Magma Evolution and Constraints on the Graphite Mineralization Hosted by the Huangyangshan Alkaline Granite Suite in the East Junggar of Xinjiang Province: Evidence from In Situ Analyses of Silicate Minerals

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Abstract: The Huangyangshan super-large graphite deposit, located in the East Junggar area of the Xinjiang Province, is hosted in and has closely temporal, spatial, and genetic relationships with the Huangyangshan alkaline granites. There are such silicate minerals as amphibole, biotite, pyroxene, and plagioclase occurring in the graphite-bearing granites. The integration of the electron microprobe analysis (EMPA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) enabled us to reveal the physicochemical conditions and evolution process, as well as the relationship of alkaline magmatism with graphite mineralization. The results show that the amphiboles generally have low Al and high Ti, K, Si, and Fe contents, as well as similar rare-earth elements (REEs) patterns and trace element distribution patterns to granites with significantly negative Eu anomalies. In the analyzed samples, primary biotite belongs to Fe-biotite and has characteristics of high Si and Fe and low Al and Mg contents. In the graphite orbicules, the pyroxene phenocrysts develop multiple zonal structures and are characterized by high Si and low Ca and Fe contents. The dominant plagioclase phenocrysts in the graphite orbicules are oligoclase and andesine, with normal and occasionally oscillatory zoning. The calculated crystallization temperature of the pyroxene, amphibole, and primary biotite in graphite orbicules are 840–1012 °C, 681–761 °C, and 658–720 °C, respectively, corresponding with their crystallization order. The pressure and depth calculation results of the amphibole, representing those of the magmatism, are 157–220 Mpa and 5.95–8.32 km, respectively. Both amphibole and biotite crystallized in a reducing environment with extremely low oxygen fugacity. The elemental compositions of these silicates indicate that the Huangyangshan pluton experienced significant mixing of mafic mantle-derived magma and felsic crust-derived magma. The cores of graphite orbicules were formed in a relatively earlier magmatic stage, while the granites and their dioritic enclaves were formed in a later magmatic stage. During magmatism, the mixing of mantle-derived basic magma had an important influence on the evolution and differentiation of the melts. According to the coexisting sulfides with graphite and compositional difference of amphibole and biotite in the granites and graphite ores, the graphite mineralization might be triggered by a magma mixing process.

Keywords: mineral elemental composition; EPMA; crystallization conditions; magma mixing; Huangyangshan graphite deposit; NW China

1. Introduction

Generally, there are three main mineralization processes that graphite crystallizes, namely, organic matter transforming by high-grade metamorphism in regional metamor-
phic graphite deposit [1–3], conversion of organic matter in contact with pyrometamorphism between igneous intrusions (mostly felsic) and coal-bearing sedimentary rocks [4–6], and carbon transforming by certain reactions in carbonaceous fluids or melts in fluid-deposited graphite [7–10]. The fluid-deposited graphite is the most complicated type due to the variability of ore-hosting rocks, melts/fluids properties, and ore-forming mechanisms [8,11–13].

In China, the first fluid-deposited graphite deposit, the Suijiquan occurring in the Kalamaili area in Xinjiang Province, was distinguished in the 1960s. In the last ten years, more crystalline graphite deposits have been discovered in this region such as the Huangyangshan super-large deposit. Then, the graphite deposits in the Eastern Junggar have attracted more attention. Some scholars have reported the ages and properties of the Huangyangshan pluton and concluded that belongs to the A-type granites formed in the Late Carboniferous [14–16]. Besides, the ore genesis of the Huangyangshan deposit has been involved in some references on the basis of fluid inclusion analysis laser Raman and graphite C isotopic analyses, as well as S and Pb isotopic analyses of associating sulfides in the graphite ores [16,17]. The C isotopic composition of the Huangyangshan graphite showed organic characteristics [16], whereas the S and Pb isotopic composition of associating sulfides showed a magmatic origin [17]. As a result, there are two major genetic viewpoints on the ore-forming mechanism of the Huangyangshan and the Suijiquan graphite deposits. One suggests that graphite is directly crystallized from magma [17–19]. The other holds that the graphite deposited from the hydrothermal process in the late stage of magma evolution [10,16]. The critical factors for the two controversial points of view are the accurate understanding on the magma evolution process and the relationship between graphite mineralization and the magmatic evolution of the ore-hosting granites.

Some magmatic minerals such as amphibole, biotite, pyroxene, and feldspar are generally used to reflect the magma composition and physicochemical condition when they precipitated according to their geochemical behavior [20–26]. As the main minerals in granitic rocks, they all have broad stability field to precipitate during the whole magmatic process and are capable of recording the temperature, pressure, and oxygen fugacity [27,28]. Our present study focuses mainly on the amphibole, biotite, pyroxene and plagioclase textures and chemical compositions in the graphite-hosting granites, the pluton microgranular dioritic enclaves, and orbicular graphite ores from the Huangyangshan deposit. We present in situ major and trace element analyses in order to reveal the physicochemical conditions of different magmatic stages and their implication on the mineralization of the investigated graphite. These studies are presumably helpful for better understanding the magma evolution process and unravel the genetic relationship between graphite and magmatism, which would have an impact on the mineral exploration for graphite deposits in China and elsewhere in the world.

2. Geological Setting and Graphite Mineralization

2.1. Regional Geology

The northern Xinjiang area, tectonically located in the southern part of the Central Asian Orogenic Belt (CAOB; Figure 1a), is split into the Altay, Junggar, and Tianshan blocks from north to south (Figure 1b). The East Junggar orogenic belt (EJOB) is situated in the northeast of the Junggar terrane and comprises the Durat–Baytag arc, the Aermantai ophiolite belt, the Yemaquan arc, the Kalamaili ophiolite belt, and the Harlik–Dananhu arc from north to south (Figure 1b); [29–32]. Based on the available geochronological data for this area, the Junggar ocean separating the Junggar and Altai block was formed at least from early Ordovician, and gradually closed during the late Paleozoic [33–38]. The Cambrian Aermantai ophiolite and early Devonian Kalamaili ophiolite witnessed the tectonic evolution process in the Paleozoic [39–42]. After its closure, the EJOB transferred into the post-collisional orogenic stage when the Huangyangshan alkaline pluton were emplaced, which is the main concern of the present study [19,43,44].
The Kalamaili area is located in the central part of the EJOB and is controlled by the NWW-trending Kalamaili fault system, which hosts typical ophiolite and several metallic deposits (Figure 1c). The exposed strata in the area mainly comprise small-scale Silurian sediments, Permian volcanogenic sediments, and a thick pile of Devonian and Carboniferous volcano-sedimentary rocks. Some Mesozoic and Cenozoic strata are distributed in the eastern and southern parts of this area. All these sediments are controlled by the Beitashan, Kubusu, Qingshui–Suijiquan, and Kalamaili faults and are deposited in a forearc basin-type sedimentary system dominated by active continental margin sediments [45–47]. The magmatic activities were characterized by late Paleozoic post-collisional granitic magmatism according to the geochronology and geochemical data from previous studies [14,32,48,49]. They produced many alkaline granitic plutons including the Laoyaquan, Beilekuduke, Yemaquan, Huangyangshan, and Yebushan plutons, as well as multiple Au, Cu, Sn, and graphite mineralization (Figure 1c); [44,50–53].

Figure 1. (a) Sketch map of the Central Asian Orogenic Belt (after [54]); (b) Geological map of the northern Xinjiang Province (after [38]); (c) Simplified geological map of the Kalamaili area, Eastern Junggar (modified after [19]).
2.2. Huangyangshan Pluton

The Huangyangshan pluton, located in the northeastern Kalamaili fault, is a typical A-type alkaline granitic pluton within the Kalamaili felsic intrusions of alkaline affinity. It roughly shows a NW–SE trend and crops out as a nearly elliptical shape on the surface, generating a concentrically zoned domain as a result of multiple phases of magmatism (Figure 2a). It intruded into the Devonian strata and shows sharp contact combined with small-scale contact metamorphism, indicating shallow depth for emplacement [14]. According to the grain sizes and main types of dark minerals, this pluton is divided into five lithofacies: medium-grained arfvedsonite granite, from medium- to fine-grained arfvedsonite granite, from medium- to fine-grained amphibole granite, medium-grained biotite granite, and fine-grained biotite granite. Their crystallizing ages show a slightly younger trend from north to south (~320–300 Ma) [16,19]. In our study, we focus on the arfvedsonite and amphibole granites, which occur near orebodies, consisting of K-feldspar (~60%), quartz (~25%), arfvedsonite (~3%–5%), hornblende (~5%–8%), plagioclase (<3%), and some accessory minerals such as zircon, titanite, ilmenite, and apatite.

Figure 2. (a) Geological map of the Huangyangshan pluton (after [15]). (b) Simplified map of the No.1 and 2 ore bodies of the Huangyangshan graphite deposit. (c) Cross-section along line 7–7′ in Figure 2b (modified after [17]).
One of the most remarkable features of the Huangyangshan granites is a great abundance of microgranular dioritic enclaves. They are arranged randomly in different sizes and develop black chilled margins (Figure 3a,b). These enclaves are mostly diorite in composition, consisting of plagioclase (~45%), amphibole (mainly richterite, ~30%), quartz (~10%), biotite (<5%), and K-feldspar (~5%). Their grain sizes (~0.2–0.5 mm) are significantly smaller than those of the host granites (~5 mm). Some gabbro and diorite porphyrite dykes are occurred inside the Huangyangshan granites and their strikes are nearly east–west, which have clear boundaries with the granites on the surface. The diorite porphyrite dykes are mainly distributed in from medium- to fine-grained amphibole granite in the north, while the gabbro dykes are mainly distributed in medium-grained biotite granite in the south of the pluton (Figure 2a).

Figure 3. Photographs (a–c) and photomicrographs (d–o) of representative granite and graphite ore samples of the Huangyangshan pluton. The pink points represent some measuring locations. (a) A dark-colored ME in arfvedsonite granite. (b) Enclaves of different sizes in amphibole granite. (c) Zoning...
graphite orbicules consisting of graphite shell, light-colored core, and fine-grained dark inner core. (d) Subhedral arfvedsonite phenocryst with ilmenite and titanite inclusions in arfvedsonite granite (−). (e) Contact zone between granite and ME containing subhedral richterite phenocryst and fine-grained richterite (−). (f) Altered amphibole phenocryst and biotite at the edge in enclaves (−). (g) Amphibole and its chloritization in amphibole granite. (h) Euhedral–anhedral hornblendes in the light-colored core of graphite orbicules (−). (i) Fine-grained hornblendes and distributed carbon materials in the dark inner core of graphite orbicules (−). (j) Altered amphibole, biotite, and chlorite in the granite collected on the surface (−). (k) Fine-grained biotite coexisting with richterite in ME (−). (l) Euhedral biotite and hornblendes in the light-colored core of graphite orbicules (−). (m) A pyroxene phenocryst besides cluster graphite aggregate (−). (n) Corona texture of pyroxene, amphibole, and biotite (BSE). (o) A plagioclase phenocryst without any alteration and inclusions in light-colored cores (+). Gr = graphite, Arf = arfvedsonite, Ilm = ilmenite, Ttn = titanite, Kfs = K-feldspar, Rct = richterite, Qtz = quartz, Pl = plagioclase, Bt = biotite, Amp = amphibole, CM = carbon materials, Chl = chlorite, Mag = magnetite, Po = pyrrhotite, and Px = pyroxene.

2.3. Graphite Mineralization

The graphite deposit hosted in the Huangyangshan pluton is a large-scale deposit with over 78 million tons predicted graphite reserves [55]. All the orebodies occur as lenticular, saddle, or irregular shapes in the middle and southern part of the pluton (Figure 2a). Among them, the No. 1 lenticular and No. 2 saddle orebodies are the largest in scale, with a predicted resource of more than 70 million tons (Figure 2b) [15,55]. The graphite ore is often characterized by the unique spherical structure and coexist with metal sulfides such as pyrrhotite and chalcopyrite (Figure 3c). The graphite orbicules are abundant and randomly oriented in the orebodies. Most of them are composed of a dark graphite shell and light color core forming typical “zonal structures”. Some of them include two cores in a dark and a light color, respectively (Figure 3c). The cores, as well as the host granites, have obvious different mineral compositions. The light-colored cores contain euhedral to anhedral amphiboles in brown or green color (Figure 3h,k). The dark-colored cores consist of fine-grained amphiboles, plagioclases, graphite, and some pyroxene phenocrysts (Figure 3i,m).

3. Sampling and Analytical Methods

Twelve samples were collected either from the surface outcrops or the drill cores, including the granites, enclaves, and graphite ore in the Huangyangshan graphite deposit (Figure 2). The HYI and HYS are the slightly weathered samples collected on surface from the arfvedsonite and amphibole granites, respectively. The HYB are the dark enclaves in arfvedsonite and amphibole granites. From ZK12 to ZK43 represents the fresh ore samples collected from the drill cores in No. 1 and No. 2 orebodies. All the samples were polished into thin sections for petrographic observation, electron microprobe analysis (EMPA), and LA-ICP-MS analysis.

Major elements compositions of amphibole, biotite, and plagioclase were analyzed using a JEOL JXA-8230 electron probe microanalyzer hosted at the State Key Laboratory of geological process and mineral resources, China University of Geosciences (Wuhan). The operating conditions were 15 kV accelerating voltage, 20 nA probe current, and 2–5 µm beam diameter. The natural minerals and oxides standards were used for calibrating the elemental X-ray intensity. A modified ZAF matrix-correction was applied during the data reduction. The analytical precision for SiO2, MgO, FeO, Al2O3, TiO2, MnO, Na2O, K2O, and Cr2O3 are all below 0.01 wt%. The analytical errors are generally less than 2%.

The trace element analysis of the amphiboles was performed using the LA-ICP-MS method at the State Key Laboratory of Ore Deposit Geochemistry, IGCAS. The 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 the ion-signal intensities. Helium (350 mL/min) was applied as a carrier gas. The ablated aerosol was mixed with Ar (900 mL/min) as a transport gas, before exiting
the cell. Each analysis incorporated a background acquisition of approximately 30 s (gas blank) followed by 60 s of data acquisition from the sample. The calibration line for each element was constructed by analyzing three USGS reference glasses (BHVO-2G, BIR-1G and BCR-2G) with Si as an internal standard element. The spot size and frequency of the laser were set to 40 µm and 7 Hz, respectively. An Excel-based software, ICPMSDataCal, (10.2, Wuhan, China) was used to perform the offline selection and integration of background and analyzed signals, time–drift correction, and quantitative calibration for the trace element analysis [56].

4. Results

4.1. Mineral Petrography

4.1.1. Amphibole

The amphibole in the Huangyangshan pluton can be divided into five types: Type-I is typical arfvedsonite in the arfvedsonite granite and occurs pervasively as phenocrysts (size up to 3 mm). It is euhedral and deep green in color (Figure 3d). There always occur some inclusions inside such as ilmenite and titanite. Type-II occurs as phenocryst at the contact zone between the arfvedsonite granite and enclaves (Figure 3e). It is from deep to light green in color, from euhedral to subhedral, has a relatively smaller size (size in 1–2 mm) than Type-I, and has no inclusions inside. Type-III amphibole is fine-grained (size in 0.2–0.5 mm) occurring in enclaves (Figure 3f). It is green-colored and mostly in a columnar or acicular shape. The common alterations such as chloritization, epidotization, and kaolinitization are mainly due to the weathering on the surface. Type-IV is the subhedral-anhedral and yellow-green amphibole developing in the amphibole granite. It is mainly short columnar or granular in shape and develops chloritization at the edge (Figure 3g). Type-V amphibole developing in the cores of the graphite orbicules is enclosed by graphite. It is from brown to green in color, mostly from euhedral to subhedral, and almost fresh (Figure 3h). The interior of the graphite orbicule is diorite, whereas the exterior is granitic. The dark-colored cores in graphite orbicules contain sparse graphite grains, whereas the graphite shells are packet aggregates (Figure 3i), possibly showing the growing process of graphite.

4.1.2. Biotite

The biotite contents in both granites and enclaves are significantly lower than the amphibole. They can be divided into two types according to the alteration degree. Altered biotite mostly occurs in enclaves and granites metasomatizing arfvedsonite and/or developing chloritization (Figure 3j). It mainly has a rough surface, reabsorbed structure, and symbiosis with secondary minerals. Some relatively fresh biotites in enclaves are fine-grained (<0.1 mm) in light brown color and coexist with amphibole (Figure 3k). Fresh biotite all occurs in the graphite orbicule core. It is commonly euhedral in flake, dark-brown, and coexists with Type-IV amphibole, plagioclase, apatite, and some pyroxene (Figure 3l).

4.1.3. Pyroxene

The pyroxene occurs only in the graphite orbicules and is mostly colorless and in a euhedral granular shape. Most of them are phenocrysts and do not coexist with or surrounded by graphite, indicating their formation was earlier. A small amount of pyrrhotite and graphite can be found in the cracks inside some pyroxene (Figure 3m). Some other pyroxene phenocrysts are wrapped by amphibole and biotite in a corona structure (Figure 3n).

4.1.4. Plagioclase

The Huangyangshan granites barely contains plagioclase resulted from the high alkalinity. The plagioclase content of the dioritic enclaves is more than 40% but the grains are too small (<0.5 mm) to observe oscillatory zones. Therefore, we mainly focused on the relatively coarse-grained plagioclase in graphite orbicules and their host granites collected in the drill cores. The plagioclase in granites are commonly 0.5–3 mm in size and distributed
in clusters, with some accessory mineral inclusions developed inside such as apatite and zircon. The plagioclase content in the graphite orbicules is significantly higher than that in the granites. They are mostly euhedral and hardly contain fine-grained amphibole and biotite as inclusions (Figure 3o). Most plagioclases in the granites are coarse-grained and develop normal zoning, while those in the graphite orbicules are medium- to fine-grained and develop inapparent normal and oscillatory zoning (Figure 3o).

4.2. Mineral Chemistry

4.2.1. Amphibole

The amphiboles in the Huangyangshan pluton and graphite ores are characterized by low Al$_2$O$_3$ (commonly < 6%, Figure 4), extremely high SiO$_2$ (mostly > 45%, Figure 4a), FeO$^{T}$ (>20%, Figure 4d), and relatively high TiO$_2$ (mostly > 0.8%), K$_2$O (0.7%–1.9%, Figure 4f). These results are shown in Table S1. The MgO, CaO, and Na$_2$O contents of the five types of amphibole are significantly different (Figure 4b,c,e). According to the major element compositions of the amphiboles, their structural formulae on a 23-cations anhydrous basis after adjusting the ferrous iron charge balance were calculated following the procedure of Leake et al. [57] The results show that Type-I amphibole has a high FeO$^{T}$ (32.54%–34.03%), Na$_2$O (6.37%–7.03%) contents, and low MgO (0.1%–0.24%), CaO (1.5%–2.5%) contents, belonging to sodic amphiboles [Na$_B$ ≥ 1.5, (Na + K)$_A$ ≥ 0.5]. It is classified as typical arfvedsonite in Figure 5a. Type-II and -III amphiboles belong to sodic–calcic amphiboles [Ca$_B$ < 1.5; (Na + K)$_A$ ≥ 0.5] and have a relatively high Na$_2$O (3.57%–4.99%) and low CaO (4.73%–7.93%) content. They are significantly different in MgO (<1% and >8%, respectively) and FeO (32.82%–33.56% and 18.87%–26.65%, respectively) contents, being consistent with the characteristics that the enclaves are neutral (rich in magnesium) and the granites are acidic (rich in iron). They are both plotted in the field of ferrorichterite in Figure 5b. Type-IV and -V amphiboles both have high CaO (9.37%–10.72%), medium MgO (4.97%–8.44%), and low Na$_2$O (1.61%–2.07%) content, showing calcic-amphiboles characteristics [Ca$_B$ ≥ 1.5; (Na + K)$_A$ < 0.5]. They both are classified as ferrohornblende in Figure 5c. The main difference between them is that Type-IV has a low Mg/(Mg + Fe$^{2+}$) value and most measuring points do not contain Fe$^{3+}$ (Table S1). There is no obvious difference between the amphiboles in light-colored and dark-colored cores.

The trace element compositions of 17 amphibole points in this study collected from enclaves and graphite orbicules and 7 arfvedsonite points reported by Ye et al. [58] are shown in Table S2. They have relatively consistent REE patterns that show significantly negative Eu anomalies and inapparent fractionation of the REEs (Figure 6a). Type-I arfvedsonite in granite and Type-II and -III richterites in enclaves have almost the same patterns with a slight HREE enrichment of Er–Tm–Yb–Lu compared with whole-rock REE patterns [19], except for one of the HYB-2 points (ΣREE = 52.67 ppm). Type-IV and -V amphiboles in amphibole granite and graphite orbicules have similar REE patterns, showing a significant enrichment in the REE content (ΣREE = 515.3–569.29 and 887.64–2126.49 ppm, respectively). The REE content of the Type-V amphibole is obviously higher than that from the Type-I to -IV amphiboles, indicating that the cores of graphite have not experienced the crystallization process of REE-rich minerals similar to the granites. The primitive mantle-normalized multi-element variation diagram patterns (Figure 6b) suggest all types of amphiboles have similar distribution characteristics to the granite with stronger Ba and Sr negative anomalies. Compared to the other four types, Type-V amphibole shows a slightly stronger La–Ce–Sm–Nd positive and Pb–Zr negative anomalies.

Note that one point in the enclaves (HYB-2) shows altered amphibole characteristics with low Nb (0.48 ppm) and REE (ΣREE = 52.67) contents and significantly different patterns in Figure 6b, hence the data were eliminated in the statistics. From calcic to sodic amphiboles, the Li content has an upward trend (average of 36, 485 and 1627 ppm, respectively), whereas the Sc–Y contents show a downward trend. The V–Cr contents also have a decreasing trend from calcic to sodic–calcic amphiboles due to the lack of sodic amphiboles data.
Figure 4. Diagrams of SiO$_2$ (a), MgO (b), CaO (c), FeO$^T$ (d), Na$_2$O (e), and K$_2$O (f) vs. Al$_2$O$_3$ of amphibole in the Huangyangshan deposit in wt%.

Figure 5. Classification diagrams of (a) sodic, (b) sodic–calcic, and (c) calcic amphiboles (after [57]). Symbols are as in Figure 4.
We obtained only three available biotite EPMA points in dioritic enclaves, two of which (23.47%–30.17%) contents. The altered and fresh biotite samples are mainly different in TiO₂ contents. The altered and fresh biotite samples are mainly different in TiO₂ and MgO (9.02%–11.48%) and low Al₂O₃ (8.75%–9.51%) and FeO (19.6%–21.87%) contents; 3 and 12 valid data were obtained from amphibole granite and graphite orbicules, respectively, which have similar compositional characteristics. They have relatively low SiO₂ (35.57%–38.51%) and MgO (4.62%–10.12%), and high Al₂O₃ (11.12%–12.95%) and FeO (23.47%–30.17%) contents. The altered and fresh biotite samples are mainly different in TiO₂ content (0.99%–1.59% and 2.09%–4.46%, respectively) and are plotted in primary biotites and re-equilibrated biotites fields, respectively (Figure 7a). In the biotite classification plot (Figure 7b), the fresh biotite is classified as an Fe-biotite, whereas the altered biotite is classified as a Mg-biotite, indicating the alteration led to the loss of Fe or Mg enrichment.

4.2.2. Biotite

The major element compositions of the biotite are shown in Table S3. The cation number and structural formulae of biotite were calculated by 22 oxygen atoms as a unit. We obtained only three available biotite EPMA points in dioritic enclaves, two of which are altered and one is relatively fresh. They have a relatively high SiO₂ (40.53%–42.32%) and MgO (9.02%–11.48%) and low Al₂O₃ (8.75%–9.51%) and FeO (19.6%–21.87%) contents; 3 and 12 valid data were obtained from amphibole granite and graphite orbicules, respectively, which have similar compositional characteristics. They have relatively low SiO₂ (35.57%–38.51%) and MgO (4.62%–10.12%), and high Al₂O₃ (11.12%–12.95%) and FeO (23.47%–30.17%) contents. The altered and fresh biotite samples are mainly different in TiO₂ content (0.99%–1.59% and 2.09%–4.46%, respectively) and are plotted in primary biotites and re-equilibrated biotites fields, respectively (Figure 7a). In the biotite classification plot (Figure 7b), the fresh biotite is classified as an Fe-biotite, whereas the altered biotite is classified as a Mg-biotite, indicating the alteration led to the loss of Fe or Mg enrichment.

Figure 6. Chondrite-normalized REE patterns (a) and primitive mantle-normalized trace element variation patterns (b) of amphiboles and granites in the Huangyangshan deposit. The normalizing values for the REEs and trace elements are from Sun and McDonough [59]. The yellow, red, blue, green lines and the shadow parts represent the trace element data of Type-I, Type-II and -III, Type-IV, Type-V and granites, respectively. The granites data are from Sun et al. [19].

Figure 7. (a) Ternary 10 × TiO₂–(FeO + MnO)–MgO discrimination diagram of primary, re-equilibrated, and epigenetic biotite (after [60]). (b) Ternary Mg–(Fe²⁺ + Mn)–(Al³⁺ + Fe³⁺ + Ti) classification diagram of biotite (after [61]).
4.2.3. Pyroxene

Due to the low content of pyroxene in the Huangyangshan pluton, 16 measuring points of the 6 pyroxene phenocrysts in the graphite orbicules were analyzed in this study. According to their major element compositions (Table S4), 6 pyroxene phenocrysts were classified into 4 clinopyroxene phenocrysts with high calcic pyroxene endmembers (Wo) and 2 orthopyroxene phenocrysts with low Wo (Figure 8). The analyzed clinopyroxenes are mainly subhedral and fine-grained, which were found in granites, graphite orbicule shells, and deep-colored cores. Their enstatite endmembers (En) are similar (18.26–27.64) and have low Al2O3 (0.32%–1.12%), MgO (5.98%–9.26%), FeO (17.24%–24.26%), and high CaO (12.09%–20.43%) contents. The orthopyroxenes only occurred in graphite orbicules in the shape of coarse phenocrysts. They have extremely lower CaO (0.36%–1.69%), higher FeO (25.49%–36.33%), MgO (7.36%–19.96%), and similar Al2O3 (0.33%–1.01%) contents compared to the clinopyroxenes.

Some orthopyroxene phenocrysts develop typical zonal structures, including orthopyroxene, amphibole, and biotite from the core to the edge (Figure 3n). In the backscattered electron photograph (Figure 9a), an orthopyroxene has high protrusion and developed cleavage at the core, but low protrusion and undeveloped cleavage at the edge, indicating the orthopyroxene may have undergone metasomatic replacement and belongs to transitional phase minerals. From the core to the edge, the Fe content decreases, whereas the Mg content increases, showing the characteristics of reversely zoned structure. However, if it continues outward, the Fe content increases and the Mg content decreases (Figure 9b), suggesting that magma have experienced multiple mixing during the formation of pyroxene.

4.2.4. Plagioclase

The plagioclase grains in both granites and graphite orbicules have similar Al2O3 contents, ranging between 22.57% and 27.67% (Table S5). The former has relatively higher SiO2 content than the latter, ranging in 59.51%–67.35% (63.48% on average) and 58.06%–66.81% (61.01% on average), respectively. The early plagioclase phenocryst in Sample ZK33 has a lower Si content (58.06%–65.36%, 59.89% on average), showing that the magma had a tendency of increasing acidity from early to late. Most plagioclases develop normal zoning characterized by dark low-An rims (30 > An > 50, oligoclase) and light high-An cores (10 > An > 30, andesine; Figure 10a–c), also suggesting the increasing magma alkalinity and acidity along with its evolution [20]. One plagioclase phenocryst enclosed by the graphite shows apparent occasional oscillatory zoning and has low a SiO2, high An, and rel-

![Figure 8. Ternary Calcic pyroxene (Wo)—Enstatite (En)—Orthoferrosilite (Fs) classification diagram of pyroxene (after [62]).](image-url)
Some orthopyroxene phenocrysts develop typical zonal structures, whereas the Mg content increases, showing the characteristics of reversely zoned structures. However, if it continues outward, the Fe content increases and the Mg content decreases. In the Huangyangshan deposit, there are rather less Ti (58.06 a.p.f.u.) and Mg/(Mg + Fe) values. For the calcic ferrohornblendes in the Huangyangshan deposit, there are relatively high Al and Mg/(Mg + Fe)2+ values. For the sodic amphibole in the Huangyangshan pluton, its temperature calculation result was not reliable for the sodic amphiboles. The accurate temperature calculation result was more likely the closure temperature and pressure of the sodic amphibole in the Huangyangshan pluton.

![BSE images illustrating the petrographic characteristics of plagioclases in the granites and the graphite orbicules and their An (anorthite composition) variation trends.](image)

**Figure 9.** (a) BSE images of an orthopyroxene phenocryst in graphite orbicule. (b) Compositional variations along the profile of the Huangyangshan orthopyroxene phenocryst (based on the data from Table S4). (c) BSE images of an orthopyroxene phenocryst in graphite orbicule. (d) Plagioclase in granites showing high-An cores and low-An rims. (e) Plagioclase in the light-colored core of graphite orbicules having andesine core and oligoclase rim. (d) A plagioclase phenocryst surrounded by graphite having relatively high An and occasional oscillatory zoning.

**5. Discussion**

### 5.1. Mineral Crystallization Conditions

Previous studies have shown that amphibole, biotite, pyroxene, and plagioclase can be used to estimate their crystallization conditions, such as temperature, pressure, and oxidation, and their applicable objects of amphiboles mainly constrain in calcic amphiboles with relatively high Ca contents [21,23,24]. Ye et al. [58] tried to estimate the temperature and pressure of the sodic amphibole in the Huangyangshan pluton using multiple formulas. However, the pressure calculation result was not reliable for the sodic amphiboles.
The accurate temperature calculation result was more likely the closure temperature for the element exchange to reach equilibrium other than the crystallization temperatures. Through amphibole-only thermometers, an estimated temperature result with errors was obtained. In this study, only Type-IV and -V belong to calcic amphiboles. The Type-IV amphibole occurs in the amphibole alkaline granite with fine granularity and chloritization at prepheries. Type-V amphibole is mainly found in the cores of graphite orbicules with an even grain size and straight edges. It is commonly euhedral and rarely has obvious ductile deformation and directional arrangement, with the Si formula number less than 7.3 a.p.f.u. (6.88 a.p.f.u.–7.08 a.p.f.u.). All this evidence suggests a magmatic origin of Type-IV and -V amphiboles [63,64]. They hardly develop oscillatory zones, indicating their crystallized process can record the evolution of magma from melt to consolidation [65]. In this paper, therefore, the quantitative estimation of these two types of amphibole are mainly carried out. Then, the characteristics of the magma system were deduced in combination with the relevant parameters of biotite and pyroxene.

5.1.1. Pressure

Most amphibole thermobarometers are only applicable for amphiboles with relatively high Al and Mg/(Mg + Fe\(^{2+}\)) values [21–23,66]. However, Type-IV and -V amphiboles have significantly low Al (0.89 a.p.f.u–1.15 a.p.f.u) and Mg/(Mg + Fe\(^{2+}\)) (0.285 a.f.p.u–0.476 a.p.f.u) values. For the calcic ferrohornblendes in the Huangyangshan deposit, therefore, we need a more universal estimation method.

After experimental simulation, Mutch et al. [67] comprehensively considered the effects of fluid, temperature, and oxygen fugacity on pressure and proposed a new calculation formula. It is widely used in the composition of symbiotic amphibole (Mg/(Mg + Fe\(^{2+}\)) = 0.32 a.p.f.u.–0.81 a.p.f.u.) and feldspar (An = 15–80), but the rock is required to have a low variance mineral assemblage: amphibole + plagioclase + biotite + quartz + alkali feldspar + ilmenite/titanite + magnetite + apatite. Most composition parameters of the amphiboles in this study meet the above conditions and the mineral assemblages are very consistent. Based on this method, the estimated pressure of Type-IV and -V amphiboles is 157–220 Mpa and the corresponding depth is 5.95–8.32 km (with a crustal density of 2700 kg/m\(^3\)). This might represent the magmatic emplacement depth at the time of crystallization.

According to the Al\(^T\)-based biotite geobarometer proposed by Uchida et al. [68], the crystallized pressure of biotite in the graphite orbicules are mostly near 0, showing quite a difference with the results of the amphibole pressure. Kang et al. [69] pointed out that the calculation of granite diagenetic pressure has the following characteristics: If there exists an amphibole + biotite mineral assembly in the granite and the amphiboles are crystallized well, the calculated pressure of the amphibole will be reliable, whereas the biotite will not be reliable. If no amphibole exists in the granite, there will also be a large error in the biotite pressure results. The results of the biotite pressure will be reliable only if the amphibole crystallized poorly and the biotite crystallized well. Therefore, this study tends to use the amphibole pressure and depth as the formation pressure and depth of the graphite orbicule cores.

5.1.2. Temperature

The cores of the graphite orbicules are characterized by dioritic lithoface rich in plagioclase and calcic amphiboles, meeting the requirements of some geothermometers [70–72]. Using the thermometer proposed by Putirka [72] based on the correlation between the Si, Fe, Mg, Ti, Na, known pressure, and temperature of amphibole, we obtained the crystallization temperatures of 681–761 °C for Type-IV and -V amphiboles, with an average of 730 °C. Their low crystallized temperature condition suggests a late stage of magmatic evolution. Given that there is no thermobarometer for sodic and sodic–calcic amphibole, it can be inferred that the formation conditions roughly through the comparison of its compositional parameters. Generally, the Al content of the amphibole is closely related to the emplace-
ment depth and low Al indicates the shallow emplacement depth [65]. The crystallization temperature has a strong negative correlation with the Si content, but negative correlations with Al, Na, and Ti contents [72]. Type-I arfvedsonite always contains some ilmenite and titanite inclusions, suggesting its high Ti content. From Type-I to -III amphiboles have significantly higher Si, Na, and lower Al than Type-IV (Figure 4). In alkaline rocks, the Na is much related to the amphibole compositions and magma components and cannot be used to estimate the temperature. Therefore, we inferred that the cores of the graphite orbicules were formed in a relatively high temperature and pressure condition compared with the granite and enclaves and may have crystallized in an earlier stage of magmatism. This is extremely consistent with the estimated temperature of the sodic amphibole (about 650 °C) and its late crystallization stage as reported by Ye et al. [58].

Under high temperature and high pressure, the content of Ti in biotite is closely related to the temperature change, which is usually used as the basis for estimating temperature [73,74]. Generally, biotite is Al-rich in peraluminous granite (S-type), Mg-rich in calc-alkaline granite (I-type), and Fe-rich in alkaline granite (A-type). The biotite in the graphite orbicules has extremely high Fe content (FeO = 23.47%–30.17%), showing typical A-type granite features. In comparison, the biotite in enclaves has a lower Fe content (FeO = 19.6%–21.87%) and higher Mg content (MgO = 9.02%–11.48%). These characteristics are similar to the compositions of amphiboles, indicating they crystallized at similar conditions. Based on the relation between the Ti content and crystallized temperature of the biotite in metapelites, Henry et al. [74] proposed a Ti-based empirical biotite geothermometer. It was later proved to be equally applicable to granite [75]. The crystallization temperature of the unaltered biotite in the enclaves is similar to that in the graphite orbicules, which yielded from 658 to 720 °C (686 °C on average). It is slightly lower than Type-IV and -V amphiboles, suggesting they crystallized slightly later than the amphiboles.

The thermometer for pyroxene is applicable when the pyroxene and the melt are in equilibrium. However, the pyroxenes in the studied graphite ore are all occurred as phenocrysts, which are not contemporaneous products with the amphibole alkaline granite. Some other scholars put forward the estimation method of pyroxene thermometer through experiments and thermodynamic principles, which is suitable for most rocks [76,77], and requires the equilibrium parameter of symbiotic clinopyroxene and orthopyroxene ($K_D$) = 1.09 ± 0.14. Through calculation, there are five dipyroxene assemblages with $K_D$ between 0.98 and 1.16, satisfying this condition. According to the formula, the crystallization temperatures of pyroxenes are 807–899 °C and 840–1012 °C, which are significantly higher than the crystallization temperatures of amphibole and biotite. This is also consistent with the pyroxene–amphibole–biotite crystallization order supported by the petrographic study.

5.1.3. Oxygen Fugacity

It is known that the oxygen fugacity of magma is positively correlated with the Mg content of amphibole and negatively correlated with the Fe content [78,79]. In addition, with the enhancement of reducibility, Fe$^{3+}$ tends to change to Fe$^{2+}$. As a result, the Fe# (Fe/(Fe + Mg)) and (Fe$^{2+}$/Fe$^{2+}$ + Fe$^{3+}$) values of amphibole can reflect the oxygen fugacity of magma. The higher these values, the lower the oxygen fugacity [78–80]. The results (Figure 11) show that Type-I and -II amphiboles have extremely high Fe# (0.951 a.p.f.u.–0.995 a.p.f.u.) and almost no Mg, indicating a very reductive condition in low oxygen fugacity. Type-III amphibole has relatively low Fe# (0.484 a.p.f.u.–0.730 a.p.f.u.) and mainly falls into the high oxygen fugacity field. Type-IV and -V amphiboles mostly have moderate Fe# (0.606 a.p.f.u.–0.741 a.p.f.u.) and are plotted in the field of intermediate oxygen fugacity. However, In Types I–IV amphiboles, all Fe elements exist in the form of Fe$^{2+}$, indicating an environment with very low oxygen fugacity. Besides, the (Fe$^{2+}$/Fe$^{2+}$ + Fe$^{3+}$) value of the Type-V amphibole ranges from 0.12 a.p.f.u. to 0.34 a.p.f.u. Such values are indicative of a range of oxygen fugacity above the QFM buffer [81], suggesting the crystallization under from low to moderate conditions.
In mineralogy, Type-I arfvedsonite is an important petrogenetic indicator of alkaline magma, which forms in the reducing condition. The Sayashk hydrothermal Sn deposit occurring in the arfvedsonite granite in this area also reflects the low magmatic oxygen fugacity [82]. A large number of metal sulfides and oxides such as pyrrhotite, chalcopyrite, and ilmenite are developed in the graphite orbicules with rarely magnetite content, which also reflects the characteristics of relatively low oxygen fugacity. However, magnetite is also rare in the enclaves and the Fe\(^{3+}\) content is very low in the component parameters (Table S1). It does not show high oxygen fugacity characteristics, which is obviously ambiguous with the high oxygen fugacity of Type-III amphiboles shown in Figure 11. Amphibole is the main carrier of Mg in magma. During magma evolution, Mg is a refractory element that tends to reside in residual melt, whereas Fe readily migrates into differentiated minerals [83]. During magma mixing, the intermediate-basic magma end member with higher Mg and Fe contents evolved as the original melt. As a result, the Mg tends to remain in the amphiboles in enclaves, showing lower Fe\(^\#\) characteristics. The Fe tends to migrate into felsic magma to form minerals with higher Fe, such as arfvedsonite and ilmenite. Therefore, we used the characteristics of Fe\(^{3+}\)/ (Fe\(^{2+}\) + Fe\(^{3+}\)) as the criterion. The enclaves were formed in a lower oxygen fugacity environment similar to the arfvedsonite granite.

Similar to those in amphiboles, the Fe\(^{2+}\), Fe\(^{3+}\), and Mg contents of biotite can also be used to estimate the oxygen fugacity of the magma and fluids [73]. In the ternary Fe\(^{2+}\)-Fe\(^{3+}\)-Mg plot (Figure 12a), the biotite in graphite orbicules is distributed near the NNO evolution line showing low oxygen fugacity, indicating it formed in a relatively reducing environment, which is consistent with the estimated results of amphibole. However, the biotite sample in the enclaves was plotted below the QFM evolution line due to its very low Fe\(^{3+}\) value, showing extremely low oxygen fugacity. In the Logf(O\(_2\))–T diagram under P\(_{H_2O}\) = 207.0 Mpa (Figure 12b), most samples are plotted near the NNO evolution line including the biotite in enclaves. Considering that the Fe\(^{3+}\)/Fe\(^{2+}\) value is more sensitive to oxygen fugacity but Figure 12b only considered the influence of the Fe\(^\#\) value, we tended to conclude that the enclaves might be formed under more reductive conditions based on Figure 12a.
In mineralogy, Type-I arfvedsonite is an important petrogenetic indicator of alkaline rocks [83]. During magma mixing, the intermediate rocks have Ca, Na, and K contents similar to the Type-III fine-grained biotite. The mixing of mafic and felsic magma is considered to be one of the most important mechanisms for forming enclaves characterized by the igneous textural features, finer grain size, and chilled margins in granites [84,85]. Up to now, some researchers have proved that the dark inclusions in the Huangyangshan pluton suggest magma mixing resulted from the injection of less differentiated mantle-derived intermediate–basic magma into the highly differentiated alkaline granitic magma [14,19,58]. The present study provides more evidence as follows: (1) The Type-II richterite phenocrysts at the contact between the enclaves and granites have Ca, Na, and K contents similar to the Type-III fine-grained richterite in enclaves (Figure 4c,e,f) but Mg and Fe contents and a crystalline form similar to the Type-I arfvedsonite phenocrysts in granites (Figure 4b,d), suggesting clear transitional characteristics. (2) Although the cores of graphite orbicules are characterized by neutral rocks with high contents of plagioclase and mafic minerals, the biotites in them have the feature of typical A-type granite (high Fe content). (3) The columnar and acicular shapes of Type-III amphibole indicate a rapid quenching possibly during fluctuations of temperature or water content of the magma [55,86]. (4) Amphiboles in dioritic-mafic rocks are commonly rich in Ca and Mg, rarely appearing Na-rich amphiboles. However, the type of amphiboles developed in dioritic enclaves is Na-rich richterite. (5) In the same magmatic system, the stronger the acidity of the rock, the higher the content of the REE. However, REE contents of Type-II, -III, and -V amphiboles in enclaves and graphite orbicules are significantly higher than Type-I amphiboles in granites (Figure 6a), indicating their different magma sources. (6) The pyroxene phenocrysts wrapped by amphibole and biotite indicates that they may be the residue of mafic magma crystallization in the early stage of magmatic evolution. (7) The reversely zoned structure developed in the pyroxenes indicate that the magma may have experienced partial mixing of basic mantle-derived magma during its evolution and then mixed with acidic crust-derived magma (Figure 9). (8) Plagioclases in oreyode matrix have obvious oligoclase to andesine cores and albite rims, indicating the trend of magma transition from neutral to acidic. This partly reflects the contamination by a felsic magma.

The cores of graphite orbicules and the host granites have obvious different mineral compositions, indicating they formed in different conditions. The type of amphibole in the granites, enclaves, and graphite orbicules is sodic, calcico-sodic, and calcic amphibole, respectively, indicating that their forming environment or parent magma was obviously different. In Si-saturated alkaline magma, the evolution sequence of amphiboles is generally from katophorite to winchite and then to ferrorichterite from early to late. Alkaline types of

Figure 12. (a) Ternary Fe$^{3+}$-Fe$^{2+}$-Mg plot for the Huangyangshan biotite (after [73]). (b) Temperature (T) vs. Log(fO$_2$) for the Huangyangshan biotite (after [73]).

5.2. Magma Mixing and Evolution

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such as arfvedsonite and riebeckite are formed at the latest stage of crystallization [87]. With the evolution of magma, the quartz content and alkalinity of amphiboles will increase. The existence of arfvedsonite in granites indicates that the magma has reached to the latest stage. The Type-III ferrorichterite contains higher SiO$_2$ but lower (Na + K)$_A$ contents than Type-I arfvedsonite. The geochemical characteristics of minerals and whole-rock show that enclaves inherited the features of host A-type alkaline granitic magma [14,19], suggesting that the enclaves have experienced sufficient magma intermingling during their formation. Although showing the same dioritic rock characteristics dominated by plagioclase and amphiboles, the Type-III ferrorichterite in enclaves has more characteristics of crust source and alkaline magma compared with Type-V ferrohornblende in graphite orbicules, indicating the enclaves were formed in the environment with a higher magma mixing degree or in the magma with higher replenishment of acid magma. In addition, the graphite orbicules contain euhedral, coarse-grained amphibole, plagioclase, and clinopyroxene, whereas the enclaves consist of fine-grained, from subhedral to anhedral ferrorichterite, and plagioclase, indicating that the cores of the graphite orbicules formed in a deep environment of higher temperature and pressure. This is also consistent with the estimated amphibole temperature and pressure mentioned above. In summary, it can be concluded that the granites and the enclaves were formed in the latest magmatic evolution stage at the same time. The crystallization temperature and pressure of cores of graphite orbicules are higher and the characteristics of alkaline magma are weaker, indicating that they crystallized relatively earlier.

The rebalancing process below the solidus will not significantly change the geochemical characteristics of the amphiboles. Therefore, its composition, especially the REEs and incompatible elements, can be used to explore the properties and petrogenesis of the parent magma. Different types of amphibole in the Huangyangshan deposit all have extremely negative Eu anomalies, which is consistent with the whole-rock compositions (Figure 6a). It suggests that the magma experienced strong plagioclase crystallization and differentiation when amphibole crystallization, which is similar to the characteristics of acid rocks originated from mantle-derived magma [88]. Whereas the enclaves have relatively weak negative Eu anomalies compared with these amphiboles, indicating that these amphiboles crystallized later than plagioclase. The Ce is more incompatible than Pb [60], so the lg(CE/Pb) value of the amphibole can reflect the degree of crustal contamination. From Type-V to Type-I amphiboles, the lg(CE/Pb) value decreases (Figure 13), suggesting the proportion of crust-derived acidic magma increased gradually. Besides, Sc, V, and Cr are transition metals that are usually enriched in mafic, untra-mafic rocks, and depleted in acidic and alkaline rocks [89]. The Sc, V, and Cr contents of Type-IV and -V amphiboles are obviously higher than those of Type-I to -III amphiboles (Table S1), further showing the melt differentiation was weaker during the formation of cores of graphite orbicules. Therefore, the mixing of mantle-derived mafic magma has an important influence on the evolution and differentiation of magma.

One of the critical issues is that the dioritic cores surrounded by a large amount of graphite and the dioritic enclaves without graphite come from the same intermediate–basic parental magma or not. Generally, the REEs are lower in mafic and untra-mafic rocks and higher in acidic and alkaline rocks [60]. According to the above discussion, the parental magma of enclaves and granites had experienced sufficient differentiation and mixing. If the parent magma was from the same source, the amphiboles in the cores of graphite orbicules were supposed to have lower REEs. However, the REE contents of Type-IV and -V amphiboles are much higher than the others (Figure 6a). In addition, some early crystallized coarse-grained clinopyroxene and plagioclase phenocrysts are developed in the cores of graphite orbicules, whereas only fine-grained amphibole, plagioclase, and a small amount of biotite occurred in the enclaves. The mineral assemblage of amphibole and some biotite is a common cumulate result of andesitic melt [90,91]. The typical cumulate rocks formed by basaltic melt are gabbro and the main minerals are clinopyroxene and plagioclase [92]. Therefore, the parental magma of graphite orbicules cores may came from
basaltic melt, while the enclaves were more likely derived from andesitic melt. Thirdly, some magmatic metal sulfides (pyrrhotite, chalcopyrite, and pentlandite assemblages) are developed along with graphite. The Type-V amphibole in the graphite orbicules has a higher oxygen fugacity (higher Fe$^{3+}$ content) and more mantle-derived components than Type-III richterite in enclaves (Figure 11) and the biotite also has higher oxygen fugacity (Figure 12). Therefore, it can be concluded that the enclaves and the cores of graphite orbicules may not originated from the same parental magma. The basic parent magma that formed graphite orbicules might be characterized by rich metal elements, rich volatiles and high oxygen fugacity that were easier to crystallize sulfides. This may be one of the reasons for the crystallization of graphite.

![Figure 13](image)

**Figure 13.** Plots of lg(Nb) vs. lg(Ce/Pb) (a) and lg(Ce/Pb) vs. lg(Nb/U) (b) of amphiboles from the Huangyangshan deposit. Symbols are as in Figure 4.

5.3. **Implications for the Graphite Mineralization**

During the evolution of magma, pyroxene, amphibole, and biotite in the Huangyangshan pluton crystallized successively with estimated crystallization temperatures of 840–1012 °C, 681–761 °C, and 658–720 °C, respectively. Their sources also evolved from the mantle source (pyroxene) to the crust–mantle mixed source (amphibole) and then to the crust source (biotite), suggesting the temperature changing trend and evolution process of magma. The early crystallized pyroxenes wrapped in the graphite orbicules were formed in an intermediate–basic magmatic environment. According to petrographic observation, the graphite is hardly direct contacts the pyroxenes, indicating that no graphite deposition occurred before the high-temperature mafic magma endmembers injected into the acid magma chamber. For melt or hydrothermal systems, graphite is usually deposited under relatively reducing conditions or precipitated and crystallized due to the reduction in the system [93,94]. The Huangyangshan pluton has significantly low oxygen fugacity and both amphibole and biotite were formed in a low oxygen fugacity environment. The reduction process of magma could be triggered by the mixing of mafic magma with the high oxygen fugacity and alkaline felsic magma.

At present, Raman graphite geothermometers have been widely used in order to determine the metamorphic grade and crystallization temperature of graphite [95–98]. Sun et al. [17] reported the crystallization temperature of the Huangyangshan graphite calculated by Raman geothermometers to be 750–800°C. It is higher than the temperature of amphibole and biotite and lower than that of pyroxene, which is also consistent with
the petrographic observation. Sun et al. [17] also concluded the graphite crystallization temperature is similar to that of magmatic graphite deposit around the world. Therefore, it can be inferred that the Huangyangshan graphite might be crystallized at the end of magma mixing and before entering the low oxygen fugacity environment of the magma condition.

In a low oxygen fugacity environment, carbon mainly occurs in the form of methane [11]. There are two main processes for the formation of graphite from methane: oxidation \((\text{CH}_4 + \text{O}_2 \rightarrow \text{C} + 2\text{H}_2\text{O})\) and decomposition \((\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2)\). They both require the mixing of oxidizing melt/fluid to drastically change the physical and chemical conditions of the system [26]. However, no evidence of foreign melts/fluids mixing in the late magmatic stage has been found so far, so the mineralization ability of the late magma needs to be further confirmed. Nonetheless, the genetic relationship between the graphite mineralization and magma mixing can still be identified by the coexisted sulfides with graphite and compositional differences of amphibole and biotite in the granites and graphite ores. Combined with the crystallization temperature of graphite, therefore, graphite mineralization might be occurred from the late stage of magma mixing to the late stage of magmatism.

6. Conclusions

The amphibole in the Huangyangshan graphite deposit can be divided into five types. It generally has low Al and high Ti, K, Si, and Fe contents and has REE patterns with negative Eu anomalies and element distribution patterns similar to granites. The primary biotite in the granites, enclaves, and graphite orbicules belongs to Fe-biotite, which has the characteristics of high Si and Fe and low Al and Mg contents. The pyroxene phenocrysts in graphite orbicules develop significant zonal structures and are characterized by high Si and low Ca and Fe contents. The plagioclase phenocrysts are mainly oligoclase and andesine, with positive and oscillating zonal structures.

The crystallization temperature of pyroxene, Type-V amphibole, and primary biotite were 840–1012 °C, 681–761 °C, and 658–720 °C, respectively, suggesting their crystallization order. The magma pressure and depth were 157–220 Mpa and 5.95–8.32 km, respectively. Both the amphibole and biotite crystallized in a reducing environment with an extremely low oxygen fugacity.

The element compositions of amphibole, biotite, pyroxene, and plagioclase suggest that the Huangyangshan pluton has experienced significant mixing of mafic mantle-derived magma and felsic crust-derived magma. The graphite mineralization might be occurred from the late stage of magma mixing to the late stage of magmatism.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12111458/s1, Table S1: EPMA results of amphibole in the Huangyangshan pluton; Table S2: LA-ICP-MS results of amphibole; Table S3: EPMA results of biotite; Table S4: EPMA results of pyroxene; Table S5: EPMA results of plagioclase.

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