppm, Ge = 2.66 ppm, As = b.d.l., Se = 47.58 ppm, Ag = 0.64 ppm, Cd = 0.3 ppm, Sn = 0.22 ppm, Sb = 0.04 ppm, Te = 0.15 ppm, Pb = 5.49 ppm, and Bi = 0.81 ppm (Table 2).

In summary, the four types of pyrrhotite are enriched in Co, Ni, Se, Ge, Cr, Te, and Pb and depleted in Ga, As, Cd, Sn, and Sb. The contents of Co, Ge, and Se in the different types of pyrrhotite are similar and high. All of the spot analyses in types I, II, and III of the pyrrhotite have similar and high Ni contents compared with the low content of type IV pyrrhotite. The Cr, Mn, Cu, Zn, Ag, Sb, Te, and Pb content in the different types of pyrrhotites vary widely (Figure 6a).

In the type I chalcopyrite, the element contents are Cr = 0.53-336.9 ppm (mean of 50.06 ppm), Mn = 0.07-9.36 ppm (mean of 1.56 ppm), Co = 0.81-6.00 ppm (mean of 2.23 ppm), Ni = 6.46-69.66 ppm (mean of 25.64 ppm), Zn = 323-725 ppm (mean of 520 ppm), Ga = 0.01-0.13 ppm (mean of 0.06 ppm), Ge = 0.93-2.58 ppm (mean of 1.84 ppm), As = 0.22-1.41 ppm (mean of 0.72 ppm), Se = 76-134 ppm (mean of 107 ppm), Ag content of 2.77-15.46 ppm (mean of 7.49 ppm), Cd = 6.48-17.34 ppm (mean of 10.29 ppm), In = 4.96-12.61 ppm (mean of 6.74 ppm), Sn = 2.58-117.85 ppm (mean of 45.41 ppm), Sb = 0.02-0.38 ppm (mean of 0.19 ppm), Te = 3.93-58.19 ppm (mean of 27.87 ppm), Pb = 1.01-48.72 ppm (mean of 15.78 ppm), and Bi = 0.03-2.05 ppm (mean of 0.87 ppm) (Table 3).

In the type II chalcopyrite, the element contents are Cr = 50.43-57.89 ppm (mean of 53.11 ppm), Mn = 0.56-1.68 ppm (mean of 1.12 ppm), Co = 4084-4881 ppm (mean of 4439 ppm), Ni = 923-1138 ppm (mean of 1053 ppm), Zn = 356-465 ppm (mean of 419 ppm), Ga = 0.05-0.12 ppm (mean of 0.08 ppm), Ge = 0.87-2.51 ppm (mean of 1.67 ppm), As = 10,784-12,572 ppm (mean of 11,616 ppm), Se = 83-121 ppm (mean of 107 ppm), Ag = 217-266 ppm (mean of 242 ppm), Cd = 7.99-9.37 ppm (mean of 8.53 ppm), In = 4.74-5.94 ppm (mean of 5.26 ppm), Sn = 17.00-18.91 ppm (mean of 17.67 ppm), Sb = 5.63-7.05 ppm (mean of 6.26 ppm), Te = 203-213 ppm (mean of 209 ppm), Pb = 22.96-24.06 ppm (mean of 23.56 ppm), and Bi = 26.12-31.47 ppm (mean of 28.9 ppm) (Table 3).

In summary, the Co, Ni, As, and Ag content in the type I chalcopyrite are substantially lower than those in the type II chalcopyrite, with a maximum difference of 2–4 orders of magnitude. The Sb, Te, and Bi content in the type I chalcopyrite are also lower than those in the type II chalcopyrite but the differences are smaller. The contents of the remaining elements (i.e., Cr, Mn, Zn, Ga, Ge, Se, Cd, In, and Pb) are similar in the two types of chalcopyrite (Figure 6b).

#### 5. Discussion

#### 5.1. Mineral Characteristics of Graphite Ores

The X-ray micro-CT scanning results show (Figure 4) that the drill cores of the graphite ores are composed mainly of low-density minerals, such as quartz and feldspar. The medium-density dark minerals, such as amphibole and biotite, are distributed mostly among the quartz and feldspar grains (Figure 4c). There is a high content of high-density metal sulfides, and these occur as massive aggregations or are disseminated in the ore (Figure 4d).

In the QEMSCAN and MAPS images, the distribution and content characteristics of various minerals, as well as the shapes and intersecting relationships of the fine-grained minerals, can be clearly identified by their mineral element components (Figure 5). According to the mass fraction values (Table 1), the plagioclase content in the ore is highest (31.03%), followed by K-feldspar (13.39%) and dark minerals (14.26%), with a quartz content of only 12.02%, which is largely lower than that of the ore-bearing granite (>50%), suggesting that the crystallization conditions of the graphite are different from those of the ore-bearing granite. The scanning results of the QEMSCAN and MAPS analyses reveal that the groundmass in the orbicular ore is mainly albite and dark minerals (such as biotite and amphibole) and that the flake graphite is distributed predominantly as bundles and banded aggregates that cut through the sulfides (Figure 5b). The Quartz occurs as xenomorphic grains that have metasomatized sulfides and contain small amounts of fine-grained disseminated graphite (Figure 5c). Some coarse-grained nodular sulfide aggregates in the analyzed section are cut by the quartz. These sulfide aggregates contain densely distributed fine-grained graphite bands (Figure 5d), but the graphite appears mainly in the form of "scalelike", with relatively low degrees of crystallization. In addition, most of the flaky graphite only coexists with the sulfide and albite, not with the quartz and K-feldspar (Figure 5a), indicating that the formation of the flake graphite was closely related to the albite and sulfide. In addition, the dark minerals show high abundance in the middle of the analyzed section in association with andesine and oligoclase but not with quartz, indicating that the crystallization conditions of these dark minerals are different from those of the ore-bearing granite, which is consistent with the mineral mass fraction results (Table 1).

## 5.2. The Origin of Sulfide

The compositional and structural characteristics of the studied sulfides from the Huangyangshan deposit reveal important information about the genesis of these minerals; (1) the sulfides are dominated by pyrrhotite, with small amounts of associated chalcopyrite and pentlandite, whereas typical hydrothermal sulfides, such as pyrite and sphalerite, are rare; (2) the contact boundaries of most of the metal sulfides are straight (Figure 3c,f) and do not display metasomatic features; (3) pentlandite is distributed within the pyrrhotite and chalcopyrite (Figure 3c,e). These characteristics are highly similar to those of magmatic Cu–Ni sulfide deposits, indicating the magmatic origin of the metal sulfides [31,32].

The crystalline shapes and textures of the sulfides from the Huangyangshan deposit are rather consistent and lack recrystallization, regrowth, and superimposed reformation by metamorphism. The sulfides are highly homogeneous in the MAPS image (Figure 5d), indicating that the trace element components contained in these sulfides did not undergo pronounced element migration and, therefore, represent the primary component characteristics when the sulfides formed [33]. An elemental spectral line diagram (Figure 7) reveals that the main elements in the pyrrhotite are Fe, S, Ni, and Co, with Ni and Co displaying stable spectral line variations without obvious crests and troughs (Figure 7a). The chalcopyrite contains Cu, Fe, S, and Zn predominantly, and the spectral lines of these elements are also stable (Figure 7b), suggesting that these elements occur as isomorphic forms rather than inclusions [34], implying the formation occurred in a stable environment. Therefore, the trace element compositions of the pyrrhotite and chalcopyrite samples from the Huangyangshan graphite deposit can be used to interpret their genesis and formation conditions, as described, in turn, below.



**Figure 7.** Examples of the time-resolved LA–ICP–MS depth profiles for the pyrrhotite and chalcopyrite from the Huangyangshan deposit. (**a**) Ablation profile for type I pyrrhotite from spot 421Po–2. (**b**) Ablation profile for type I chalcopyrite from spot 423Ccp–1.

## 5.2.1. Pyrrhotite

Previous studies have shown that Co and Ni replace Fe in pyrrhotite as isomorphic forms, and pyrrhotite is a major carrier mineral of Co and Ni. The contents of Co and Ni in pyrrhotite are predominantly affected by the physicochemical conditions applied during their formation, meaning that these elements can be used to infer the genetic type of pyrrhotite [35–37]. During magmatic evolution, Ni and Co are preferentially enriched in the early- and late-crystallized minerals, respectively [38]. Therefore, the Co/Ni ratio of magmatic-origin pyrrhotite tends to be lower than that of hydrothermal-origin pyrrhotite. The contents of Co and Ni are similar between types I–III of the pyrrhotite from the Huangyangshan deposit, and most of the Co/Ni values range from 0.07 to 0.12 (Table 2). All these values plot within the range of magmatic origin for types I–III of the pyrrhotite. Type IV pyrrhotite has higher Co and lower Ni contents compared with the other three types, with a mean Co/Ni ratio of 1.69, and it plots within the range of magmatic-hydrothermal deposits, indicating that this pyrrhotite might have formed during late hydrothermal metasomatic processes.

In general, Pb, Zn, Ge, and Te are enriched in hydrothermal pyrrhotite as micro inclusions [38,39]. The contents of these elements in the pyrrhotite from the graphite ore of the Huangyangshan deposit are extremely low, mostly below the detection limit, suggesting that these pyrrhotites were formed in a relatively stable, closed, and high-temperature magmatic environment. In addition, all of the analyzed pyrrhotites have low contents of low-temperature elements, such as As, Sb, Ag, and Au, which is in marked contrast to porphyry-type, skarn-type, and hydrothermal-vein–type deposits [40,41]. In summary, types I–III nodular and xenomorphic–granular pyrrhotite are of the same magmatic origin, whereas the type IV pyrrhotite in granitic groundmass is of hydrothermal origin, as discussed above.



**Figure 8.** Co–Ni genetic discrimination diagram of the pyrrhotite from the Huangyangshan deposit (modified after [37]).

#### 5.2.2. Chalcopyrite

Previous studies of the trace-element characteristics of chalcopyrite have proposed that the Co/Ni ratio is an important indicator reflecting the origin of chalcopyrite [37,42]. The trace element analytical results for chalcopyrite from the Huangyangshan deposit in this study reveal that type I chalcopyrite has low Co and Ni contents and low Co/Ni ratios, ranging from 0.04 to 0.24, whereas type II chalcopyrite contains abundant Co and Ni and has Co/Ni values ranging from 3.82 to 4.44. Previous studies have reported low Ni contents in chalcopyrite from hydrothermal deposits (averaging 1–5 ppm), with Co/Ni values >1, whereas the Ni contents of chalcopyrite from magmatic Cu–Ni sulfide deposits fluctuate widely (10–10<sup>4</sup> ppm), with Co/Ni values of <1 [37,43,44]. Therefore, the Co/Ni values of type I chalcopyrite from the Huangyangshan deposit are consistent with those of chalcopyrite from magmatic Cu-Ni sulfide deposits. The low Ni contents in type I chalcopyrite may have resulted from the low Ni content in the ore-forming melt itself or from Ni enrichment in the pre-existing pyrrhotite and pentlandite before the chalcopyrite was dissolved. Type II chalcopyrite from the Huangyangshan deposit has high Ni and very high Co contents in comparison with type I chalcopyrite, which is consistent with the characteristics of late hydrothermal chalcopyrite. The high contents of Ni in the type II chalcopyrite may have been caused by hydrothermal enrichment. Type II chalcopyrite also has substantially higher As and Ag contents relative to type I chalcopyrite. These two elements generally exist in chalcopyrite through the substitution of Cu by Ag and of S by As [45,46], which usually takes place at a low temperature. Therefore, the high contents of As and Ag suggest that the type II chalcopyrite underwent low-temperature replacement. In addition, low-temperature elements, such as Sb, Te, and Bi are enriched in type II chalcopyrite relative to type I, which further suggests a low-temperature environment for the formation of type II chalcopyrite. In summary, we believed that the type I chalcopyrite was of magmatic origin, coexisting with types I-III pyrrhotite, while type II chalcopyrite was of hydrothermal origin.

Types I–III pyrrhotite have high contents of Se (>80 ppm), Ge (>2.5 ppm) and low contents of Zn (mostly <1.5 ppm), Cd (mostly <0.5 ppm), and Sn (<0.5 ppm). The I-type chalcopyrite has high contents of Zn (mostly >500 ppm) and Se (mostly >100 ppm) and low contents of Sb (mostly <0.3 ppm) and Te (more than <20 ppm). These properties are similar to the trace element characteristics of Cu–Ni sulfide deposits in other regions, such

as Jinchuan (China), Creighton (Canada), and Bushveld (South Africa), but they are clearly distinct from the hydrothermal deposits of skarn and porphyry types [47–51].

#### 5.3. Implications of Metal Sulfides for Graphite Mineralization

The genetic type of the Huangyangshan graphite deposit has been debated since its discovery. The occurrence of the graphite ore in alkaline granite, the organic carbon source of the graphite (carbon isotopic compositions: -20.9 to -20.5%), and the cutting of transparent minerals by flake graphite has led some previous studies to classify the Huangyangshan deposit as magmatic–hydrothermal in origin [2,10,12]. However, the results of the present study reveal that the metal sulfides closely associated with graphite are of magmatic origin, indicating the occurrence of a magmatic mineralization event related to mafic magmatism in the deposit.

Various lines of evidence in this study show that the formation of the Huangyangshan graphite deposit is closely related to the development of sulfides: (1) the graphite and metal sulfides occur mostly along the edges of the orbicular structures, whereas ores lacking graphite and granitic groundmass do not contain sulfides (Figure 3b); (2) the banded graphite coexists with the granular sulfides (Figure 5b) (3) the microscopy revealed that the sulfides and graphite cut through the biotite that crystallized during the late magmatic stage (Figure 3d); (4) hydrothermal-origin type IV pyrrhotite and type II chalcopyrite occur in the silicate mineral cores lacking graphite or replaced types I–III pyrrhotite and type I chalcopyrite (Figure 3h,i); (5) the Os isotope composition of the graphite indicates that its carbon was sourced at least partly from mantle-derived magma, which is the same as the sulfides in the deposit [6]; (6) the crystallization temperature of the graphite was about 750–800 °C, which is approximately similar to the crystallization temperature of high-temperature pyrrhotite and chalcopyrite from a magmatic system [12,52]. The above evidence shows that the graphite in the Huangyangshan deposit should have the same magmatic origin as sulfide. Moreover, the comparison studies showed that the intergrowth relationship between the graphite and sulfides, the orbicular mineralization characteristics of the graphite, the mineral assemblage of the sulfides, and the crystallization temperature of graphite from the Huangyangshan deposit were highly similar to the mineralization characteristics of the graphite hosted in the ultramafic rocks of the Ronda (Spain) and Beni-Bousera (Morocco) deposits [53]. These similar characteristics also indicate that the graphite in the Huangyangshan deposit is of magmatic origin.

In addition, Luque et al. [54] considered that metal sulfides have a catalytic effect on carbon's crystallization to graphite, for which pyrrhotite has the strongest catalytic effect. Graphite is commonly associated with sulfides in the Huangyangshan deposit (Figure 3e), which is consistent with the effect of catalysis on graphite mineralization. Based on all the above data, therefore, it can be proposed that the graphite in the Huangyangshan deposit has the same magmatic origin as the sulfide associated with graphite, and this sulfide acts as a catalyst to promote graphite mineralization.

## 6. Conclusions

In the Huangyangshan deposit of East Junggar, China, the graphite ores show an orbicular structure characterized by an inner core and an outer circle. The inner core is composed mainly of felsic minerals and dark minerals, whereas the outer circle is composed of graphite and associated metal sulfides, including pyrrhotite, chalcopyrite, and pentlandite. The results of the micro-CT and section-scanning electron microscopy of the drill core showed that the graphite ore has higher plagioclase and dark mineral content and substantially lower quartz content than the granitic wall rock. Flake graphite occurs mostly as bundles and banded aggregates, cutting through the sulfides. The formation of flake graphite is closely related to the formation of albite and sulfide.

Four types of pyrrhotite and two types of chalcopyrite were identified, with types I–III pyrrhotite and type I chalcopyrite being genetically related to graphite mineralization. Types I–III pyrrhotite are associated with graphite and have similar Co and Ni contents and

low Co/Ni values, as well as generally low Au, Ag, Pb, Zn, As, Sb, Ge, and Te contents, suggesting a magmatic origin. Type IV pyrrhotite has higher Co and lower Ni contents compared with the other three types, suggesting a hydrothermal origin. Type I chalcopyrite has low Co and Ni contents and low Co/Ni values, implying a magmatic origin. Type II chalcopyrite has high Ni and very high Co contents and high Co/Ni values, as well as high low-temperature elements such as Sb, Te, and Bi, implying a hydrothermal origin. Graphite has the same origin as types I–III of pyrrhotite and type I of chalcopyrite, and the metal sulfides play a catalytic role, leading to graphite crystallization.

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