

Article

Chronology and Geochemistry of the Sijiaying Iron Deposit in Eastern Hebei Province, North China Craton: Implications for the Genesis of High-Grade Iron Ores

Xinyu Gao ^{1,2}, Denghong Wang ^{2,*}, Fan Huang ^{2,*}, Yan Wang ² and Chenghui Wang ²

¹ School of the Earth Sciences and Resources, China University of Geosciences (Beijing), Beijing 100083, China; gaoxinyugeology@outlook.com

² Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China; wangyan@mail.cgs.gov.cn (Y.W.); wangchenghui131@sina.com (C.W.)

* Correspondence: wangdenghong@vip.sina.com (D.W.); fhymn@163.com (F.H.)

Abstract: The Sijiaying iron deposit is located in the Eastern Hebei area of the southern section of the northern margin of the North China Craton (NCC) and is the largest single iron deposit in China. The deposit contains many banded iron formations (BIFs) and was proven to have more than 3 million tons of high-grade iron ore resources. This study carried out geochemistry and zircon U–Pb analysis of normal-grade iron ore, high-grade iron ore, and wall rock (biotite–leptynite, chlorite–sericite schist) in the Sijiaying deposit and discussed the genesis and metallogenic age of high-grade iron ore. BIFs have low concentrations of Al₂O₃ and TiO₂ and high field strength element (HFSE) depletion, indicating almost no contamination via terrestrial debris. The standardized post-Archean Australian shale (PAAS) rare earth element (REE) distribution pattern indicates that the iron formation exhibits positive Eu, Y, and heavy rare earth element (HREE) anomalies and lacks negative Ce anomalies, indicating that the Sijiaying BIF was enriched with iron sources via high-temperature hydrothermal fluids from the seabed and deposited in an anoxic ancient marine environment. In addition, geological field work identified two types of high-grade iron ore in the mining area: primitive sedimentary and hydrothermally altered high-grade iron ore. Further ore geochemical research showed that the primitive sedimentary-type iron ore is similar in geochemistry to the BIF. In addition to low Eu/Eu* values, the hydrothermally altered high-grade iron ore shows geochemical characteristics similar to those of the BIF, suggesting that they share the same iron source but did not form at the same time. The total large ion lithophile element (LILE) (Sr, Ba, Pb) contents in primitive sedimentary-type high-grade iron ore are higher than those in hydrothermally altered high-grade iron ore, indicating that LILEs are carried away via fluids during the hydrothermal alteration process in normal-grade iron ore. The geochemical characteristics of biotite–leptynite and chlorite–sericite schist include high contents of SiO₂ and Al₂O₃, light rare earth elements (LREEs), LILE enrichment (Rb, Ba, Sr, Zr), and HFSE depletion (Nb, Ta, P, Ti), characteristics that are similar to island arc volcanic rocks. The reconstruction of the original rock indicates that the wall rock is a product of volcanic sedimentary cycles in an island arc setting. Zircon cathodoluminescence images and LA–ICP–MS zircon U–Pb dating can be divided into four age groups (3283 Ma, 2547 Ma, 2500 Ma, and 2407 Ma), which correspond to the earliest volcanic activity in eastern Hebei, the main mineralization age of the Sijiaying BIF (the mineralization age of primitive sedimentary high-grade iron ore), a regional tectonic–metamorphic event, and the occurrence of migmatization (the mineralization age of hydrothermally altered high-grade iron ore), respectively. Therefore, the Sijiaying BIF and primitive sedimentary high-grade iron ores were deposited and mineralized at 2547 Ma, and the iron orebody was later altered via the hydrothermal solution at 2407 Ma, forming large-scale high-grade iron ores.

Keywords: banded iron formation; high-grade iron ore; Zircon U–Pb dating; North China Craton



Citation: Gao, X.; Wang, D.; Huang, F.; Wang, Y.; Wang, C. Chronology and Geochemistry of the Sijiaying Iron Deposit in Eastern Hebei Province, North China Craton: Implications for the Genesis of High-Grade Iron Ores. *Minerals* **2023**, *13*, 775. <https://doi.org/10.3390/min13060775>

Academic Editor: Urs Klötzli

Received: 10 May 2023

Revised: 31 May 2023

Accepted: 2 June 2023

Published: 7 June 2023



Copyright: © 2023 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/>).

1. Introduction

Banded iron formation (BIF) is a marine chemical sedimentary rock formed in the Pre-Cambrian era and is mainly composed of iron-bearing minerals, with iron contents greater than 15%, and the iron minerals are interbedded with quartz, chert, and carbonate and silicate minerals. When the iron content is more than 25%, it becomes a BIF deposit with industrial value. According to the different sedimentary environments, BIFs are often divided into two subtypes: Algoma-type and Superior-type. Algoma-type BIFs formed in a deep-sea volcanic sedimentary environment and are often found in the volcanic sedimentary sequence of an Archean greenstone belt. Superior-type BIFs were mainly formed in the Paleoproterozoic era and deposited in a shallow sea continental shelf environment. They are usually interbedded with carbonate rock, quartz sandstone, and black shale, with only a small amount of volcanic rock [1]. The earliest BIF in the world was formed 3.8 billion years ago, BIF reached its mineralization peak between 2.7 and 2.5 billion years ago, and large-scale BIF mineralization began to gradually decline about 1.85 billion years ago [2]. Since the mineralization period of BIFs was very early, BIFs were reformed via tectonism, metamorphism and magmatism after mineralization; thus, the iron orebody locations, ore structure and structure have changed greatly.

BIFs in China are mainly distributed in the North China Craton, with iron ore resources accounting for approximately 80% of the total national resources, and they are especially concentrated in iron ore-rich areas, such as Anshan–Benxi, Eastern Hebei, Luxi, Huoqiu, and Wuyang [3–5]. The main deposit type is Algoma-type BIF. The ore is mainly normal-grade (~40%) magnetite–quartzite and shallow hematite–quartzite [6,7]. In addition, most large iron ore deposits, such as Gongchangling, Nanfen, Xingshan and Sijiaying [8], contain a certain number of high-grade iron ore resources. High-grade iron ore mainly includes two types (primitive sedimentary and hydrothermally altered); however, the hydrothermal origins are still controversial, with origins mainly in metamorphic hydrothermal or migmatized hydrothermal environments [9–14]. Many geologists constrain the metallogenic age of BIF volcanic interbeds based on their zircon ages. The research results show that BIF began forming in Northern China in 3.5 Ga, and the late Neoproterozoic era (~2.5 Ga) was the peak era of BIF mineralization [3,15].

The Sijiaying iron deposit in eastern Hebei is in the eastern section of the northern margin of the North China Craton, with a proven iron ore resource of nearly 2.4 billion tons. It is the largest BIF in China, with more than 3 million tons of high-grade iron ore developed within the mining area [8,16]. However, research on the genesis of the high-grade iron ore in the Sijiaying BIF is not sufficiently detailed, and there is still some controversy over the mineralization age [17,18]. On the basis of work accomplished in one year in the mining area, this paper comprehensively summarizes the geological characteristics of the Sijiaying iron deposit, conducts systematic microscopic identification and major and trace element geochemical analysis of iron ores of different grades, and conducts LA–ICP–MS zircon U–Pb dating and major and trace element analysis of the roof and floor wall rocks (biotite–leptynite, chlorite–sericite schist) of the main orebody. It explores the genesis and mineralization age of Sijiaying’s high-grade iron ore and establishes a clear mineralization model to facilitate mineral exploration.

2. Geological Setting

2.1. Regional Geology

The North China Craton (NCC) is the largest and oldest land block in China, containing abundant iron ore resources. The early formation and evolution of the NCC is a focus of debate among geoscientists. One point of view is that the basement of the ancient land of Northern China is divided into two blocks—the east block and the west block (Figure 1a)—with the central collision tectonic zone (TNCO) as the boundary, and the cratonic continent was formed via suture during the ~1.85 Ga collision event [19,20]. Another view suggests that the North China Craton was formed through the assembly of at least seven microlandmasses at 2.7–2.5 Ga, including Jiaoliao (JL), Qianhuai (QH),

Ordos (OR), Jining (JN), Xuchang (XCH), Xuhuai (XH), and Alxa (ALS) [21–23]. After the formation of a unified continental crystalline basement, it was covered by Mesoproterozoic-to-Phanerozoic era sedimentary cover.

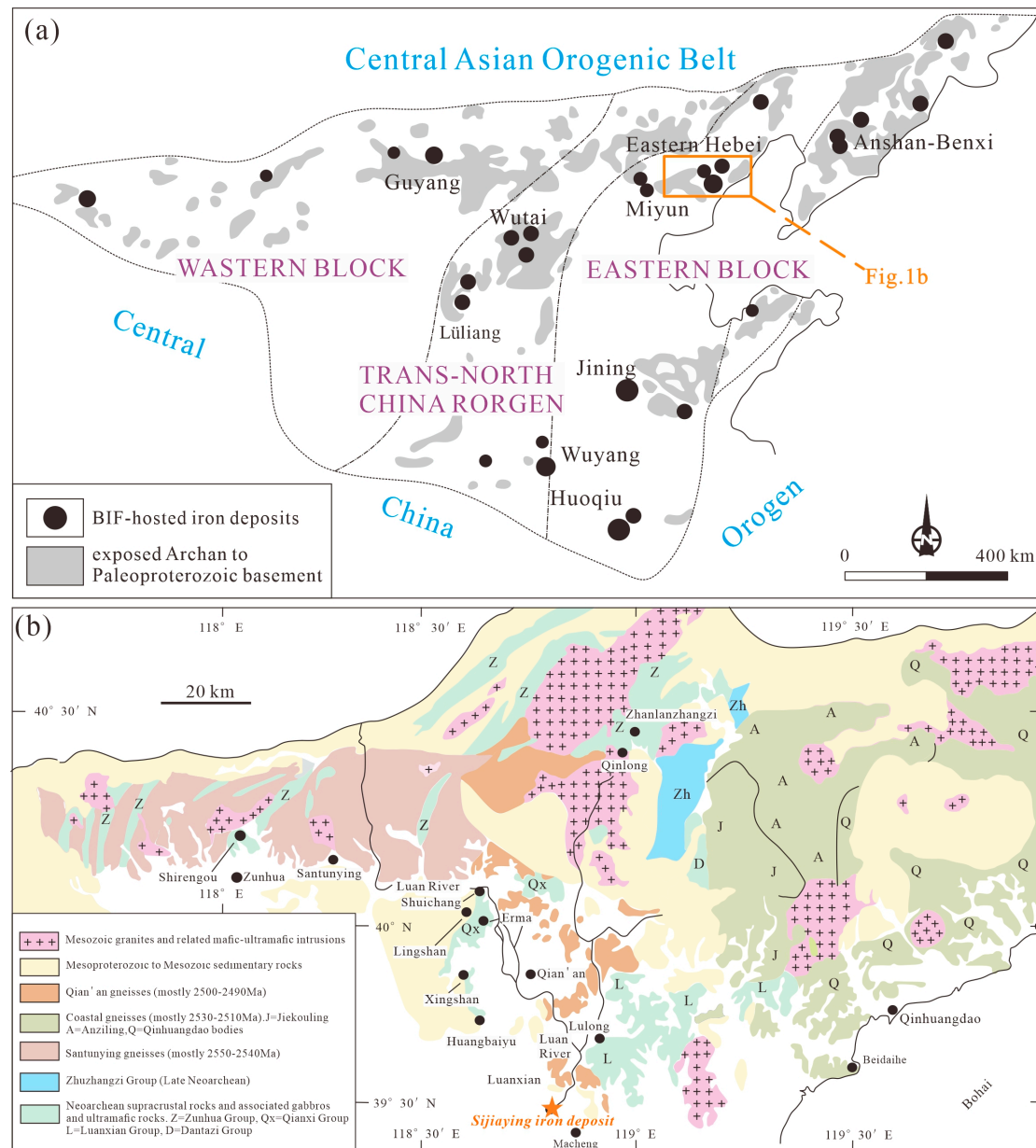


Figure 1. (a) Major tectonic units and BIF in NCC (modified based on Zhao et al. (2005) [20] and Shen et al. (2005) [24]). (b) Distribution of banded iron formations in eastern Hebei province (based on Nutman et al. (2011) [25]).

The eastern Hebei area is in the eastern section of the northern margin of the NCC and is one of the most important BIF iron deposit distribution areas in China. It contains iron ore reserves totaling more than 6 billion tons and contains a series of large BIF iron deposits, such as Sijiaying, Macheng, Shachang, Shuichang, Shirengou, Xingshan, and Zhanlanzhangzi (Figure 1b), as well as a batch of small- and medium-sized iron deposits [4,6,8]. Unlike other areas with concentrated iron deposits, the ore-hosting strata in eastern Hebei Province are complex, and the Zhuzhangzi Group in the east, the Qianxi Group in the west, and the Luanxian Group in the south all contain areas of BIF development of varying sizes. The earliest stratum is the Caozhuang Formation, which is distributed in the

Caozhuang–Huangbaiyu–Naoyumen area of Qian'an; this formation formed in the early-Archean era (3830–3470 Ma) and resulted in BIF deposits, such as Xingshan, Naoyumen, and Huangbaiyu [26–28]. The remaining BIF-hosting strata were mainly formed in the late-Neoproterozoic era [29]. The zones of Zunhua–Qianxi, Qinglong–Kuancheng, Qian'an, Sijiaying–Macheng–Changning, and Zhuzhangzi can be divided according to the distribution range of ore-controlling strata and BIF. The zones are controlled by regional fault structures and have strong folding. Early-Archean era fold structures in the nearly EW and NNE directions superimpose the nearly north–south horizontal folding that occurred in the late Neoproterozoic era [16,17]. The crystalline basement in eastern Hebei has a high overall metamorphic degree, reaching granulite–greenschist facies metamorphism and strong migmatization, and various migmatitic granites are widely developed.

2.2. Deposit Geology

2.2.1. Associated Rocks

The Sijiaying iron deposit is located on the southern edge of eastern Hebei, with a mining area of approximately 20 km². The basement stratum is the Neoproterozoic Luanxian Group, and the caprocks are the middle–upper Proterozoic Changcheng System, Jixian System, and Qingbaikou System; the Cambrian system, the Ordovician system, the Carboniferous system, the Permian system, and the Quaternary system. The metamorphic degree of the Luanxian Group reaches low amphibolite facies, which is divided into three parts: the lower part is mainly composed of plagioclase amphibolite and plagioclase amphibolite–gneiss, mixed with thin layers of biotite–leptynite and leptyte; the middle part is mainly composed of interbedded biotite–leptynite and plagioclase amphibolite; and the upper part is dominated by biotite–leptynite, with many thin layers of interbedded magnetite quartzite and plagioclase amphibolite. In addition, Archean migmatite–granite is widely developed in the region, generally weak in the east and north and strong in the west and south, and dominated by “injection” and “permeability” migmatization. The iron orebodies near the migmatite–granite often contain chlorite schist, chlorite–sericite schist, and biotite–chlorite schist.

2.2.2. Geometry of Orebodies

In the mining area, the horizontal distribution is divided into four orebodies from east to west, and the orebodies are distributed in parallel bands (Figure 2b). The orebodies strike E–W; dip westward, with inclination angles of 40–50°; and are in a layered or quasilayered form. A portion of the orebody is lenticular in shape, with stable layers and significant changes in thickness. Along the strike and dip, sudden pinching-out, branching and compounding, and swelling and shrinking phenomena are present (Figure 2b). The characteristics of the orebodies are described as follows: (1) orebody I is in the eastern part of the mining area, with a total length of 8.4 km and relatively stable changes in morphology and occurrence. The burial depths are 0–600 m, and the thicknesses are generally 50–80 m, making it the largest orebody in the entire area. (2) Orebody II is small and located on the west side of the central mining area. The orebody is discontinuous along the strike and dip, with significant changes in thickness and extension. The burial depths are mostly between 200 and 600 m, with thicknesses of 30 to 60 m. The extension depth is relatively deep, and it has not experienced pinch-out below 700 m. (3) Orebody III is in the central–northern part of the mining area, with a total length of 2.8 km, and is in the form of an ore belt. It is composed of multiple layers of ore with varying thicknesses of interbedded rocks. Obvious swelling, shrinkage, and composite branching phenomena are present along strike, with a thickness of 100–200 m. The orebody extends deeper and tends to thicken toward the deeper part of the orebody. (4) Orebody IV is distributed in the central part of the mining area, with a total length of 2.6 km. It is layered in shape, with gentle inclination angles of roughly 35–50°. The thicknesses of the orebody are 20–40 m, with moderate depths (300–500 m), and the orebody is mostly covered by the Quaternary and Great Wall systems. Local orebody sections are eroded.

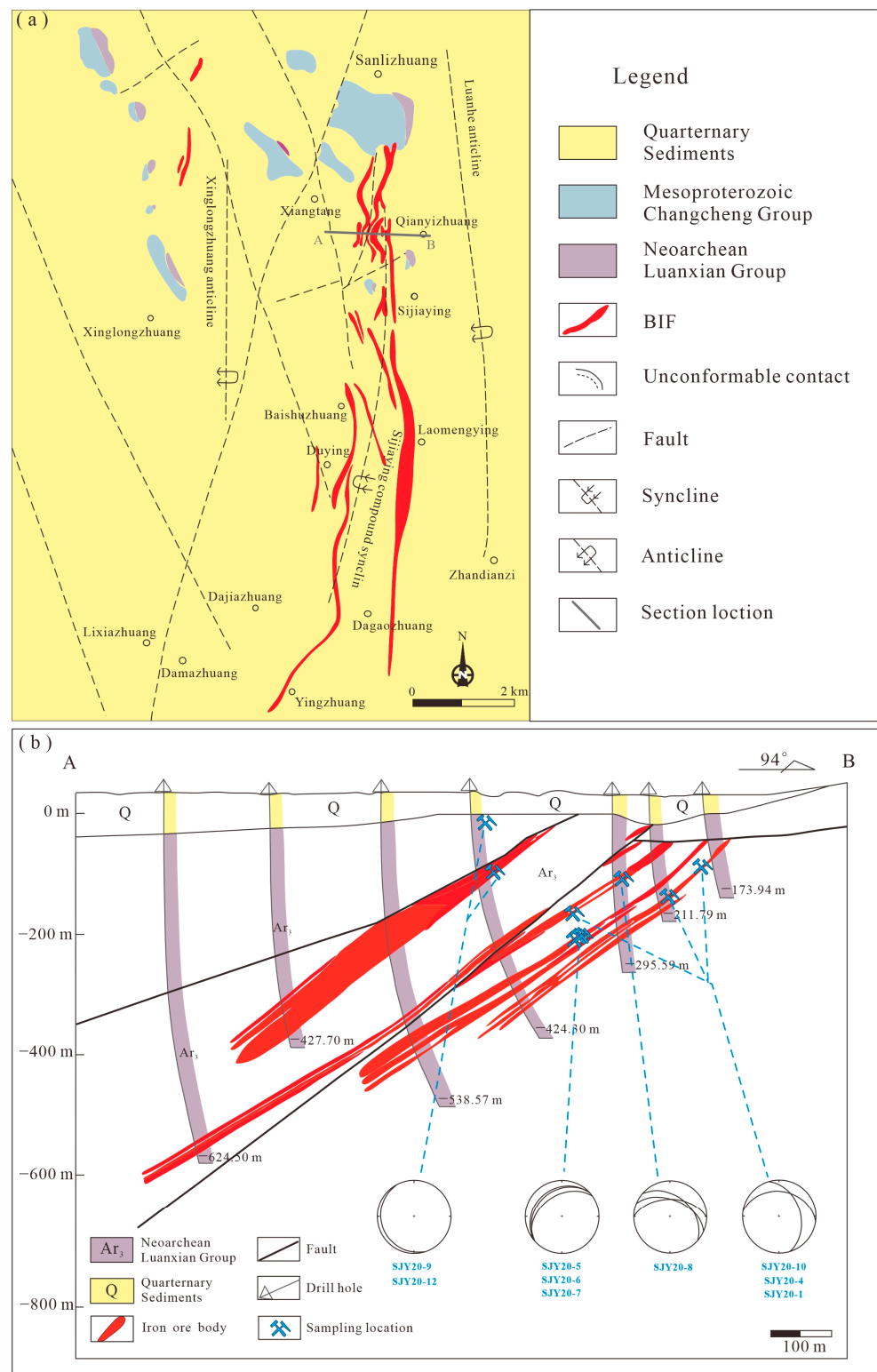


Figure 2. (a) Geological map of Sijiaying deposit (based on Wang et al. (2017) [18]). (b) Measured section showing sample locations for zircon U–Pb dating and iron orebodies with occurrences parallel to their wall rocks.

The vast majority of high-grade ore developed more in the deeper parts of normal-grade orebodies, with smaller volumes of high-grade ore in the shallow parts. High-grade orebodies are mostly found in lean orebodies, with clear and abrupt boundaries

with normal-grade orebodies. There are also portions of high-grade orebodies that are mostly found in the middle and lower parts of thick normal-grade orebodies, with gradual boundaries [7,30]. The high-grade orebodies are mostly layered and lenticular in shape and mainly occur along the layers (Figure 3d); they have relatively thin thicknesses, with single-layer thicknesses of 1–3 m and a maximum thickness of 12 m. The extension and depth are mostly in the tens of meters.

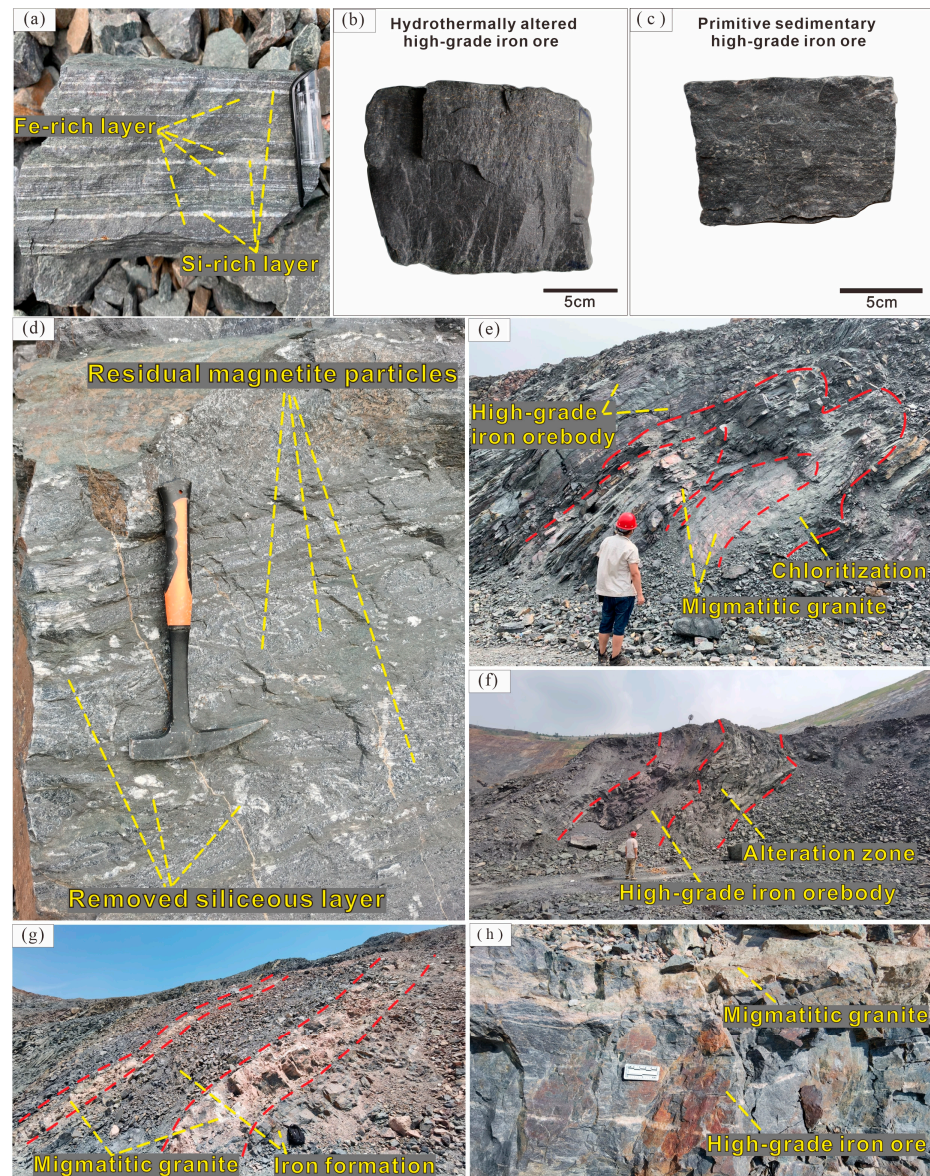


Figure 3. Photographs of rocks and iron ores in Sijiaying deposit: (a) magnetite–quartzite (normal-grade); (b) primitive sedimentary-type iron ore; (c) hydrothermally altered high-grade iron ore; (d) desilication phenomenon of hydrothermal alteration; (e) grade of iron ore increases near the migmatization hydrothermal solution; (f) contact between iron orebody and altered wall rock; (g,h) contact between migmatitic granite and iron orebody.

2.2.3. Ore Mineralogy

The magnetite–quartzite BIFs are mainly composed of iron-rich bands and silicon-rich bands, with an average FeO_T of approximately 35% (Figure 3a). The main metal minerals are magnetite (30%~40%), hematite (~5%), and martite (~5%). The gangue minerals are mainly quartz (40%~50%), followed by actinolite, tremolite, hornblende, and pyroxene.

The trace minerals are mainly apatite, pyrite, and chalcopyrite, with small amounts of chlorite, calcite, biotite, and other later-formed alternating minerals.

High-grade iron ores can be divided into two types based on the ore structure: hydrothermal alteration and primitive sedimentation. The hydrothermally altered high-grade iron ore resources in the mining area have an advantage, being mainly composed of dense- and fine-grained structures and massive structures (Figure 3b), and the FeO_T content is approximately 60%. The ore minerals are magnetite (>60%) and a small amount of hematite (~10%), and the gangue minerals are quartz (~20%) and pyrite (~10%) (Figure 4c). Magnetite is usually euhedral to subhedral (20~700 μm), showing a slightly oriented structure (Figure 4a). The altered minerals are mainly carbonate minerals (Figure 4d), pyrite, chlorite (Figure 4f), and biotite (Figure 4g). The second type of high-grade iron ore has a striped or banded structure (Figure 3c) and contains almost no hydrothermal minerals. The metal minerals are mostly fine magnetite (10~400 μm) (>80%), and the gangue mineral is quartz (~20%) (Figure 4b).

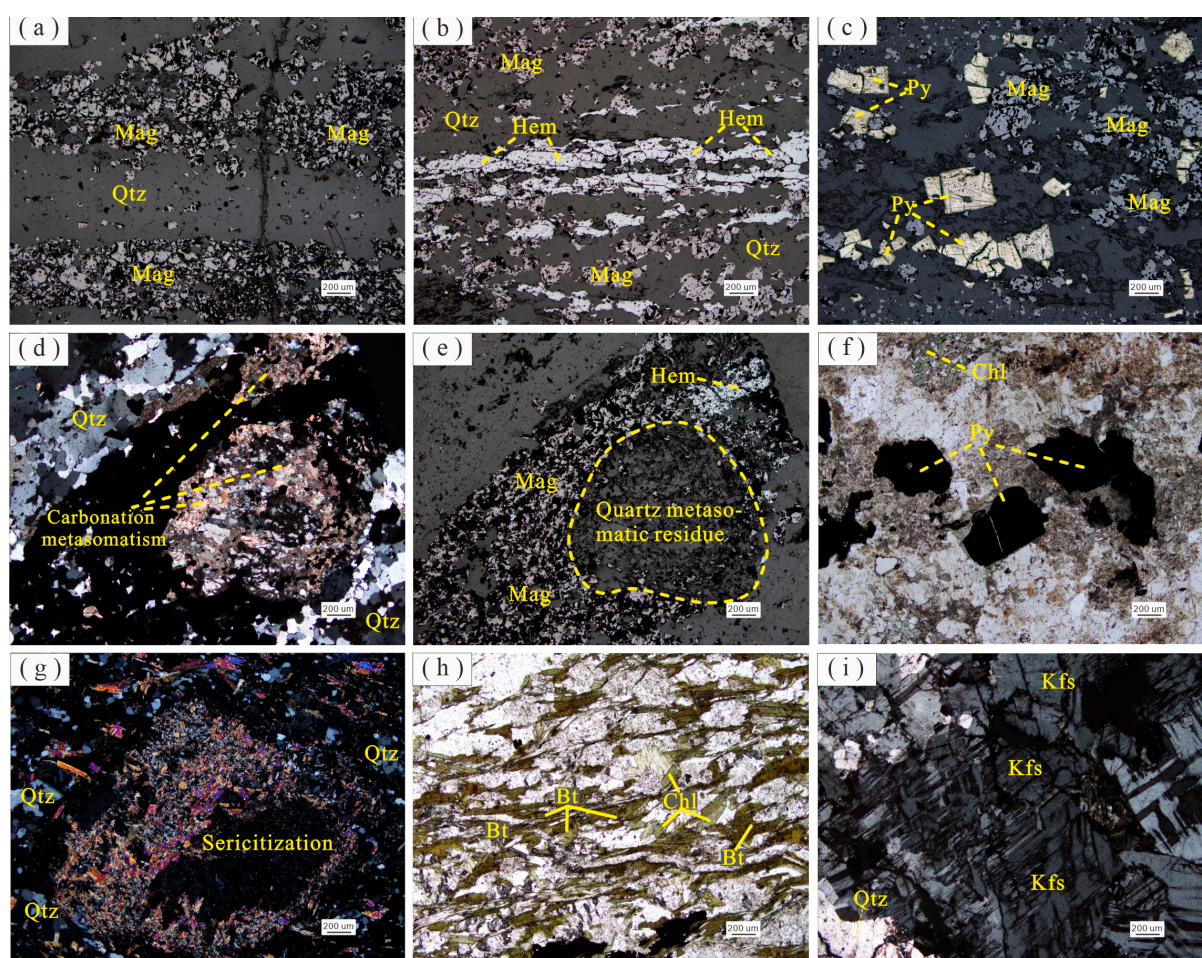


Figure 4. Photomicrographs of wall rocks and iron ores in Sijiaying deposit. (a) Magnetite and quartz bands (Sample SJY20-5-1, reflected-light); (b) anhydrous magnetite partially replaced by hematite (Sample SJY20-7-2, reflected-light); (c) pyrite brought via hydrothermal solution partially replaced magnetite (Sample SJY20-10-5, reflected-light); (d) carbonation hydrothermal metasomatism of quartz particles (Sample SJY20-10-5, reflected-light); (e) carbonation metasomatism (Sample SJY20-10-5, cross polarized light); (f) typical microscopic characteristics of chlorite–sericite schist (Sample SJY20-13-1, single polarization); (g,h) typical microscopic characteristics of biotite–leptynite (Sample SJY20-10-2, cross polarized light and single polarization); (i) typical microscopic characteristics of migmatitic granite (cross polarized light). Abbreviations: Mag, magnetite; Hem, hematite; Qtz, quartz; Py, pyrite; Chl, chlorite; Bt, biotite; Kfs, feldspar.

3. Sample and Analytical Techniques

3.1. Sampling

3.1.1. Quartz-Magnetite BIFs

The geological field survey and research work were mainly completed on the N16 exploration line (Figure 2b line AB) in the northern area of the Sijiaying deposit, and the samples were mostly taken from this section. The ore samples were mainly magnetite–quartzite BIFs (Figure 3a) of varying ore grades. SJY20-5-1 is a low-grade iron ore that was widely present in the mining area. Samples from SJY20-7-2 to SJY20-10-5 were extracted from ore layers that are relatively close to alteration. The iron ore samples were identified in the field as hydrothermally altered high-grade iron ore, while SJY20-11-1 was a banded ore located at the bottom of the orebody. SJY20-11-1 was a banded ore located on the floor layer of an orebody, and it was found to be a primitive sedimentary high-grade iron ore based on the structure of the iron ore. In addition, this article used typical ore samples obtained by Xu et al. (2014, 2015) [31,32] by drilling in the Sijiaying south mining area as points of reference.

3.1.2. Wall Rock

The wall rock was mainly biotite–leptynite, with chlorite–sericite schist found at the altered location. Six samples of biotite–leptynite and four samples of chlorite–sericite schist were taken at the roof and floor of orebody III in the open pit of the Sijiaying North District. Most of the biotite–leptynite samples were not affected by alteration and weathering, and only SJY20-10-6 and SJY20-11-5 were contaminated by potassic migmatization and alteration. The chlorite–sericite schist was taken from the surrounding locations of altered high-grade orebodies. The sampling location is shown in Table 1, and a stereographic projection of the sampling point's occurrence is drawn in Figure 2b.

Table 1. Samples collected from Sijiaying iron deposit.

Sample Type	N	Sample Name	Location	Coordinates		Depth (m)	BIF Facies	Texture	Major Mineral Assemblage
				East	North				
BIF (Open Pit)	1	SJY20-5-1	Near Prospecting Line 16	118.751825	39.681657	−187	Oxide	Black quartz bands	Magnetite and quartz, a little chlorite
	2	SJY20-6-1	Near Prospecting Line 16	118.752249	39.679825	−217	Oxide	Black and white quartz bands	Magnetite and quartz
	3	SJY20-7-2	Near Prospecting Line 16	118.751478	39.681492	−189	Oxide	Medium coarse-grained bands cut by green alternating veins	Magnetite, quartz, chlorite, and pyrite
	4	SJY20-8-6	Near Prospecting Line 16	118.753249	39.674220	−112	Oxide	Fine quartz bands	Magnetite and quartz
	5	SJY20-9-4	Near Prospecting Line 16	118.750482	39.681629	−164	Oxide	Fine and little quartz bands	Magnetite and quartz
	6	SJY20-9-5	Near Prospecting Line 16	118.750482	39.681629	−164	Oxide	Banded gray–brown, crosscutting veins	Magnetite and quartz
	7	SJY20-10-5	Near Prospecting Line 16	118.751900	39.681886	−167	Oxide	Banded green alternating bands	Magnetite, quartz, and chlorite
	8	SJY20-11-1	Near Prospecting Line 16	118.755412	39.675196	−124	Oxide	Fine black–grey alternating bands	Magnetite and quartz

Table 1. Cont.

Sample Type	N	Sample Name	Location	Coordinates		Deth (m)	Sampling Site	Texture	Major Mineral Assemblage
				East	North				
Biotite leptynite	1	SJY20-7-4	Near Prospecting Line 16	118.751478	39.681492	−189	The wall rock of the roof of ore body III	Fine-grained flake-like granoblastic structure, as well as a parallel granular structure	Biotite, quartz, plagioclase, and a small amount of magnetite
	2	SJY20-8-1	Near Prospecting Line 16	118.753249	39.674220	−112	The wall rock of the floor of orebody III		Biotite, quartz, plagioclase, and a small amount of magnetite
	3	SJY20-8-3	Near Prospecting Line 16	118.753249	39.674220	−112	The wall rock of the floor of orebody III		Biotite, quartz, plagioclase, and a small amount of magnetite
	4	SJY20-10-2	Near Prospecting Line 16	118.751900	39.681886	−167	The wall rock of the roof of orebody III		Biotite, quartz, plagioclase, and a small amount of magnetite
	5	SJY20-10-7	Near Prospecting Line 16	118.751900	39.681886	−167	The wall rock of the floor of orebody III		Biotite, quartz, plagioclase, and a small amount of magnetite
	6	SJY20-11-5	Near Prospecting Line 16	118.755412	39.675196	−124	The wall rock on the north side of the orebody		Biotite, quartz, plagioclase, and pyrite
Chlorite-sericite schist	7	SJY20-9-2	Near Prospecting Line 16	118.750482	39.681629	−164	The wall rock on the north side of the orebody	Scaly granular crystalline structure; schistose structure	Feldspar, quartz, biotite, sericite, and chlorite
	8	SJY20-13-1	Near Prospecting Line 16	118.753480	39.687973	−186	Near the orebody in the northern mining area		
	9	SJY20-13-2	Near Prospecting Line 16	118.753480	39.687973	−186			
	10	SJY20-13-3	Near Prospecting Line 16	118.753480	39.687973	−186			

3.2. Analytical Methods

3.2.1. Whole-Rock Geochemistry

The ore and wall rock (biotite–leptynite and chlorite–sericite schist) were subjected to 200 mesh fragmentation samples at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. Geochemical analysis of major elements was carried out at the National Research Center for Geo-Analysis, Chinese Academy of Geological Sciences (CAGS). The standard X-ray fluorescence (XRF) (PW4400) was used to determine the main elements. The accuracy of XRF analysis was estimated to be less than 1% for silicon dioxide and less than 2% for other major oxides, and the FeO content was determined using the standard GB/T 14506.14-2010. The inductively coupled plasma mass spectrometry (ICP-MS) was used to determine trace elements and rare earth elements (REEs) on the Jena plasma MS instrument of the Key Laboratory of Mineralization and Resource Evaluation, Ministry of Natural Resources, Institute of Mineral Resources, Chinese Academy of Geological Sciences. Powered samples were digested in high-pressure teflon bombs using a mixture of super-pure HF–HNO₃ for 2 days at ~100 °C. The procedure involved evaporation to near dryness, refluxing with super-pure HNO₃, and drying twice until the powders were completely dissolved. Duplicate analyses of samples and rock standards yielded relative standard derivations of <5% for most trace elements.

3.2.2. Zircon U–Pb Geochronology

U–Pb dating analyses were completed using a LA–ICP–MS at the Key Laboratory of Mineralization and Resource Assessment of the Ministry of Land and Resources, CAGS. Referring to Hou et al. (2009) [33] for details on the operating conditions required for the laser ablation system, the multi-collector inductively coupled to the plasma mass spectrometer (MC–ICP–MS) instrument. Laser ablation was performed using a new wave UP213 laser ablation system. A Thermo Finnigan Neptune MC–ICP–MS instrument was

used to acquire ion-signal intensities. Zircon GJ1 was used as an external standard for U–Pb dating and was analyzed twice every 5–10 analyses. In all analyzed zircon grains, the common Pb correction was not necessary due to the low signal of common ^{204}Pb and high $^{206}\text{Pb}/^{204}\text{Pb}$ values. The U, Th, and Pb concentrations were calibrated using zircon M127 (U: 923 ppm; Th: 439 ppm; Th/U: 0.475) [34]. Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 [35].

4. Geochemical Results

4.1. Iron Ores

Normal-grade BIF mainly consists of magnetite and quartz; thus, it has very high SiO_2 (50.61~64.51 wt.%) and FeO_T (33.91~44.58 wt.%) contents (Table 2). The main element differences in high-grade BIF are relatively significant, with SiO_2 (4.25~47.18 wt.%) and FeO_T (45.23~85.0 wt.%). However, with increasing grade, the contents of MnO and MgO increase, while the contents of Al_2O_3 and K_2O decrease (Figure 5a–c). The abundances of rare earth elements and Y in medium- and low-grade iron ores range from 21.66 to 56.18 ppm, with an average value of 36.43 ppm. The rare earth element and yttrium (REY) contents in high-grade iron ores are relatively high, ranging from 14.82 to 92.98 ppm, with an average value of 49.92 ppm. The iron ores from the Sijiyang deposit have a positive Eu anomaly, while the positive Eu anomaly of high-grade iron ores is relatively low, and the Ce anomaly and Y/Ho ratio values are more dispersed. The distribution patterns of rare earth and trace elements in the standardized post-Archean Australian shale (PAAS) values of BIF ore samples (Figure 6) are as follows: (1) heavy rare earth elements are enriched relative to light rare earth elements ($(\text{La}/\text{Yb})_{\text{SN}} = 0.34\text{--}2.67$); (2) positive La anomalies ($\text{La}/\text{La}^* = 1.04\text{--}3.78$) are present; (3) strong positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.25\text{--}2.82$) are present; (4) positive Y anomalies ($\text{Y}/\text{Y}^* = 1.28\text{--}2.01$) are present; and (5) the Y/Ho ratio of iron ores exceeds the Y/Ho ratio range of chondrites (32.05–44.75). However, the trace element contents of most iron ores are generally low (<5 ppm), though the contents of Ba (3.12–258.07 ppm), Li (1.63–95.3 ppm), Cu (0.89–27.5 ppm), Zn (4.34–43.90 ppm), and compatible elements (V (2.63–68.30 ppm), Cr (1.89–26.34 ppm), and Ni (1.13–12.50 ppm)) are slightly higher. On the normalized trace element distribution map of the primitive mantle (PM) (Figure 5b), both high- and normal-grade iron ores show high field strength element (HFSE) (e.g., Nb, Ta, Zr, Hf, and Ti) depletion.

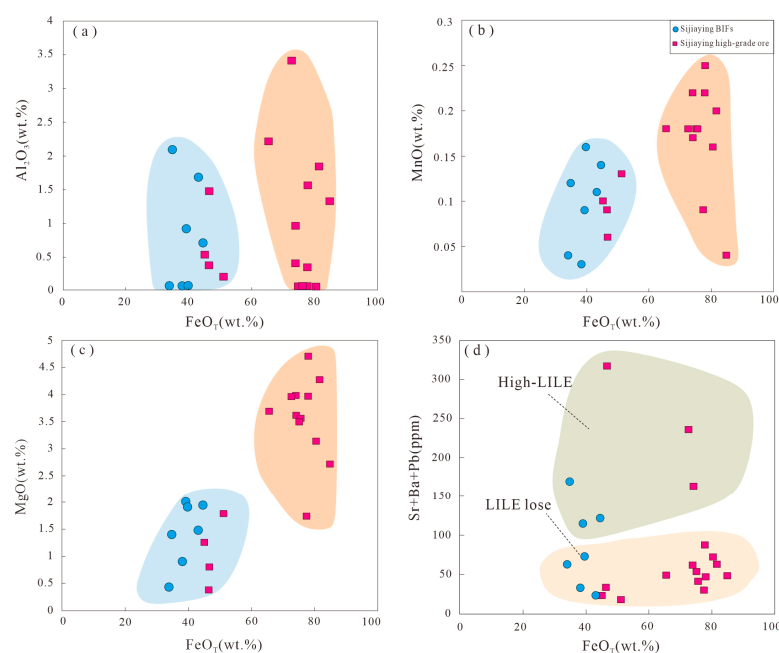


Figure 5. Binary diagrams (a–d) of magnetite in Sijiyang BIF. Partial data of iron ore from Xu et al. (2014, 2015) [31,32].

Table 2. Major (wt.%) and trace element (ppm) compositions of iron ores in Sijiaying iron deposit.

Sample Name	SJY20-5-1	YS-2	SJY-2-1	SJY-ZK601-591.3	SJY20-7-2	SJY20-8-6	SJY20-6-1	SJY20-9-4	SJY20-9-5	SJY20-10-5	SJY20-11-1	SJY-19	SJY-ZK602-717.2	SJY-ZK602-747	SJY-ZK602-750.5	SJY-ZK602-778	SJY-ZK602-789.7	SJY-ZK602-794.7	SJY-ZK602-805.5	SJY-ZK602-809	SJY-ZK602-822	SJY-ZK602-797	SJY-ZK602-735.5
Lithology	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	Normal-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite	High-grade magnetite-quartzite
References	This study	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	This study	This study	This study	This study	This study	This study	This study	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	Data from Xu et al., 2014 [31]	
wt.%																							
SiO ₂	55.30	64.51	58.69	53.28	51.02	50.61	48.77	48.68	51.58	51.56	47.18	6.51	15.77	16.59	17.18	16.42	6.59	17.57	11.22	4.25	6.09	25.63	15.95
Al ₂ O ₃	2.09	<0.10	<0.10	<0.01	0.90	1.68	0.69	1.46	0.36	0.51	0.18	1.31	3.43	<0.01	<0.01	<0.01	1.84	0.94	<0.01	1.55	0.32	2.21	0.38
CaO	1.97	0.37	0.97	3.22	2.68	0.92	2.13	0.86	0.90	0.97	0.88	0.44	2.39	4.1	3.08	3.43	2.93	2.17	3.28	5.42	5.86	2.17	5.01
TFe ₂ O ₃	34.84	33.91	38.12	39.68	39.18	43.24	44.58	46.67	46.53	45.23	51.17	85.05	72.7	75.23	77.57	75.74	81.63	74.25	80.61	78.08	77.96	65.58	74.09
FeO	8.59	1.5	2	13.1	7.36	8.77	11.68	8.98	6.79	10.53	12.90	2.4	24.8	23.1	20.7	23.8	26	23.6	24.2	24.1	23.9	20.7	23.2
K ₂ O	1.30	0.06	0.07	<0.01	0.05	1.22	0.52	0.68	0.02	0.15	0.01	0.03	1	<0.01	<0.01	0.02	0.02	0.54	0.05	0.03	0.02	0.04	0.01
MgO	1.41	0.43	0.9	1.92	2.01	1.48	1.95	0.80	0.38	1.26	1.79	2.71	3.97	3.51	1.74	3.57	4.28	3.62	3.15	4.72	3.98	3.7	3.99
MnO	0.12	0.04	0.03	0.16	0.09	0.11	0.14	0.06	0.09	0.10	0.13	0.04	0.18	0.18	0.09	0.18	0.2	0.22	0.16	0.25	0.22	0.18	0.17
Na ₂ O	<0.01	0.14	0.19	0.08	<0.01	0.03	0.05	<0.01	<0.01	0.01	0.03	0.09	0.19	0.14	0.11	0.11	0.09	0.14	0.11	0.19	0.19	0.2	0.17
P ₂ O ₅	0.11	0.14	0.12	0.15	0.13	0.17	0.17	0.21	0.23	0.01	0.05	0.13	0.29	0.16	0.19	0.31	0.44	0.25	0.25	0.12	0.34	0.23	0.17
TiO ₂	0.05	0.02	0.07	0.02	0.04	0.05	0.05	0.05	0.02	0.03	0.02	0.05	0.07	0.09	0.01	0.09	0.08	0.07	0.05	0.04	0.12	0.06	0.03
LOI	2.37	1.47	1.41	1.7	2.42	0.04	0.39	0.03	0.03	−0.53	−1.37	3.37	<0.10	<0.10	<0.10	<0.10	1.74	0.26	1.93	5.15	4.62	<0.10	<0.10
CO ₂	3.16	-	-	-	4.61	0.17	1.88	0.34	0.17	0.17	0.17	-	-	-	-	-	-	-	-	-	-	-	-
H ₂ O ⁺	1.02	-	-	-	0.68	0.60	0.42	0.64	0.36	0.42	0.28	-	-	-	-	-	-	-	-	-	-	-	-
ppm																							
Li	14.06	19.30	11.60	5.44	14.53	13.78	11.84	8.16	5.41	12.00	1.63	95.30	26.10	3.69	4.44	4.19	13.50	35.40	31.70	11.50	20.40	19.80	5.58
Be	0.76	0.48	0.70	0.70	0.60	0.29	0.67	0.34	0.20	0.44	0.39	1.78	1.41	1.71	0.51	1.70	0.29	0.80	0.94	0.38	0.43	0.44	1.04
V	6.51	8.95	8.01	6.94	22.48	16.51	10.22	12.42	5.70	13.71	2.63	68.30	61.40	30.10	22.20	24.80	46.00	40.10	26.50	43.90	48.10	36.40	33.80
Ni	2.04	8.15	2.91	9.08	5.37	5.37	2.34	3.05	1.13	1.38	1.25	6.93	12.50	12.20	3.07	5.15	6.24	10.40	6.51	3.71	9.70	3.75	9.39
Co	0.63	3.24	0.83	3.91	1.43	0.88	0.85	1.28	0.31	0.69	0.18	3.97	3.55	2.93	1.48	1.90	2.67	4.25	1.68	1.11	3.86	1.56	2.53
Cr	9.42	7.95	4.07	13.60	26.34	13.86	7.92	11.03	6.09	6.83	10.69	7.05	16.50	2.97	2.90	12.50	13.30	16.00	14.50	1.89	14.90	6.12	1.94
Sc	1.66	1.68	0.89	0.46	2.28	2.47	1.90	2.55	1.33	1.37	0.50	1.86	2.14	0.84	0.28	1.77	1.54	1.89	0.59	1.01	1.82	1.49	0.54
Rb	50.80	3.62	2.42	0.53	18.60	2.67	49.27	16.52	0.66	5.69	0.38	1.30	57.10	0.28	0.24	0.87	1.12	30.40	1.11	0.83	1.12	1.73	0.40
Ba	127.93	45.50	5.61	30.40	63.95	6.51	100.29	258.07	4.63	11.18	6.89	28.00	79.40	8.47	3.12	7.71	9.04	111.00	25.10	6.42	5.81	9.55	3.61
Sr	39.08	10.20	8.17	38.80	45.73	15.19	16.80	56.01	24.68	11.05	6.44	12.40	155.00	44.10	26.10	33.00	52.80	48.70	43.10	38.90	80.70	37.70	57.40
Th	1.21	0.53	0.34	0.23	1.14	0.67	1.33	1.25	0.46	0.35	0.04	0.39	1.56	0.43	0.25	0.57	1.29	2.06	0.25	0.10	0.42	1.36	0.28
Zr	18.59	7.37	9.26	1.19	23.06	6.61	18.84	18.99	3.65	5.49	0.68	10.90	1.27	0.82	0.66	1.89	0.50	1.46	0.91	0.24	1.46	0.56	0.54
Cu	1.88	17.50	16.00	24.20	3.82	9.34	2.00	25.85	1.66	2.09	1.45	14.00	1.27	27.50	20.20	1.02	1.14	2.16	13.40	7.86	2.42	0.94	0.89
Zn	12.66	12.10	5.62	43.90	9.94	7.47	25.43	6.50	10.43	9.58	4.34	29.20	32.10	24.90	20.10	19.60	32.60	24.40	35.50	16.80	15.90	22.90	15.10
Ga	2.30	1.45	1.48	1.29	0.97	1.24	1.67	1.89	0.57	1.09	0.19	11.10	6.34	2.46	1.63	3.00	5.65	5.82	2.48	4.56	6.15	4.29	2.51
Nb	1.15	0.38	0.28	0.28	0.78	0.41	0.48	1.01	0.23	0.47	0.10	0.27	1.22	0.38	0.48	0.59	0.49	1.62	0.99	0.62	0.48	0.60	0.63
Cs	0.77	0.33	0.29	0.16	0.15	0.38	0.33	0.21	0.04	0.26	0.07	0.56	9.67	0.06	0.03	0.13	0.20	4.88	0.31	0.14	0.26	0.79	0.10
La	3.22	2.64	4.63	3.45	12.00	10.41	6.63	20.90	13.36	4.76	1.68	34.00	12.70	5.35	3.02	5.90	8.37	15.90	3.69	3.89	12.10	6.79	4.62
Ce	7.21	5.61	6.53	5.33	24.58	22.75	13.51	38.15	9.29	22.04	2.86	23.50	25.10	9.57	5.40	13.10	16.60	29.00	6.23	6.32	24.10	12.50	7.73
Pr	0.80	0.65	0.70	0.67	2.74	2.16	1.46	3.75	2.10	1.00	0.34	1.83	2.89	1.11	0.63	1.73	1.96	3.32	0.71	0.72	2.98	1.46	0.89
Nd	3.22	2.88	2.90	2.36	10.57	8.12	5.58	13.50	8.03	4.03	1.53	6.33	11.80	4.45	2.30	7.60	7.60	11.90	3.04	3.21	11.60	5.92	3.72
Sm	0.78	0.67	0.55	0.48	1.89	1.45	1.03	2.21	1.34	0.78	0.29	1.09	2.03	0.76	0.38	1.75	1.51	2.03	0.67	0.51	2.12	1.18	0.87
Eu	0.22	0.22	0.15	0.31	0.49	0.37	0.30	0.57	0.38	0.28	0.18	0.40	0.51	0.30	0.18	0.39	0.53	0.59	0.26	0.17	0.65	0.28	0.27
Gd	0.94	0.85	0.74	0.60	1.69	1.34	1.13	2.00	1.40	0.86	0.38	1.71	1.86	0.71	0.47	1.58	1.60	1.82	0.69	0.83	2.02	1.18	0.87
Tb	0.15	0.16	0.12	0.09	0.23	0.18	0.16	0.25	0.18	0.12	0.05	0.27	0.33	0.15	0.09	0.30	0.28	0.33	0.14	0.11	0.32	0.17	0.17
Dy	0.97	0.90	0.64	0.62	1.22	1.02	1.02	1.27	1.00	0.80	0.37	6.41	1.60	2.06	0.72	0.55	1.99	1.69	0.87	0.74	1.72	1.22	1.00
Y	7.55	5.86	4.03	6.51	8.66	6.81	8.38	8.49	8.19	6.41	11.60	14.10	7.05	4.94	4.94	13.70	12.70	12.90	8.19	9.27	12.00	9.75	8.95
Ho	0.20	0.17	0.11	0.16	0.23	0.20	0.21	0.24	0.20	0.17	0.09	0.29	0.44	0.18	0.13	0.39	0.36	0.37	0.22	0.21	0.35	0.23	0.20
Er	0.65	0.54	0.36	0.43	0.72	0.64	0.71	0.78	0.66	0.55	0.29	0.83	1.33	0.50	0.40	1.20	1.08	1.21	0.67	0.65	0.98	0.78	0.67
Tm	0.09	0.08	0.05	0.07	0.09	0.08	0.10	0.10	0.08	0.08	0.04	0.13	0.21	0.08	0.07	0.22	0.15	0.19	0.10	0.12	0.13	0.14	0.10
Yb	0.60	0.53	0.31	0.50	0.58	0.56	0.70	0.67	0.55	0.52	0.28	0.86	1.19	0.46	0.49	1.41	1.03	1.28	0.60	0.85	0.90	0.82	0.70
Lu	0.09	0.08	0.05	0.08	0.09	0.08	0.11	0.10	0.08	0.08	0.04	0.13	0.18	0.07	0.09	0.21	0.17	0.23	0.10	0.15	0.15	0.13	0.12
Hf	0.54	0.20	0.08	0.06	0.51	0.20	0.55	0.52	0.12	0.15	0.03	0.20	0.10	0.05	0.03	0.15	0.02	0.09	0.04	0.01	0.07	0.03	0.04
Ta	0.12	0.03	0.03	0.03	0.04	0.04	0.06	0.07	0.02	0.04	0.01	0.15	0.01	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.04	0.01	-
Pb	2.72	7.21	19.50	4.15	5.64	2.19	5.31	2.99	4.24	1.12	4.76	8.05	1.55	0.90	0.53	0.77	1.06	2.95	3.49	1.50	1.04	1.24	0.80
U	0.83	0.79	0.63	0.21	0.47	1.85	0.50	0.99	0.86	0.28	0.07	2.29	0.72	0.18	0.14	0.28	0.41	0.72	0.22	0.13	0.14	0.37	0.10

Table 2. Cont.

Sample Name	SJY20-5-1	YS-2	SJY-2-1	SJY-ZK601-591.3	SJY20-7-2	SJY20-8-6	SJY20-6-1	SJY20-9-4	SJY20-9-5	SJY20-10-5	SJY20-11-1	SJY-19	SJY-ZK602-717.2	SJY-ZK602-747	SJY-ZK602-750.5	SJY-ZK602-778	SJY-ZK602-789.7	SJY-ZK602-794.7	SJY-ZK602-805.5	SJY-ZK602-809	SJY-ZK602-822	SJY-ZK602-797	SJY-ZK602-735.5
ΣREE	19.13	15.98	17.84	15.15	57.11	49.38	32.66	84.49	51.40	23.33	8.41	72.97	62.63	24.41	14.20	37.77	42.93	70.10	17.99	18.51	60.12	32.80	21.93
LREE	15.46	12.67	15.46	12.60	52.28	45.27	28.52	79.08	47.25	20.14	6.87	67.15	55.03	21.54	11.91	30.47	36.57	62.74	14.60	14.85	53.55	28.13	18.10
HREE	3.67	3.31	2.38	2.55	4.83	4.11	4.14	5.41	4.15	3.19	1.54	5.82	7.60	2.87	2.29	7.30	6.36	7.36	3.39	3.66	6.57	4.67	3.83
LREE/HREE	4.21	3.83	6.50	4.94	10.83	11.02	6.90	14.61	11.39	6.32	4.45	11.54	7.24	7.51	5.20	4.17	5.75	8.52	4.31	4.06	8.15	6.02	4.73
La _N /Yb _N	0.37	0.34	1.01	0.47	1.40	1.25	0.64	2.10	1.64	0.61	0.41	2.67	0.72	0.79	0.42	0.28	0.55	0.84	0.42	0.31	0.91	0.56	0.45
δEu	1.40	1.55	1.25	3.07	1.47	1.40	1.50	1.43	1.47	1.80	2.82	1.56	1.39	2.17	2.26	1.25	1.81	1.63	2.03	1.35	1.67	1.26	1.65
δCe	1.08	1.03	0.87	0.84	1.03	1.16	1.05	1.04	1.00	1.03	0.91	0.72	1.00	0.95	0.94	0.99	0.99	0.96	0.93	0.91	0.97	0.96	0.92
Y/Ho	37.99	34.47	36.64	40.69	38.29	34.08	39.45	35.22	40.35	37.87	74.28	40.00	32.05	39.17	38.00	35.13	35.28	34.86	37.23	44.14	34.29	42.39	44.75
REY	26.68	21.84	21.87	21.66	65.76	56.18	41.04	92.98	59.59	29.74	14.82	84.57	76.73	31.46	19.14	51.47	55.63	83	26.18	27.78	72.12	42.55	30.88

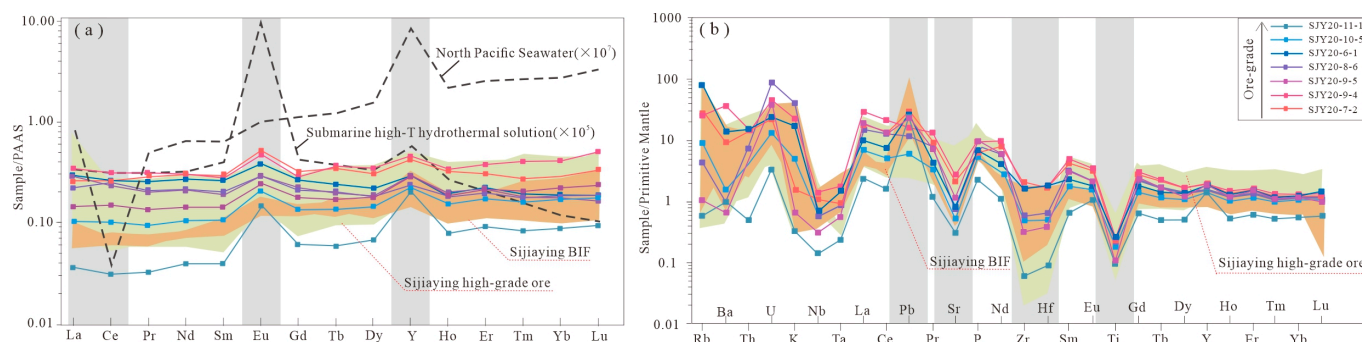


Figure 6. PAAS-normalized REE (a) and PM-normalized trace element patterns (b) of high-grade iron ore and quartz-magnetite BIF. Values of PAAS and primitive mantle follow Pourmand, A. et al. (2012) [36] and Sun and McDonough (1989) [37], respectively, and data for Sijiaying BIF and high-grade iron ore are shown as yellow and red line zones from Xu et al. (2014, 2015) [31,32]. Deep-sea water and high-temperature hydrothermal fluid in North Pacific are derived from Alibo and Nozaki (1999) [38] and Bau, M. and Dulski, P. (1999) [39], respectively.

4.2. Wall Rock

4.2.1. Biotite–Leptynite

The biotite–leptynite rock is grayish black, relatively dense and hard, and appears yellow–brown after weathering. The rock has a fine granoblastic texture (Figure 4g); parallel grain arrangement; fine mineral grain size, generally from 0.1–0.3 mm; a relatively uniform mineral distribution; and biotite and felsic minerals that are directionally arranged (Figure 4h). The main minerals are feldspar (~40%), quartz (20%–30%), biotite (~15%), and hornblende (<5%); the rock also contains small amounts of muscovite and microcline, and the accessory minerals are apatite, magnetite, epidote, and tourmaline.

The SiO₂ contents of biotite–leptynite range from 56.14 to 67.20 wt.%, Al₂O₃ contents range from 13.79 to 17.11 wt.%, Na₂O contents range from 2.43 to 4.41 wt.%, K₂O contents range from 2.74 to 4.24 wt.%, and FeO_T values range from 5.01 to 8.57 wt.% (Table 3). The total rare earth element (REE) contents in the sample vary slightly (111.45–176.26 ppm) and show a slight negative Eu anomaly (Eu/Eu* = 0.78–0.94) on the normalized rare earth element map of chondrites (Figure 7a). REEs show a right-leaning distribution, which is similar to that of granitic rocks [40,41], with (La/Yb)_N values ranging from 8.16 to 22.33. The rock has high concentrations of Rb (74.04–144.53 ppm), Ba (478.82–1216.48 ppm), Sr (8.59–358.08 ppm), and Zr (119.85–158.52 ppm). The primitive mantle standardized trace element map shows negative Nb, Ta, P, K, and Ti anomalies and positive Rb, Ba, Pb, and U anomalies (Figure 7b).

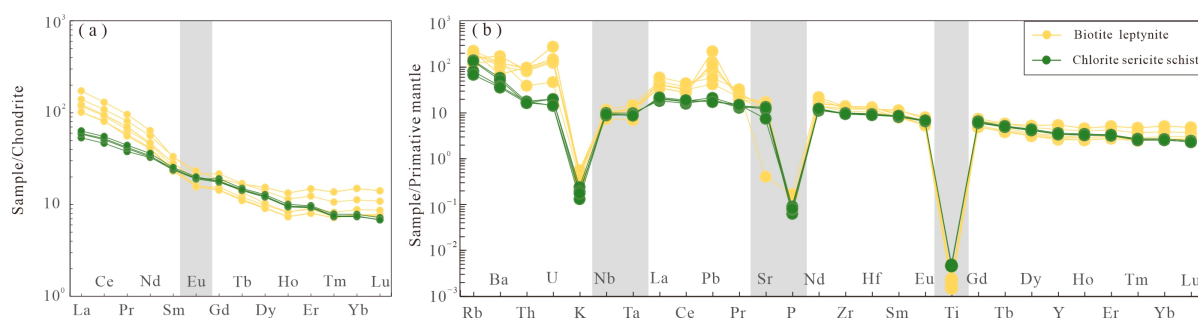


Figure 7. (a,b) Chondrite-normalized REE and primitive mantle-normalized trace element patterns of the biotite–leptynite and chlorite–sericite schists, with values of chondrite and primitive mantle based on Taylor and McLennan (1985) [42] and Sun and McDonough (1989) [37], respectively.

Table 3. Major (wt.%) and trace element (ppm) compositions of wall rocks in Sijiaying iron deposit.

Sample Name	SJY20-10-2	SJY20-10-7	SJY20-7-4	SJY20-8-1	SJY20-8-3	SJY20-11-5	SJY20-13-1	SJY20-13-2	SJY20-13-3	SJY20-9-2
Lithology	Biotite leptynite	Biotite leptynite	Biotite leptynite	Biotite leptynite	Biotite leptynite	Biotite leptynite	chlorite–sericite schist	chlorite–sericite schist	chlorite–sericite schist	chlorite–sericite schist
location	On the roof of the main orebody	On the floor of the main orebody	On the roof of the main orebody	On the floor of the main orebody	On the roof of the main orebody	In the north of the main orebody	On the roof of the main orebody	On the roof of the main orebody	On the floor of the main orebody	On the floor of the main orebody
SiO ₂ (%)	66.29	64.94	65.77	67.20	60.44	56.14	48.20	47.79	48.50	47.43
Al ₂ O ₃ (%)	15.45	14.59	13.79	14.65	16.06	17.11	10.42	10.61	9.82	10.10
CaO (%)	2.02	3.16	1.44	1.85	2.09	5.81	6.48	7.11	7.60	6.71
TFe ₂ O ₃ (%)	5.01	6.37	5.55	5.30	8.57	6.98	12.60	13.04	13.54	12.35
FeO (%)	3.48	4.06	3.92	3.77	6.72	3.70	9.09	9.59	9.30	8.51
K ₂ O (%)	3.21	3.50	3.68	4.15	4.24	2.74	1.82	1.48	1.00	1.32
MgO (%)	2.52	3.00	3.38	2.67	3.52	3.64	14.95	14.84	14.76	15.32
MnO (%)	0.06	0.08	0.07	0.07	0.09	0.09	0.14	0.16	0.17	0.17
Na ₂ O (%)	3.92	2.87	3.66	2.43	2.71	4.41	1.32	1.36	1.60	1.49
P ₂ O ₅ (%)	0.14	0.16	0.16	0.16	0.18	0.35	0.19	0.13	0.16	0.17
TiO ₂ (%)	0.42	0.46	0.45	0.42	0.59	0.66	1.40	1.30	1.31	1.30
CO ₂ (%)	0.26	0.43	0.34	0.17	0.43	0.85	0.34	0.85	0.77	0.43
H ₂ O ⁺ (%)	1.00	1.24	1.70	1.66	1.32	1.22	2.56	1.78	1.22	3.54
LOI (%)	0.82	1.22	1.61	1.06	1.06	1.67	1.80	1.54	1.03	3.03
ppm										
Li	25.69	41.56	32.49	41.68	44.31	19.72	72.58	35.53	11.93	58.72
Be	1.52	1.86	2.03	1.72	1.77	1.36	0.84	0.73	0.70	0.84
V	101.68	139.24	154.20	128.10	161.03	124.82	794.61	816.18	784.90	822.67
Ni	41.90	50.93	60.10	45.90	59.23	36.26	488.21	552.93	564.63	541.39
Co	14.86	15.21	20.44	16.07	19.02	19.34	63.72	70.79	64.43	62.77
Cr	100.38	131.12	163.47	123.00	130.44	34.68	1540.58	1620.43	1552.27	1635.78
Sc	10.64	13.76	12.95	11.48	14.96	11.36	32.55	30.53	28.29	29.08
Rb	97.99	141.58	122.32	129.12	144.53	74.03	89.06	85.73	51.68	43.09
Ba	1216.48	478.82	848.13	720.52	869.64	989.54	408.16	363.40	269.37	251.45
Sr	358.08	321.43	366.22	262.73	275.38	8.59	286.70	252.84	273.97	157.65
Th	7.22	8.30	8.21	6.94	7.81	3.34	1.52	1.41	1.51	1.40
Zr	137.29	158.52	156.02	119.85	138.33	153.70	111.65	106.19	109.87	106.49
Cu	40.15	26.70	28.20	36.73	25.22	24.24	88.62	95.18	101.21	90.07
Zn	70.32	67.47	68.59	79.21	92.47	66.32	99.27	104.74	104.59	99.75
Ga	18.82	17.65	18.52	17.92	20.62	19.94	16.30	15.68	14.55	15.31
Nb	6.68	7.32	6.47	6.16	8.41	5.26	7.12	6.27	6.79	6.68
Cs	5.36	8.88	5.91	6.40	9.28	7.76	6.92	7.80	4.51	3.40
La	24.02	28.88	27.89	23.92	33.10	40.91	12.62	13.82	14.10	14.98
Ce	49.65	57.83	56.41	49.12	66.21	79.43	28.40	31.05	31.96	33.68
Pr	5.29	6.67	6.19	5.52	7.67	9.10	3.58	3.87	3.98	4.20
Nd	18.94	21.86	21.25	19.32	26.25	29.85	15.16	15.38	15.93	16.83
Sm	3.52	4.32	3.95	3.62	5.11	5.01	3.79	3.63	3.72	3.88
Eu	0.91	1.09	0.90	0.95	1.24	1.35	1.10	1.10	1.13	1.16
Gd	2.94	3.92	3.18	2.96	4.43	3.85	3.92	3.59	3.67	3.70
Tb	0.41	0.62	0.45	0.43	0.63	0.51	0.56	0.53	0.54	0.54
Dy	2.31	3.90	2.50	2.33	3.56	2.61	3.25	3.06	3.07	3.14
Y	12.67	24.77	13.53	11.92	19.96	14.68	16.54	15.54	15.47	15.84
Ho	0.42	0.75	0.47	0.42	0.65	0.47	0.57	0.53	0.54	0.54
Er	1.33	2.45	1.52	1.33	2.05	1.48	1.61	1.52	1.54	1.56
Tm	0.18	0.35	0.21	0.18	0.27	0.19	0.20	0.19	0.19	0.19
Yb	1.31	2.54	1.50	1.32	1.91	1.31	1.33	1.25	1.27	1.27
Lu	0.20	0.36	0.22	0.19	0.28	0.19	0.18	0.17	0.17	0.17
Hf	3.70	4.00	4.13	3.27	3.74	3.69	2.94	2.76	2.83	2.76
Ta	0.51	0.52	0.51	0.47	0.61	0.29	0.40	0.38	0.37	0.36
Pb	41.13	20.34	7.86	23.21	16.04	10.63	3.59	3.51	3.95	3.21
U	2.87	5.88	3.14	2.63	3.14	0.99	0.42	0.42	0.30	0.31
ΣREE	111.45	135.54	126.63	111.60	153.35	176.26	76.27	79.70	81.79	85.86
LREE	102.34	120.65	116.59	102.44	139.57	165.65	64.66	68.85	70.81	74.73
HREE	9.10	14.89	10.04	9.16	13.77	10.61	11.61	10.86	10.97	11.13
LREE/HREE	11.24	8.10	11.61	11.18	10.14	15.62	5.57	6.34	6.45	6.72
LaN/YbN	13.12	8.16	13.36	13.03	12.45	22.33	6.82	7.92	7.97	8.45
δEu	0.86	0.81	0.78	0.88	0.80	0.94	0.87	0.93	0.93	0.94
δCe	1.08	1.02	1.05	1.05	1.02	1.01	1.04	1.04	1.05	1.04

4.2.2. Chlorite–Sericite Schist

The appearance of chlorite–sericite schist is blackish green, with a scaly granular crystallo-blastic texture and schistose structure. The content of flaky minerals is greater than 30%, while the content of granular minerals (feldspar and quartz) is less than 70%. Among them, biotite and hornblende are often altered to chlorite (Figure 4f), feldspar is often altered to sericite (Figure 4g), and accessory minerals include apatite, magnetite, sphene,

and zircon. The formation of such rocks is related not only to regional metamorphism, but also to migmatization and dynamic tectonic processes.

The chlorite–sericite schist is mainly developed around the ore bed or near the roof and floor and is usually thin or lenticular with narrow thicknesses, which is consistent with the occurrence of the ore bed, and it is often distributed in the alteration belt. The SiO₂ contents of the rock range from 47.43 to 48.50 wt.%, Al₂O₃ contents range from 9.82 to 10.61 wt.%, MgO contents range from 14.76 to 15.32 wt.%, CaO contents range from 6.48 to 7.60 wt.%, Na₂O contents range from 1.32 to 1.60 wt.%, K₂O contents range from 1.0 to 1.82 wt.%, FeO_T contents range from 12.35 to 13.54 wt.%, and FeO contents range from 8.51 to 9.59 wt.%. The loss on ignition (LOI) of the samples is generally larger than that of biotite–leptynite, indicating that there may be more water-bearing minerals, such as chlorite and sericite (Table 3).

The total REE contents of chlorite–sericite schist are lower than those of biotite–leptynite schist (76.27–85.86 ppm), and slightly negative Eu anomalies are shown on the chondrite-normalized REE partition diagram. The REE fractionation method is similar to that of biotite–leptynite, with smaller light–heavy rare earth fractionation and (La/Yb)_N values ranging from 6.82 to 8.45. The rock has high contents of compatible elements (Cr average of 1587.26 ppm, Co average of 65.42 ppm, Ni average of 536.79 ppm, V average of 804.59 ppm), but Rb (43.09–89.06 ppm), Ba (251.45–408.16 ppm), Sr (157.65–286.70 ppm), and Zr (106.19–111.65 ppm) contents are lower than those of biotite–leptynite, indicating that there are more basic components present. The trace element map of primitive mantle homogenization is similar to that of biotite–leptynite, with negative Nb, Ta, P, K, and Ti anomalies and positive Rb, Ba, Pb, and U anomalies (Figure 7b).

4.3. LA–ICP–MS Zircon U–Pb Dating

This study used the LA–ICP–MS method to analyze zircons in the roof and floor biotite–leptynite of orebody III in the Sijaying open pit. Two samples (SJY20-10-2 and SJY20-10-6) were tested for U–Pb 20 and 18 times, respectively (Table 4).

Table 4. U–Pb results of LA–ICP–MS zircon in host rocks in Sijaying iron deposit.

SJY20-10-2												
Sample Spot	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age	1σ	Concordance
spot.5	100.48	85.77	0.85	0.16839	0.00277	11.40404	0.24943	0.49332	0.00902	2538	29	98.29
spot.7	113.42	64.21	0.57	0.18293	0.00244	13.56690	0.21552	0.54285	0.00844	2674	22	95.76
spot.9	148.36	99.69	0.67	0.16780	0.00249	11.17271	0.20038	0.48448	0.00652	2529	25	99.38
spot.10	170.42	75.61	0.44	0.17821	0.00218	11.10259	0.16094	0.45614	0.00667	2632	20	91.28
spot.11	104.48	50.29	0.48	0.16954	0.00228	10.58300	0.21966	0.45527	0.00842	2548	23	94.54
spot.15	146.69	103.41	0.70	0.17486	0.00220	12.27662	0.17982	0.51192	0.00653	2600	21	97.62
spot.20	30.05	20.18	0.67	0.16479	0.00395	11.18630	0.37162	0.49232	0.01210	2496	43	96.93
spot.21	71.09	51.31	0.72	0.17273	0.00291	11.46805	0.25801	0.48229	0.00734	2576	28	98.37
spot.22	148.14	59.24	0.40	0.16932	0.00250	11.60372	0.17145	0.49875	0.00627	2545	24	97.61
spot.23	141.25	95.59	0.68	0.16862	0.00231	11.33147	0.18201	0.48856	0.00650	2538	23	99.05
spot.26	116.25	86.05	0.74	0.16858	0.00242	11.76116	0.20508	0.50712	0.00816	2541	23	96.19
spot.27	202.65	117.31	0.58	0.17045	0.00205	11.45603	0.18549	0.48624	0.00651	2558	20	99.81
spot.29	179.83	103.37	0.57	0.16859	0.00196	11.26849	0.18203	0.48363	0.00742	2545	19	99.82
spot.30	92.22	74.61	0.81	0.18524	0.00260	12.97982	0.25334	0.50734	0.00735	2695	23	98.06
spot.31	104.87	62.26	0.59	0.18822	0.00270	13.72893	0.25148	0.52820	0.00732	2721	24	99.59
spot.32	200.45	167.65	0.84	0.16818	0.00216	10.60670	0.15158	0.45690	0.00598	2535	22	95.46
spot.33	110.65	78.35	0.71	0.17011	0.00264	12.07263	0.23783	0.51551	0.00799	2552	26	95.29
spot.34	186.76	114.67	0.61	0.16897	0.00224	10.75917	0.18412	0.45994	0.00679	2542	22	95.70
spot.36	125.71	101.53	0.81	0.17171	0.00204	11.32024	0.16965	0.47686	0.00639	2570	20	97.69
spot.38	127.25	123.25	0.97	0.17050	0.00241	11.16960	0.18439	0.47217	0.00579	2560	25	97.26

Table 4. Cont.

SJY20-10-6												
Sample Spot	U (ppm)	Th (ppm)	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ	$^{207}\text{Pb}/^{206}\text{Pb}$ Age	1σ	Concordance
spot.1	169.66	62.64	0.37	0.17313	0.00194	11.80878	0.19493	0.49050	0.00660	2590	20	99.43
spot.5	154.72	102.18	0.66	0.18240	0.00620	12.42505	0.60462	0.48626	0.00788	2650	47	96.14
spot.8	109.75	75.84	0.69	0.26216	0.00344	21.95509	0.64670	0.60526	0.01457	3255	21	93.06
spot.11	225.78	138.11	0.61	0.16732	0.00177	10.12759	0.19588	0.44003	0.00814	2527	17	92.36
spot.15	101.78	38.47	0.38	0.27032	0.00305	23.42254	0.43638	0.63013	0.01118	3304	18	94.97
spot.16	201.83	206.10	1.02	0.17553	0.00258	10.87217	0.23523	0.44984	0.01129	2609	26	90.82
spot.17	136.98	90.34	0.66	0.16971	0.00233	10.89254	0.24973	0.46676	0.00978	2553	22	96.47
spot.18	69.91	79.67	1.14	0.16708	0.00302	11.30578	0.24830	0.49281	0.00906	2519	31	97.65
spot.19	184.03	106.73	0.58	0.16993	0.00231	10.61513	0.25060	0.45311	0.00947	2555	24	93.79
spot.20	208.42	134.60	0.65	0.16837	0.00187	11.38212	0.13789	0.49057	0.00646	2541	18	98.80
spot.21	164.33	69.25	0.42	0.16995	0.00218	10.80472	0.30527	0.46181	0.01199	2552	21	95.48
spot.22	91.61	68.59	0.75	0.17290	0.00305	11.62594	0.23693	0.48776	0.00797	2577	29	99.27
spot.23	129.95	119.65	0.92	0.17055	0.00223	12.16836	0.18055	0.52032	0.00791	2561	21	94.92
spot.25	96.45	75.71	0.78	0.16627	0.00272	11.33251	0.19176	0.49717	0.00675	2517	27	96.80
spot.26	166.36	93.38	0.56	0.21818	0.00314	17.41854	0.40168	0.57895	0.00874	2961	24	99.33
spot.27	143.22	82.20	0.57	0.20610	0.00242	16.28574	0.24471	0.57423	0.00755	2874	18	98.31
spot.30	204.16	128.17	0.63	0.18278	0.00219	11.66460	0.21631	0.46400	0.00815	2674	20	91.07
spot.31	293.18	194.87	0.66	0.16668	0.00177	10.19212	0.28303	0.44407	0.01194	2521	18	93.31

The SJY20-10-2 sample was taken from the biotite–leptynite on the roof of orebody III, which is less affected by metamorphism. Zircon particles are mostly short and columnar, and a few are long and columnar. The zircons are euhedral or subhedral, with length/width ratios of 2:1 to 3:1. According to the cathodoluminescence (CL) image characteristics of zircons and the U–Pb analysis results, these zircons can be divided into two types: (1) the first type of zircon (e.g., spots 4, 22, 26, 33 and 28) (Figure 8a) has low cathodoluminescence brightness, obvious oscillatory bands, different band widths, and relatively clear and relatively high Th/U ratios (0.4–0.92); these results are indicative of magmatic zircons [43], which may be less affected by late metamorphism, with an age of 2550 ± 22 Ma (MSWD = 0.22, $n = 7$) (Figure 8c, blue area). (2) The second type of zircon shows low cathodoluminescence brightness without typical oscillatory bands (e.g., spots 9, 15, 32, 36 and 38) (Figure 8a). The oscillatory zonings of zircon occasionally change in lightness and shade, which means that the trace elements of zircon have a certain degree of change during crystallization [44]. The boundaries of some zircon particles are disturbed in the late stage, showing that the cathodoluminescence of the zircon edge is bright, which may represent the superimposition of late metamorphism/migmatization. The Th/U ratios of these zircons range from 0.67 to 0.97, indicating that they are of magmatic origin, and have an age range of 2552 ± 23 Ma (MSWD = 0.62, $n = 6$) (Figure 8c, purple area), suggesting the presence of inherited zircons affected by metamorphism. Due to the similar ages of the two types of zircons, we consider that they are both zircons that formed during the same mineralization process [29]. The $^{207}\text{Pb}/^{206}\text{Pb}$ weighted average age of ancient geological materials was more representative of the formation age, and the $^{207}\text{Pb}/^{206}\text{Pb}$ weighted average age of the two types of zircons was 2547 ± 6 Ma (MSWD = 1.04, $n = 13$).

The SJY20-10-6 sample was collected from the biotite–leptynite on the roof of orebody III, which is highly affected via hydrothermal alteration. The zircon particles are more numerous and fragmented, and only a few are mostly complete. Most zircon crystals are euhedral, with length/width ratios of 2:1. According to the CL image characteristics of zircons and the U–Pb analysis results, these zircons can be divided into three types: (1) the first type has a complex structure, the zircon core has dark cathodoluminescence and no oscillatory zoning (e.g., spots 8, 15, 26 and 27) (Figure 8b), and the Th/U ratios are 0.38–0.69. The obtained $^{207}\text{Pb}/^{206}\text{Pb}$ age range was 2873–3304 Ma ($n = 4$), making it the oldest inherited zircon in the eastern Hebei area. The zircon rim shows bright cathodoluminescence characteristics (low U contents), with occasional oscillatory zoned growth. The growth domain of light gray-CL is usually uniform, which can be explained by the regrowth in ancient inherited zircons during later anatexis events. (2) The cathodoluminescence of the core of the second type of zircon is relatively dark, and there are occasionally small and dense oscillatory zonings (e.g., spots 5, 11, 17, 18, 20, 23, and 25) (Figure 8b). The

Th/U ratios were 0.61–1.14, and the apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages were 2516–2650 Ma ($n = 7$), representing magmatic zircons affected by late metamorphism. (3) The third type of zircon exhibits obvious oscillatory zoning (e.g., spots 12, 19, 21, 22, and 30) in the CL image (Figure 8b), with Th/U ratios ranging from 0.42 to 1.02. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages range from 2540 to 2673 Ma ($n = 5$), representing the magmatic zircons of the ore-forming source rock. The zircon concordance diagram (Figure 8d) of the three types of zircons shows an upper intercept age at 3283 ± 280 Ma and a lower intercept age at 2404 ± 170 Ma, which represent the times of the oldest magmatism and migmatization in the eastern Hebei area.

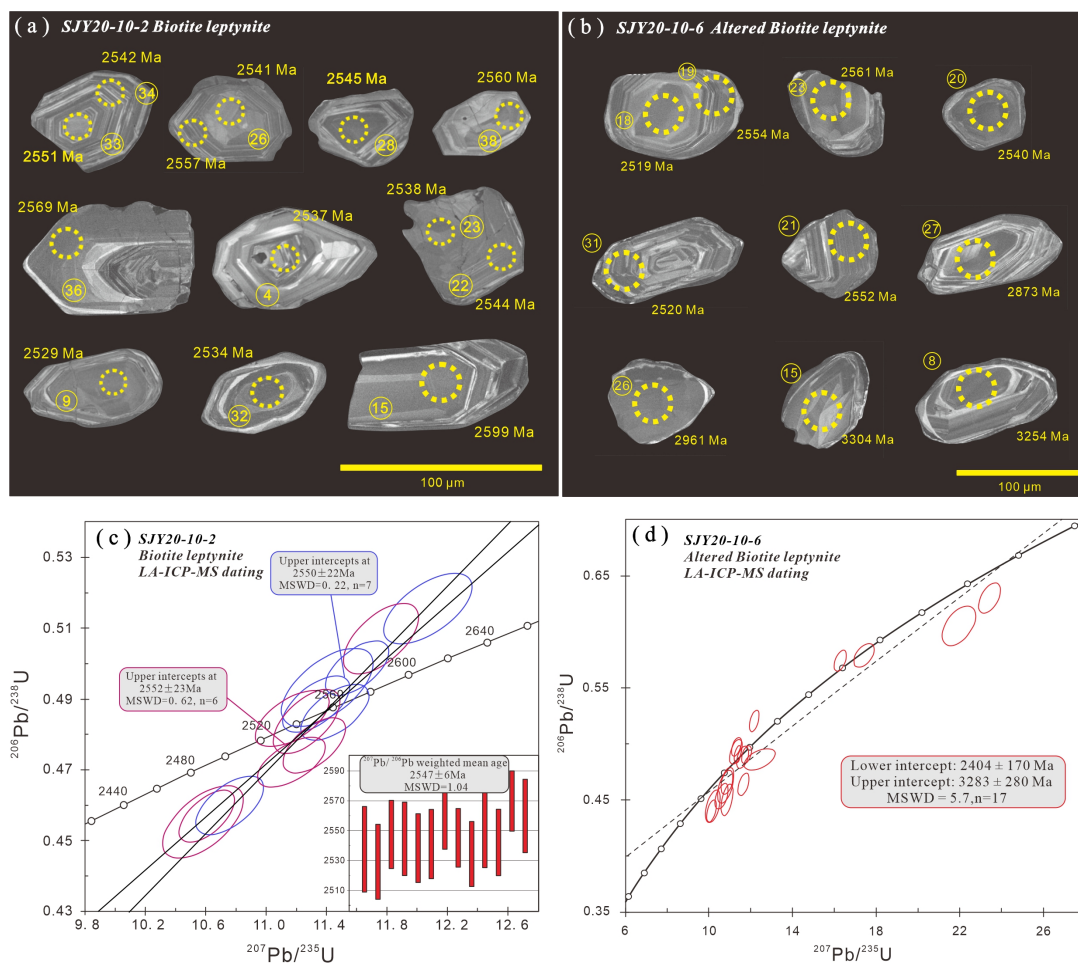


Figure 8. Concordia plots of zircon U–Pb data and representative CL images with corresponding apparent ages for biotite–leptynite. Small circles (20–30 μm diameter) represent analytical points. (a) Representative zircon CL images of SJY20-10-2 (biotite leptynite); (b) Representative zircon CL images of SJY20-10-6 (altered biotite leptynite); (c) U–Pb concordia diagrams of zircons of SJY20-10-2 (biotite leptynite); (d) U–Pb concordia diagrams of zircons of SJY20-10-6 (altered biotite leptynite).

In the REE normalization diagram of zircons (Figure 9a), all zircons show significant positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 1.43\text{--}60.04$ in SJY20-10-6; $\text{Ce}/\text{Ce}^* = 5.46\text{--}129.14$ in SJY20-10-2), as well as negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.21\text{--}0.95$ in SJY20-10-6; $\text{Eu}/\text{Eu}^* = 0.19\text{--}0.59$ in SJY20-10-2), and the distribution characteristics of rare earth elements are more enriched in heavy REEs (HREEs) than in light REEs (LREEs) (Table 5). In the $(\text{Sm}/\text{La})_{\text{CN}}$ La and $\text{Ce}/\text{Ce}^* - (\text{Sm}/\text{La})_{\text{CN}}$ discrimination diagrams (Figure 9b,c), most zircons are plotted close to the magmatic zircon region. Although some zircon data deviate, they show a trend of transition from a magmatic zircon region to a hydrothermal zircon region, which is consistent with the CL image of zircon and may be caused by the influence of late regional metamorphism and migmatization on zircon.

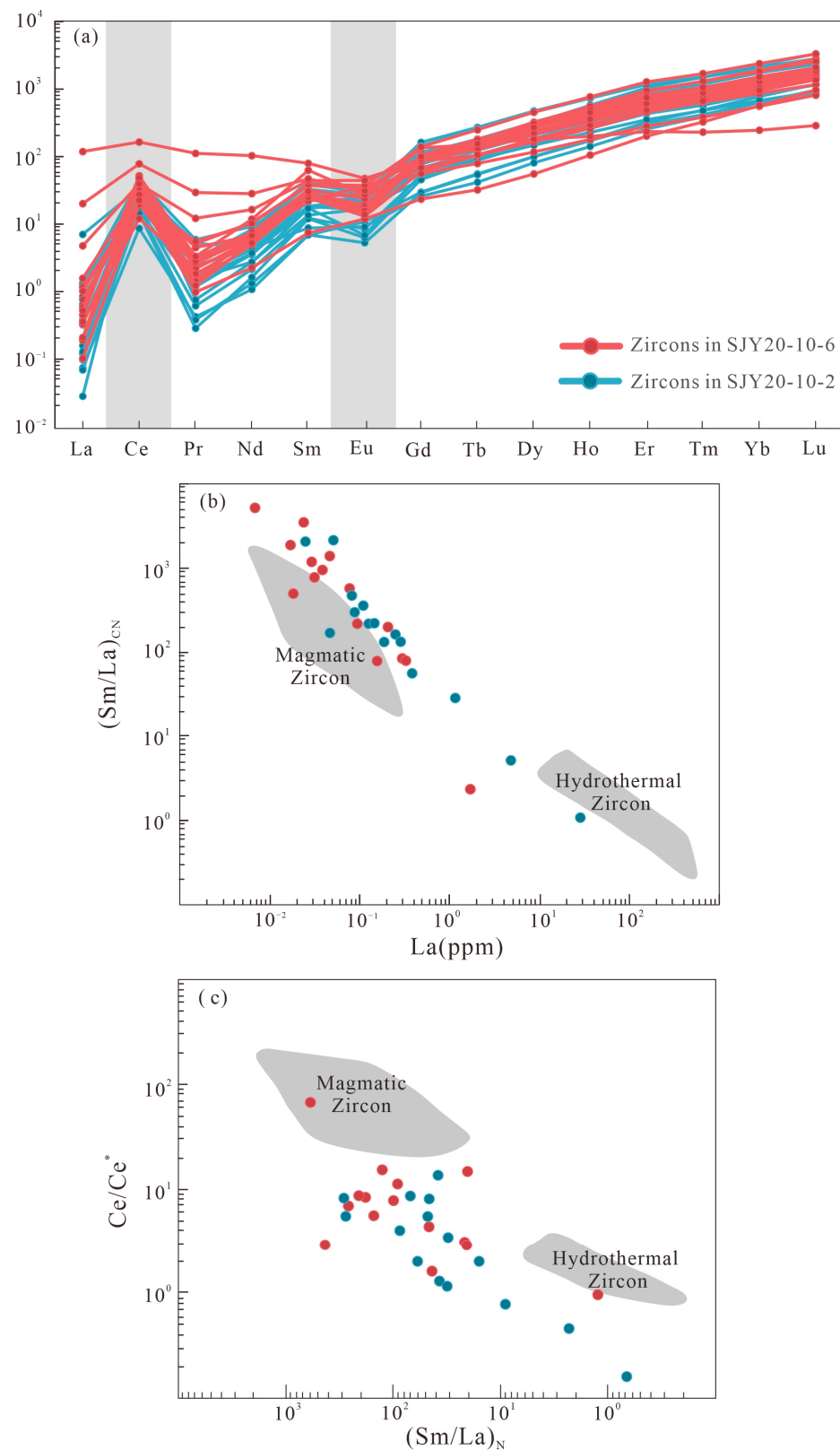


Figure 9. (a) Chondrite-normalized REE patterns of zircons from biotite-leptynite and sericite-chlorite schist, with values for chondrite following Taylor and McLennan (1985) [42]. (b,c) $(\text{Sm}/\text{La})_{\text{CN}}\text{-La}$ and $\text{Ce}/\text{Ce}^*\text{--}(\text{Sm}/\text{La})_{\text{CN}}$ diagrams for zircons (after Hoskin, 2005 [45]). Values for chondrite follow Taylor and McLennan (1985) [42].

Table 5. Analysis results of trace elements in zircon in host rocks in Sijiaying iron deposit.

SJY20-10-2																			
Test Points	Spot.7	Spot. 9	Spot.10	Spot.15	Spot.20	Spot.21	Spot.22	Spot.23	Spot.26	Spot.27	Spot.29	Spot.30	Spot.31	Spot.32	Spot.33	Spot.34	Spot.36	Spot.38	
La	0.00	0.03	0.33	0.02	0.02	0.02	0.00	0.04	0.30	1.71	0.10	0.21	0.00	0.08	0.03	0.16	0.01	0.05	
Ce	11.61	13.94	27.93	11.80	5.42	9.71	9.82	11.87	16.98	20.98	14.49	10.03	8.97	23.53	17.63	29.18	32.28	26.90	
Pr	0.06	0.15	0.57	0.29	0.04	0.12	0.04	0.17	0.29	0.51	0.23	0.31	0.03	0.25	0.12	0.15	0.07	0.28	
Nd	1.03	1.78	4.41	3.98	0.52	1.71	0.64	2.01	3.25	2.14	2.17	3.85	0.79	3.21	1.79	1.32	1.31	3.90	
Sm	1.91	3.44	4.38	6.69	1.08	2.89	1.09	3.83	4.20	1.37	2.83	5.87	1.87	5.12	2.66	2.11	2.67	6.25	
Eu	0.51	1.43	1.49	1.58	0.64	1.32	0.31	0.84	1.06	0.54	0.97	1.81	0.37	1.59	1.24	0.99	0.41	1.68	
Gd	10.73	18.64	13.86	33.59	6.22	16.29	6.09	16.07	19.90	5.39	12.24	29.78	9.60	22.81	12.67	9.52	11.41	24.00	
Tb	3.32	6.13	4.65	10.16	2.10	5.67	2.05	5.08	6.25	1.58	3.87	9.66	3.60	6.82	3.93	3.35	3.47	6.55	
Dy	39.73	75.32	53.38	120.08	25.60	78.94	25.45	57.25	72.41	20.71	44.61	115.70	46.88	80.98	45.33	40.17	37.64	71.97	
Ho	14.88	28.42	19.60	42.83	10.23	32.62	9.81	20.15	26.42	8.04	17.00	41.20	18.69	29.16	16.67	15.75	12.95	23.96	
Er	71.43	140.87	98.86	194.13	53.30	171.50	49.31	95.51	128.59	42.63	84.78	192.17	98.40	140.73	86.85	78.61	58.39	110.88	
Tm	14.65	30.11	21.31	38.05	12.42	37.99	10.65	19.37	26.61	9.94	19.27	38.37	21.60	30.19	19.54	18.52	12.21	23.61	
Yb	143.17	292.96	221.19	342.23	130.90	382.85	107.51	178.23	251.31	107.46	192.42	355.84	217.25	291.69	203.58	190.69	115.17	225.97	
Lu	29.05	58.77	47.74	65.10	29.84	83.58	21.85	35.86	52.02	24.37	42.11	70.87	46.30	62.12	46.08	42.85	23.26	46.39	
SJY20-10-6																			
Test points	spot.1	spot.5	spot.8	spot.11	spot.15	spot.16	spot.17	spot.18	spot.19	spot.20	spot.21	spot.22	spot.23	spot.25	spot.26	spot.27	spot.30	spot.31	
La	0.39	0.19	0.28	0.08	0.09	0.11	0.14	-	28.31	0.03	0.05	0.13	0.00	0.00	0.05	0.25	1.16	4.85	
Ce	17.94	13.92	12.25	14.91	7.55	32.06	20.30	21.30	101.12	12.18	14.61	28.06	27.02	17.05	30.10	14.02	24.51	48.17	
Pr	0.44	0.23	0.50	0.26	0.21	0.31	0.26	0.15	10.68	0.18	0.10	0.28	0.14	0.12	0.32	0.54	1.18	2.84	
Nd	3.22	2.38	5.09	3.01	2.81	3.64	3.16	2.98	48.57	2.54	1.09	3.25	2.39	2.52	5.64	4.89	7.81	13.40	
Sm	3.95	3.80	5.79	4.58	3.44	4.98	4.40	4.28	12.31	4.60	1.16	3.90	4.40	4.76	9.70	6.04	6.80	7.25	
Eu	0.82	0.77	2.05	0.95	2.17	1.41	1.14	1.07	2.79	0.95	0.71	1.65	0.93	0.83	1.60	2.19	2.62	1.84	
Gd	17.80	12.48	18.33	20.03	11.64	18.67	20.80	18.70	17.86	21.65	4.91	14.19	19.72	21.26	27.84	28.82	19.24	20.77	
Tb	5.87	3.94	4.78	5.85	2.99	5.64	6.51	5.06	3.92	6.75	1.22	4.01	5.68	6.63	5.67	9.35	5.07	5.84	
Dy	74.12	44.94	54.40	68.50	29.92	61.37	82.21	56.20	42.26	74.11	14.20	45.93	68.22	78.03	46.22	115.19	57.17	68.84	
Ho	29.48	16.58	18.99	24.39	10.22	22.08	31.14	19.77	14.82	26.56	6.01	16.70	25.00	28.05	11.33	43.41	20.34	25.46	
Er	151.59	78.02	90.30	113.40	46.89	102.85	156.42	92.52	75.16	124.90	33.49	80.61	124.60	133.41	38.93	209.87	100.85	123.55	
Tm	33.29	16.23	18.98	23.21	9.77	21.25	33.10	19.19	16.33	26.10	8.33	17.04	26.11	26.96	5.89	42.85	22.37	26.82	
Yb	319.98	145.52	182.40	216.05	94.28	195.59	306.06	175.94	160.37	235.97	96.36	162.23	239.87	242.94	41.98	400.87	220.19	256.94	
Lu	70.26	29.59	39.12	43.13	20.55	39.13	64.42	35.93	34.54	48.58	24.47	34.55	49.86	47.89	7.33	82.87	47.68	52.58	

5. Discussion

5.1. Stages of Iron Formation

The Luanxian Group is the main ore-bearing horizon of the Sijiaying iron deposit, and biotite–leptynite, as the wall rock of the iron orebody, is closely related to mineralization. Due to the lack of direct dating minerals in BIF orebodies, the zircon U–Pb method has the characteristics of a high blocking temperature and long half-life period. The zircon U–Pb ages of the roof and floor wall rock of BIF orebodies are usually used as the main means to constrain the mineralization age [46,47]. According to the zircon CL images, zircon domains that stretch from the core to the mantle and, finally, to the edge, combined with the cathodoluminescence characteristics of low and high CL brightness, can be categorized into the following four stages, as listed and described in Figure 10.

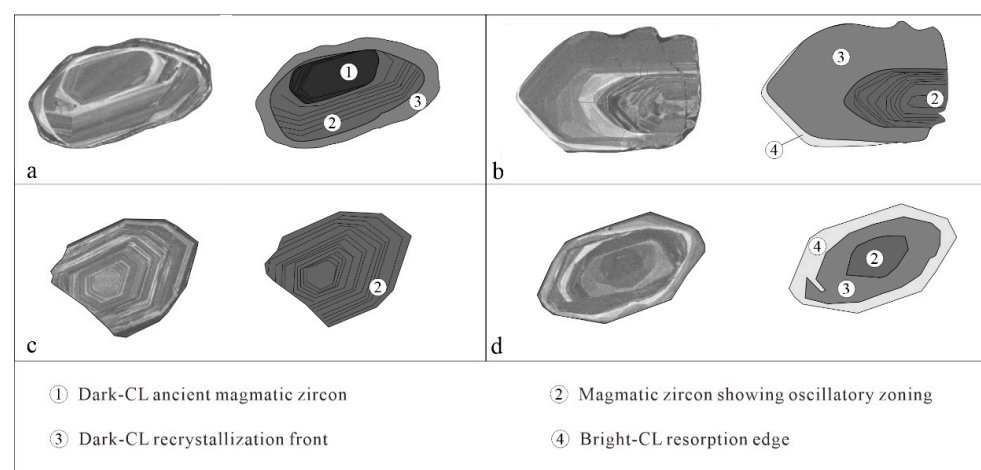


Figure 10. Cathodoluminescence images and schematic sections showing textures and stages of zircon growth of biotite leptynite from Luanxian Group. See text for discussion. (a) Zircons from the earliest volcanism in eastern Hebei; (b,d) Zircons from the main mineralization period superimposed by regional metamorphism and migmatization; (c) Magmatic zircons from the main mineralization period of Sijiaying iron deposit.

5.1.1. Dark-CL Ancient Magmatic Zircons

The zoning characteristics of zircon at this stage are not obvious, and the zircon in the CL image is relatively dark (Figure 8a). The zircon domain commonly exhibits sector or fir-tree zoning, and, occasionally, the zircon core shows planar zoning (Figure 8b), indicating inconsistent rates of elemental adsorption during the development of crystal domain [48]. The Th/U ratios of this crystal domain are relatively large ($\text{Th/U} = 0.38\sim 0.69$), showing the overall characteristics of magmatic zircons. The analyses yield an upper intercept at 3283 ± 280 Ma (Figure 8d), representing the precursory magmatic zircon and the earliest volcanic sedimentary event in the eastern Hebei region (Figure 10a,d).

5.1.2. Magmatic Zircons Showing Oscillatory Zoning

The zircons in this stage are mainly magmatic zircons, which are relatively euhedral and have a uniform oscillatory banded structure, indicating an uneven distribution of trace elements, which, in turn, indicates a typical magmatic crystallization origin [49,50]. In addition, a number of zircon particles show inherited old residual zircons in their cores, exhibiting dissolution and rounding characteristics and forming dense rhythmic growth bands at the edges. The zircon crystal domain at this stage usually displays a uniformly bright CL image (Figure 8c) because of its low trace element content [51]. This type of zircon is extensively developed in the wall rock of the orebody, with an age of 2547 ± 6 Ma, indicating the development of large-scale magmatic activity during this period (Figure 10c).

5.1.3. Dark-CL Recrystallization Front

At this stage, there is no clear zoning in the zircon domain, which tends to be in contact with inherited zircon cores. Occasionally, this crystal domain inherits zircons through inward metasomatism, with sharp and bright CL boundaries (Figure 8b). These boundaries represent the recrystallization process at the zircon edges, which are extracted from the zircon cores, which are rich in trace elements and present black-CL images, indicating the existence of a dissolution–recrystallization process. They can be interpreted as newly formed metamorphic edges formed through the transformation of inherited zircons under the influence of regional metamorphism [44,52]. The formation age of zircons at this stage was slightly later than that of the Sijiaying BIF, being approximately 2500 Ma (Figure 10b) [53,54].

5.1.4. Bright-CL Resorption Edge

The zircon domains at this stage are usually distributed at the edges of zircon particles, showing low U and less than $5\ \mu\text{m}$ bright-CL image features (Figure 8b,d). Such zircon domains are generally recrystallization domains formed via the fluid transformation of zircon edges in the late stage of migmatization, which may represent the age of anatexis. The zircon age was taken as the lower intercept age of SJY20-10-6, which was 2404 ± 170 Ma (Figure 10b,d).

5.1.5. Timing of Deposition

The subtypes of BIF deposits play important roles in determining the mineralization age of the Sijiaying iron deposit. From a regional perspective, the lower part of the protolith formation of the Luanxian Group is dominated by basic volcanic rocks, and the middle and upper parts are transitional to acidic volcanic rocks, alkaline volcanoclastic rocks, and clayey siltstone, forming a volcanic sedimentary cycle from bottom to top. The iron formation is located at the transitional part from basic volcanic rocks to acidic volcanic rocks or sedimentary rock [16,31,32,55]. Geochemical analysis of plagioclase amphibolite and biotite–leptynite in the deep western portion of the deposit shows that the wall rock has volcanic affinity [17]. In the Al_2O_3 vs. $\text{K}_2\text{O} + \text{Na}_2\text{O}$ (Figure 11a) [56] and Zr/TiO_2 vs. Nb/Y (Figure 11b) [57] diagrams, most of the biotite–leptynite samples are plotted in the magma field, indicating mainly intermediate–felsic volcanic rocks. The protolith of chlorite–sericite schist is a volcanoclastic rock related to calcium–alkaline basic volcanism. In addition, the

rare earth distribution pattern of BIFs is similar to that of high-temperature hydrothermal fluids on the seabed (Figure 6a). Moreover, Huston et al. (2004) [58] compared the Eu/Eu^* ratios of different types of BIFs, indicating that Algoma-type BIFs usually have relatively high Eu/Eu^* ratios, while Sijiyang BIFs have Eu/Eu^* ratios of 1.25 to 3.09, with an average of 1.7, which is much higher than Proterozoic BIFs (Eu/Eu^* ratios of late-Paleoproterozoic era BIFs are 1.15 to 2.46 [59]; Eu/Eu^* ratios of Neoproterozoic era BIFs are 0.47 to 0.86 [60]). Thus, we propose that the Sijiyang BIF is an Algoma-type BIF, and its mineralization is related to volcanic activity.

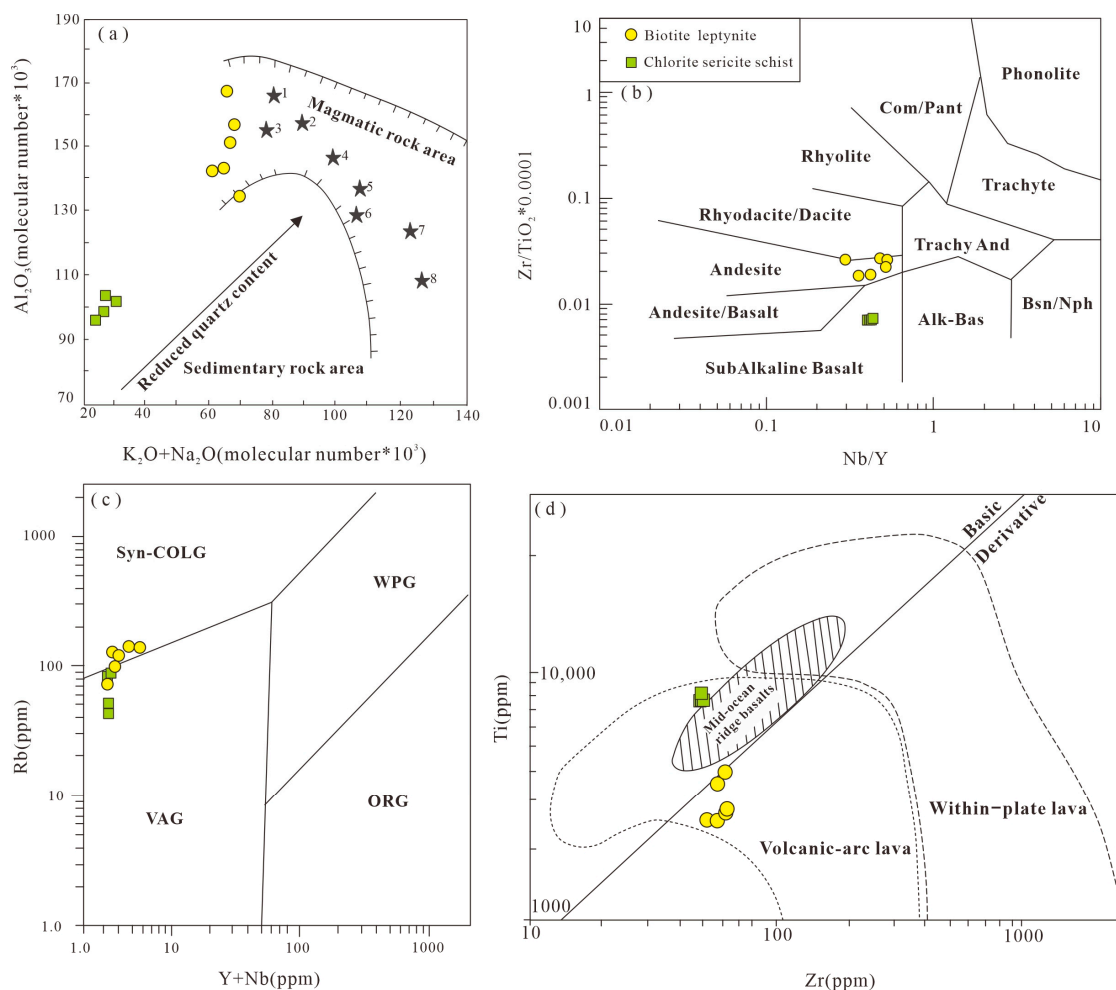


Figure 11. (a) Al_2O_3 –($\text{K}_2\text{O} + \text{Na}_2\text{O}$) diagram of metamorphic rocks (after Wang, 1987 [56]): 1-andesite; 2-Dacite; 3-Quartz diorite; 4-Rhyodacite; 5-Quartz coarse andesite; 6-rhyolite; 7,8-Alkaline granite [$\text{Al}_2\text{O}_3 = 1000 \times n(\text{Al}_2\text{O}_3)$; and $\text{K}_2\text{O} + \text{Na}_2\text{O} = 1000 \times n(\text{K}_2\text{O}) + 1000 \times n(\text{Na}_2\text{O})$]. (b) Zr/TiO_2 – Nb/Y discriminant diagram (after Winchester and Floyd, 1977 [57]). (c) Rb – $\text{Y} + \text{Nb}$ diagram showing fields of volcanic-arc granite (VAG), ocean-ridge granite (ORG), within-plate granite (WPG), and syn-collisional granite (Syn-COLG) (after Pearce et al., 1984 [61]). (d) Ti – Zr diagram (after Pearce et al., 1982 [62]).

The marine volcanic sedimentary process provided the basic material source for mineralization, and the iron orebody and wall rock were deposited simultaneously and produced in an interlayer. Therefore, the zircon U–Pb age of the wall rock has a potential constraint on the mineralization age. This study conducted LA–ICP–MS zircon U–Pb analysis on biotite–leptynite, and the results showed that there are two types of magmatic zircons and two stages of tectonic–metamorphic events in the Sijiyang deposit. The oldest magmatic zircon age is 3283 ± 280 Ma, which represents the time when the earliest volcanic magma activity occurred in eastern Hebei Province. The Xingshan deposit in the

Caozhuang–Huangbaiyu–Naoyumen area of Qian'an in eastern Hebei was formed during this period (3830–3470 Ma), and is the earliest such deposit in Northern China [26–28].

The formation age of the second type of magmatic zircon is 2547 Ma, which is the main formation age of the biotite–leptynite, represents the mineralization age of the Sijiaying BIF, rather than the older 2692–2847 Ma [18]. At approximately 2550 Ma, large-scale volcanic activity developed in the eastern Hebei region, and many Algoma-type BIFs were deposited and mineralized during this period. Meanwhile, similar age data were obtained for BIFs in the eastern Hebei region, including Shirengou [63], Shuichang [64], and Malanzhuang [65].

Regional metamorphism occurred at 2.5 Ga, shortly after mineralization, and this tectonic–metamorphic event is a unifying tectonic feature in eastern Hebei Province. Shen et al. (1981) [53] analyzed the Rb–Sr values of various types of leptynites in Sijiaying and suggested that 2.5 Ga was the end of the latest regional metamorphism of amphibolite facies in the whole region. Qian et al. (1985) [16] perceived that the nearly N–S folds that were commonly developed in the Luanxian Group were formed in the late-Neoproterozoic era, and the tectonic movement was similar to the formation age of large-scale regional metamorphism. Furthermore, the dark CL image of the metamorphic edge of the Sijiaying magmatic zircon may be a reflection of the 2.5 Ga tectonic–metamorphic event in the eastern Hebei region.

Migmatization is a deep melting event developed on the basis of regional metamorphism and formed a series of migmatitic granite and pegmatite that is widely developed in the Luanxian Group. The migmatitic granite is in fuzzy contact with the biotite–leptynite in the deposit, and there is often the phenomenon of oblique cutting or destruction of the orebody (Figure 3g), which indicates that migmatization occurred later than mineralization. Zircons usually show active facies in the migmatization stage, which can constrain the age of migmatization [66,67]. The bright-CL domains at the zircon edges in the biotite–leptynite were formed in the migmatization stage, with a lower intercept age of 2404 ± 170 Ma, which was the time of the anatexis event, and this value could also represent the age of the formation of the hydrothermally altered high-grade iron ore [30,68]. Li et al. (2011) [65] performed zircon SHRIMP U–Pb dating in the gneissic granite of the Malanzhuang BIF in the Qian'an area, showing that 2484 ± 23 Ma was the time of anatexis of the Qian'an Group, while the migmatization of the Luanxian Group may be slightly later.

5.2. Depositional Conditions of BIF

Pure chemical sedimentary rocks are generally rich in Fe and Mn. If terrigenous clastic materials are contaminated, their Al and Ti contents increase [69]. The magnetite–quartzite of the Sijiaying deposit has very low concentrations of Al_2O_3 and TiO_2 ($\text{Al}_2\text{O}_3 + \text{TiO}_2 = 0.01\sim 3.5$ wt.%, Table 2) and low contents of HFSEs (Figure 6b). Al_2O_3 and TiO_2 are not correlated with each other (Figure 12b). The Eu/Eu* ratio is negatively correlated with Al_2O_3 . Most samples have the characteristics of low Al and high Eu (Figure 12c) and high Fe/Ti and Fe/Al ratios ($\text{Fe/Ti} > 1000$; $\text{Fe/Al} = 29.91\sim 512.19$), indicating that the contamination of terrigenous debris has a relatively small impact on positive Eu anomalies. These geochemical characteristics indicate that crustal materials rarely participate in the mineralization process of the Sijiaying BIF, while high-temperature hydrothermal solutions contribute more to mineralization.

The PAAS-standardized REY partitioning model of the Sijiaying BIF indicates a relative depletion in light rare earth elements and relative enrichment in medium-to-heavy rare earth elements, along with positive Eu and Y anomalies (Figure 6a). The Y/Ho ratios of the ore range from 32.05 to 44.75, with an average value of 37.88, which is higher than that of chondrites (26–28) [70] and closer to that of modern seawater (>44) [38,71]. As Eu anomalies are mainly controlled by temperature [72], the strong positive Eu anomalies in the Sijiaying BIF indicate that high-temperature hydrothermal fluids from the seabed are involved in the mineralization process [39,73]. In the SiO_2 – Al_2O_3 discrimination diagram (Figure 12a), most ore samples plot in the hydrothermal and seawater regions, indicating a close relationship with seafloor hydrothermal activity. It is generally believed that Fe and REEs are not

fractionated during transport from the eruption center of submarine volcanoes [74]; thus, positive Eu is abnormal, stable ΣREEs indicate that Fe in BIF is obtained from hydrothermal solutions [75], and periodic upward currents cause Fe to precipitate in a recurring layer [5]. In the Sm/Yb–Eu/Sm discrimination diagram (Figure 12e), a seafloor high-temperature hydrothermal solution of less than 0.1% is sufficient for the Sijiaying BIF to show the characteristics of a positive Eu anomaly, while the Y/Ho–Sm/Yb discrimination diagram (Figure 12d) shows that there may be a high volcanic hydrothermal fluid flux (1%–5%). Wang et al. (2017) [18] found that the ore has positive $\varepsilon\text{Nd}_{(t)}$ values and high Ge/Si ratios, indicating that Fe originates from high-temperature hydrothermal fluids on the seabed. Therefore, the Sijiaying BIFs are the products of marine chemical deposition and the sources of ore-forming materials provided via submarine volcanic hydrothermal solution.

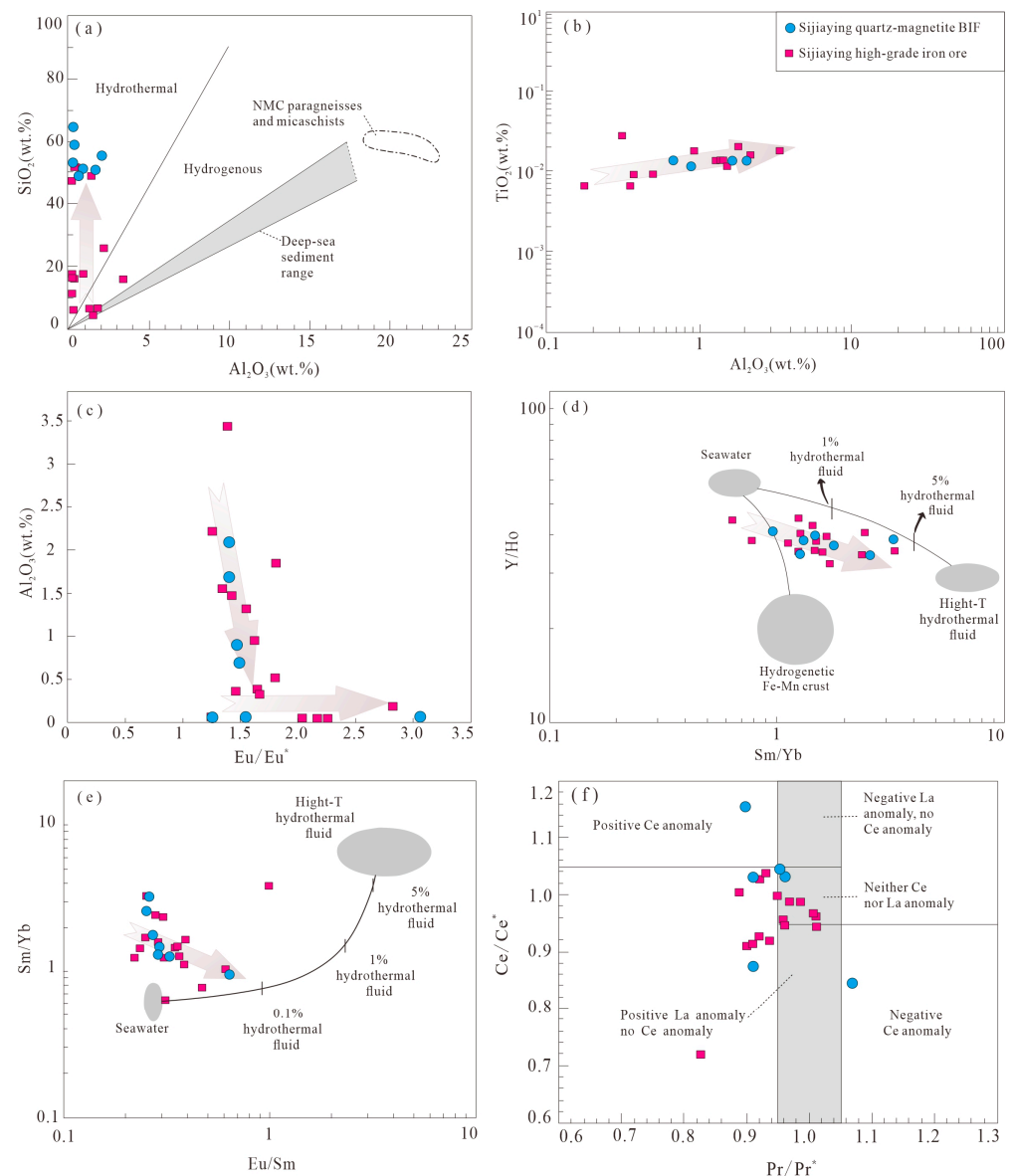


Figure 12. Diagrams: (a) SiO_2 – Al_2O_3 diagram (Wonder et al., 1988) [76]; (b) TiO_2 – Al_2O_3 diagram; (c) Al_2O_3 – Eu/Eu^* diagram; (d) Y/Ho–Sm/Yb diagram (after Alexander et al., 2008) [77]; (e) Sm/Yb–Eu/Sm diagram (after Alexander et al., 2008) [77]; (f) Ce/Ce^* – Pr/Pr^* diagram (after Bau and Dulski, 1996) [78]. PAAS normalization values in (f) are after Pourmand, A. et al. (2012) [36]. Partial data of iron ore from Xu et al. (2014, 2015) [31,32].

Ce anomalies are commonly used to determine the redox state of seawater [57,58]. Under oxidizing conditions, Ce^{3+} is oxidized to low-solubility Ce^{4+} and absorbed by the surfaces of Fe–Mn hydroxides, organic matter, and clay particles in the water [79], resulting in significant negative Ce anomalies in the water. In the Ce/Ce*–Pr/Pr* diagram (Figure 12f) [78], most of the geochemical data of iron ore are plotted in the area without a negative Ce anomaly, indicating that the paleo-seawater in the depositional process of the Sijiaying BIFs experienced low-oxygen or anoxic conditions.

BIF and wall rock are the products of contemporaneous marine volcanic sedimentary processes; therefore, the surrounding rocks can serve as a basis for distinguishing the mineralization background [80]. The biotite–leptynite and chlorite–sericite schist samples are depleted in high field strength elements (HFSEs), such as Nb, Ta, Ti, and P, being consistent with normal-grade island arc volcanic rocks formed via fluid metasomatic mantle wedges [81]. In the Rb–Y and Nb (Figure 11c) and Ti–Zr (Figure 11d) diagram, most biotite–leptynite and chlorite–sericite schist are plotted in the volcanic arc area, and their genesis is closely related to arc magma. In addition, the Shuichang and Shirengou BIFs, which are similar to the Sijiaying BIF in the eastern Hebei region, also formed in an island arc setting [63,64], and similar results were obtained in the Anshan–Benxi region [82,83]. Consequently, the Sijiaying BIF potentially formed in an island arc setting and was most likely formed through sedimentation and mineralization in the ancient back-arc basin.

5.3. Genesis of High-Grade Iron Ores

The high-grade iron ore of the Sijiaying deposit is in integrated contact with BIFs, with clear boundaries (Figure 3e,h). Their REE distribution patterns and trace element distributions show similar geochemical characteristics, indicating that the initial material sources are the same. However, there are also differences in some aspects, such as (1) that fact that they have different textures and structures. The normal-grade iron ore is mainly composed of medium-to fine-grained textures (particle sizes of 0.02–0.3 mm) and banded structures (Figure 3a), while the high-grade ore has mostly medium-to coarse-grained textures (particle sizes of 0.1–1 mm) and massive structures (Figure 3b), followed by disseminated structures and residual fine-grained structures (Figure 3c). (2) In terms of the mineralogy, quartz is the main gangue mineral of normal-grade iron ore, while in high-grade ore, it is a minor or trace mineral. Biotite, chlorite, and carbonate minerals (Figure 4d) are the main gangue minerals of high-grade iron ore, while in normal-grade iron ore, they are present in small or trace amounts. (3) In terms of the spatial distribution, most of the wall rock near the ore-rich iron ore has wall rock alteration, such as chloritization, carbonatization, biotization, and muscovite. Generally, the orebody near the altered wall rock has a higher grade (Figure 3e) and gradually decreases outward. (4) Due to the active chemical nature and strong geochemical activity of large ion lithophile elements (LILEs), they easily migrate in the fluid system, while Fe is a relatively stable component in the fluid system [74]. Through the comparison of LILEs and TFeO (Figure 5d), some high- and normal-grade iron ores have similar LILEs, indicating that both are products of primitive sedimentation, while the LILE contents in the other high-grade iron ores are relatively lower than those of normal-grade iron ores, indicating that the fluid hydrothermal system altered the normal-grade iron ore in the later stage. (5) The Eu/Eu* values of high-grade iron ore (1.25–2.82, with an average of 1.72) are slightly higher than those of low-grade iron ore (1.25–3.07, with an average of 1.66), indicating that the primitive sedimentary high-grade iron ore has high Eu/Eu* values, while the later hydrothermal alteration of the normal-grade iron ore reduces the Eu/Eu* values [84]. Frei et al. (2008) [85] proposed that the Pre-Cambrian BIF showed a significant decrease in Eu/Eu* values as the Earth cooled and the hydrothermal activity decreased; thus, the Eu/Eu* values of the Sijiaying BIF are generally lower than 1.8. Thus, the Sijiaying deposit has high-grade iron ores of primitive sedimentation and hydrothermal alteration, and the geological and geochemical field characteristics can adequately distinguish between the two types of high-grade iron ores.

Metamorphism has little influence on the migration of REYs; however, high-temperature hydrothermal alteration may lead to decreases in REEs, Sr and Eu in ores and corresponding increases in Mn and Fe in rocks [86,87]. In this study, as the iron ore grade increases, the REE partitioning curve gradually decreases (Figure 5a), indicating that hydrothermal activity is a key factor affecting the iron ore grade. Pb and Sr, as two important LILEs, are generally lower in content in high-grade iron ore than in BIF, indicating that the fluid removes them during the process of iron formation. In addition, the zircon particles in the wall rock of the roof and floor are euhedral, with the influence of zircon edge dissolution recrystallization, a decrease in the Th/U ratio, and weak positive Ce anomalies. Moreover, the $(\text{Sm}/\text{La})_{\text{CN}}\text{-La}$ and $\text{Ce}/\text{Ce}^*-(\text{Sm}/\text{La})_{\text{CN}}$ discrimination diagrams (Figure 9b,c) show a distribution trend from magmatic zircon to hydrothermal zircon, indicating that it was mainly magmatic zircon that underwent multiple hydrothermal alterations. The lower intercept age of these zircons was 2404 ± 170 Ma, which corresponds to the time of migmatization after regional metamorphism. The zircon SHRIMP U–Pb dating results of the Sijiaying potassic granite by Zhang et al. (2012) [88] indicate that the late-Neoproterozoic era was the main period of migmatization. Hence, the 2404 ± 170 Ma migmatization was most likely the provider of the hydrothermal solution that altered the Sijiaying normal-grade iron ore.

In eastern Hebei, the location of high-grade iron ore is closely related to migmatization [89]. Large-scale development of high-grade iron ore is visible in the Qianxi and Luanxian rock groups, where migmatization is present, while no high-grade iron ore is visible in the Zhuzhangzi Group without migmatization [16]. Furthermore, there are high-grade orebodies adjacent to migmatite in the mining area, and hydrothermal alteration near the high-grade orebodies is significant (Figures 3e and 4e,f). Potassium migmatization occurs more readily at the location where interlayer faults and fractures are developed, and the grade of the surrounding iron formation is also significantly improved [30] (Figure 3d). Accordingly, this study identified the primitive sedimentary type and hydrothermally altered type of high-grade iron ore from the ore texture, structure, and geochemical characteristics. Although the detailed alteration process and mechanism are not clear, we preliminarily suggest that the genesis of high-grade ores is probably related to the hydrothermal process of migmatization, which may lead to the desilication of adjacent BIFs [14].

5.4. Genetic Model of Ore Deposits

As mentioned in Sections 5.1–5.3, marine volcanic activity occurred in the eastern Hebei region during the Paleoproterozoic; however, no large-scale BIFs were formed in the southern Luanxian area. Our study supports the view that a stable basement was formed in the NCC through the merging of several microblocks in the late-Neoproterozoic era [21–23,90]. Meanwhile, an ancient island arc setting developed in eastern Hebei, and back-arc extension formed a hot spot in the basin. Along the hot spot spreading center, the hydrothermal fluid of submarine volcanic activity brought a large amount of Fe^{2+} to the deep seawater. When the hydrothermal flux exceeded the oceanic oxidation state, the deep seawater was in an anoxic reductive state [74], which was conducive to the aggregation and migration of Fe^{2+} [91,92]. However, when Fe^{2+} was transported via ocean currents to a shallow water setting at the edge of a back-arc basin, which was far from the hydrothermal vent, and the hydrothermal flux was insufficient to change the ocean's oxidation state, Fe^{2+} would quickly be oxidized to Fe^{3+} , which could deposit together with Si supplied by the surrounding seawater to form BIFs (Figure 13a) [18].

After mineralization, a regional tectonic–metamorphic event occurred. The BIF experienced regional metamorphism of amphibolite facies and developed multistage fold deformation. Some primitive sedimentary-type high-grade iron ores were distributed in favorable structural positions (Figure 13b). When regional metamorphism developed to a certain stage, intense migmatization occurred. The migmatization hydrothermal fluid migrated along the fold and fault structures formed in the early stage and accelerated iron

formation, meaning that the magnetite in the primitive iron layer was reorganized and enriched, forming hydrothermally altered high-grade iron ores (Figure 13c) [6,93–96].

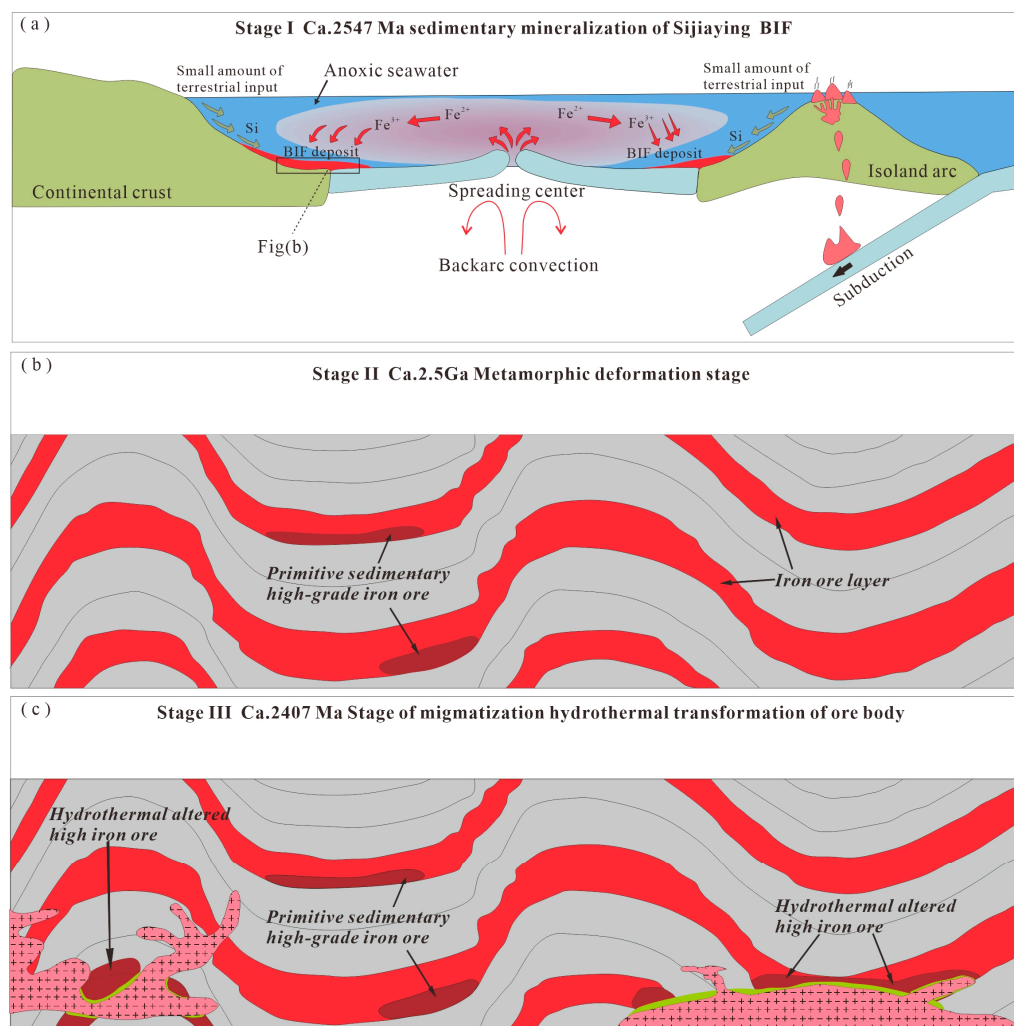


Figure 13. Depositional model for Sijiaying BIF. (a) Sedimentary metallogenic model of Sijiaying iron deposit; (b) BIF is affected by regional tectonic-metamorphic events; (c) the genetic model of altered high-grade iron ores.

6. Conclusions

On the basis of a detailed geological field survey of the Sijiaying BIF, this study conducted geochemical analysis of the iron orebody and ore-bearing strata. Our research draws the following conclusions:

- (1) The Sijiaying BIF is the source of ore-forming materials provided via submarine volcanic hydrothermal solution, which was mineralized in an anoxic paleo-ocean.
- (2) There are two types of high-grade iron ores in the deposit: primitive sedimentary and hydrothermally altered iron ores. Primitive sedimentary high-grade iron ores are of the same mineralization age as BIFs, while hydrothermally altered high-grade iron ores were formed later than BIFs.
- (3) The biotite–leptynite that is closely related to the orebody was formed at 2547 ± 6 Ma, which represents the main mineralization age of the iron formation. After mineralization, it underwent regional metamorphism (~ 2500 Ma) and migmatization (2407 ± 170 Ma). Migmatization is the process that most likely provided a hydrothermal solution to alter iron orebodies and improve ore grades.

In summary, the Sijiaying iron deposit is an Algoma-type BIF of the late-Neoproterozoic era that formed in an island arc setting and is closely related to volcanic marine sedimentation.

Author Contributions: Conceptualization, X.G. and D.W.; Data curation, X.G.; Formal analysis, X.G.; Funding acquisition, D.W. and Y.W.; Investigation, X.G. and D.W.; Project administration, D.W., F.H. and Y.W.; Resources, D.W. and F.H.; Software, X.G.; Validation, X.G., D.W., F.H., Y.W. and C.W.; Visualization, X.G.; Writing—original draft, X.G.; Writing—review and editing, X.G. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the project of “Geology of mineral resources in China” from China Geological Survey (Grant No. DD20221695, DD20190379, DD20160346).

Acknowledgments: This study was funded by “Geology of mineral resources in China” project from China Geological Survey (Grant No. DD20221695, DD20190379, DD20160346). The fieldwork was strongly supported by the Hebei Iron and Steel Group Mining Company, which is hereby acknowledged.

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

References

1. Gross, G.A. A classification of iron formations based on depositional environments. *Canad. Miner.* **1980**, *18*, 215–222.
2. Klein, C. Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, meta-morphism, geochemistry, and origin. *Am. Miner.* **2005**, *90*, 1473–1499. [CrossRef]
3. Shen, B.F.; Zhai, A.M.; Miao, P.S.; Sima, X.Z.; Li, J.J. Geological character and potential resources of iron deposits in the north China block. *Geol. Surv. Res.* **2006**, *29*, 244–252. (In Chinese with English Abstract)
4. Zhang, Z.C.; Hou, T.; Santosh, M.; Li, H.M.; Zhang, Z.H.; Song, X.Y.; Wang, M. Spatio-temporal distribution and tectonic settings of the major iron deposits in China: An overview. *Ore Geol. Rev.* **2014**, *57*, 247–263. [CrossRef]
5. Li, H.M.; Zhang, Z.J.; Li, L.X.; Zhang, Z.C.; Chen, J.; Yao, T. Types and general characteristics of the BIF-related iron deposits in China. *Ore Geol. Rev.* **2014**, *57*, 264–287. [CrossRef]
6. Li, H.M.; Wang, D.H.; Li, L.X.; Chen, J.; Yang, X.Q.; Liu, M.J. Metallogeny of iron deposits and resource potential of major iron minerogenetic units in China. *Geol. China* **2012**, *39*, 559–580. (In Chinese with English Abstract)
7. Zhang, L.C.; Zhai, M.G.; Wan, Y.S.; Guo, J.H.; Dai, Y.P.; Wang, C.L.; Liu, L. Study of the Precambrian BIF-iron deposits in the North China Craton: Progresses and questions. *Acta Petrol. Sin.* **2012**, *28*, 3431–3445. (In Chinese with English Abstract)
8. Gao, X.Y.; Wang, D.H.; Chen, Y.C.; Huang, F.; Wang, C.H.; Di, Y.J. Metallogenic series and prospecting direction of iron deposits in north China block. *Acta Geosci. Sin.* **2022**, *10*, 1–16. Available online: <http://kns.cnki.net/kcms/detail/11.3474.P.20221019.1629.002.html> (accessed on 7 May 2023). (In Chinese with English Abstract)
9. Chen, G.Y.; Li, M.H.; Wang, X.F.; Sun, D.S.; Sun, C.M.; Wang, Z.F.; Su, Y.X.; Lin, J.X. The genetical mineralogy of garnets from Gongchangling, China. *Mineral. Petrol.* **1984**, *4*, 1–254. (In Chinese with English Abstract)
10. Wan, Y.S. *Formation and Evolution of Iron Bearing Rock Series in Gongchangling, Liaoning*; Beijing Science and Technology Press: Beijing, China, 1993; pp. 1–108. (In Chinese)
11. Li, Y.H.; Zhang, Z.J.; Hou, K.J.; Duan, C.; Wan, D.F.; Hu, G.Y. The Genesis of Gongchangling High-Grade-Iron Ores, Anshan-Benxi Area, Liaoning Province, NE China: Evidence from Fe-Si-O-S Isotopes. *Acta Geol. Sin.* **2014**, *88*, 2351–2372. (In Chinese with English Abstract) [CrossRef]
12. Cheng, Y.Q. Problems on the genesis of the high-grade ore in the pre-sinian (precambrian) Banded iron ore deposits of the Anshan-type of Liaoning and Shantung provinces. *Acta Geol. Sin.* **1957**, *37*, 153–178. (In Chinese with English Abstract)
13. Guan, G.Y. On the significance of metamorphism in the formation of Anshan type iron ore deposits. *Acta Geol. Sin.* **1961**, *1*, 65–76. (In Chinese with English Abstract)
14. Li, H.M.; Li, Y.H.; Li, L.X.; Li, Z.H.; Fu, J.F.; Hou, K.J.; Fan, C.F. Re-forming conditions of the sedimentary metamorphic iron deposit and metallogenesis of the high-grade iron deposit. *Acta Geol. Sin.* **2022**, *96*, 3211–3233. (In Chinese with English Abstract). [CrossRef]
15. Chen, Y.C.; Xue, C.J.; Wang, D.H.; Li, H.Q.; Lu, Y.F. A discussion on the regional mineralizing pedigree of the ore deposits in the northern margin of the north China landmass. *Geol. J. China Univ.* **2003**, *9*, 520–535.
16. Qian, X.L.; Cui, W.Y.; Wang, S.Q.; Wang, G.Y. *Geology of Precambrian Iron Deposits in Eastern Hebei Province*; Hebei Science and Technology Press: Shijiazhuang, China, 1985; pp. 1–273. (In Chinese)
17. Cui, M.L.; Zhang, L.C.; Wu, H.Y.; Xu, Y.X.; Li, W.J. Timing and tectonic setting of the Sijiaying banded iron deposit in the eastern Hebei province, North China Craton: Constraints from geochemistry and SIMS zircon U–Pb dating. *J. Asian Earth Sci.* **2014**, *94*, 240–251. [CrossRef]

18. Wang, C.L.; Wu, H.Y.; Li, W.J.; Peng, Z.D.; Zhang, L.C.; Zhai, M.G. Changes of Ge/Si, REE+Y and Sm-Nd isotopes in alternating Fe- and Si-rich mesobands reveal source heterogeneity of the ~2.54 Ga Sijiaying banded iron formation in Eastern Hebei, China. *Ore Geol. Rev.* **2017**, *80*, 363–376. [\[CrossRef\]](#)
19. Zhao, G.C.; Wilde, S.A.; Cawood, P.A.; Sun, M. Archean blocks and their boundaries in the North China Craton: Lithological, geochemical, structural and P-T path constraints and tectonic evolution. *Precamb. Res.* **2001**, *107*, 45–73. [\[CrossRef\]](#)
20. Zhao, G.C.; Sun, M.; Wilde, S.A.; Li, S.Z. Late Archean to Paleoproterozoic evolution of the North China Craton: Key issues revisited. *Precamb. Res.* **2005**, *136*, 177–202. [\[CrossRef\]](#)
21. Zhai, M.G.; Santosh, M. The early Precambrian odyssey of the North China Craton: A synoptic overview. *Gondwana Res.* **2011**, *20*, 6–25. [\[CrossRef\]](#)
22. Zhai, M.G.; Santosh, M. Metallogeny of the North China Craton: Link with secular changes in the evolving Earth. *Gondwana Res.* **2013**, *24*, 275–297. [\[CrossRef\]](#)
23. Zhai, M.G. Multi-stage crustal growth and cratonization of the North China Craton. *Geosci. Front.* **2014**, *5*, 457–469. [\[CrossRef\]](#)
24. Shen, B.F.; Zhai, A.M.; Yang, C.L.; Cao, X.L. Temporal-spatial distribution and evolutionary characters of Precambrian iron deposits in China. *Geol. Surv. Res.* **2005**, *28*, 196–206. (In Chinese with English Abstract)
25. Nutman, A.P.; Wan, Y.S.; Du, L.L.; Friend, R.L.; Dong, C.Y.; Xie, H.Q.; Wang, W.; Sun, H.Y.; Liu, D.Y. Multistage late Neoproterozoic crustal evolution of the North China Craton, eastern Hebei. *Precambrian Res.* **2011**, *189*, 43–65. [\[CrossRef\]](#)
26. Jahn, B.M.; Auvray, B.; Cornichet, J.; Bai, Y.L.; Shen, Q.H.; Liu, D.Y. 3.5 Ga old amphibolites from eastern Hebei Province, China: Field occurrence, petrography, Sm-Nd isochron age and REE geochemistry. *Precambrian Res.* **1987**, *34*, 311–346. [\[CrossRef\]](#)
27. Liu, D.Y.; Nutman, A.P.; Compston, W.; Wu, J.S.; Shen, Q.H. Remnants of ≥ 3800 Ma crust in the Chinese part of the Sino-Korean craton. *Geology* **1992**, *20*, 339. [\[CrossRef\]](#)
28. Han, C.M.; Xiao, W.J.; Su, B.X.; Chen, Z.L.; Zhang, X.H.; Ao, S.J.; Zhang, J.E.; Zhang, Z.Y.; Wan, B.; Song, D.F.; et al. Neoproterozoic Algoma-type banded iron formations from Eastern Hebei, North China Craton: SHRIMP U-Pb age, origin and tectonic setting. *Precambrian Res.* **2014**, *251*, 212–231. [\[CrossRef\]](#)
29. Wan, Y.S.; Dong, C.Y.; Jie, H.Q.; Wang, S.J.; Song, M.C.; Xu, Z.Y.; Wang, S.Y.; Zhou, H.Y.; Ma, M.Z.; Liu, D.Y. Formation Ages of Early Precambrian BIFs in the North China Craton: SHRIMP Zircon U-Pb Dating. *Acta Geol. Sin.* **2012**, *86*, 1447–1478. (In Chinese with English Abstract)
30. Gao, X.Y.; Wang, D.H.; Huang, F.; Wang, Y.; Guo, W.M. Discussion on deep prospecting of Sijiaying iron deposit in eastern Hebei Province. *Acta Geol. Sin.* **2022**, *96*, 2494–2505. (In Chinese with English Abstract) [\[CrossRef\]](#)
31. Xu, Y.X.; Zhang, L.F.; Gao, X.M.; Li, H.M.; Jia, D.S.; Li, L.X. Metallogenic Conditions of High-grade Ores in the Sijiaying Sedimentary Metamorphic Iron Deposit, Eastern Hebei Province. *Geol. Explor.* **2014**, *50*, 675–688. (In Chinese with English Abstract)
32. Xu, Y.X.; Zhang, L.F.; Li, H.M.; Li, L.X.; Gao, X.M.; Jia, D.S. The Exploration Model of the Sijiaying Sedimentary Metamorphic Iron Deposit in Eastern Hebei Province. *Geol. Explor.* **2015**, *51*, 23–35. (In Chinese with English Abstract)
33. Hou, K.; Li, Y.; Tian, Y.Y. In situ U-Pb zircon dating using laser ablation-multi ion counting-ICP-MS. *Miner. Depos.* **2009**, *28*, 481–492. (In Chinese with English Abstract)
34. Nasdala, L.; Hofmeister, W.; Norberg, N.; Mattinson, J.M.; Corfu, F.; Dor, W.; Kamo, S.L.; Kennedy, A.K.; Kronz, A.; Reiners, P.W.; et al. Zircon M257—A homogeneous natural reference material for the ion microprobe U-Pb analysis of zircon. *Geostand. Geoanal. Res.* **2008**, *32*, 247–265. [\[CrossRef\]](#)
35. Ludwig, K.R. *User's Manual for Isoplot3.0: A Geochronological Toolkit for Microsoft Excel*; Berkeley Geochronology Center: Berkeley, CA, USA, 2003; pp. 1–71.
36. Pourmand, A.; Dauphas, N.; Ireland, T.J. A novel extraction chromatography and MC-ICP-MS technique for rapid analysis of REE, Sc and Y: Revising CI-chondrite and Post-Archean Australian Shale (PAAS) abundances. *Chem. Geol.* **2012**, *291*, 38–54. [\[CrossRef\]](#)
37. Sun, S.S.; McDougall, W.F. Chemical and Isotopic Systematics of Oceanic Basalts: Implications for Mantle Composition of the Earth and Mantle Evolution. *Earth Planet. Sci. Lett.* **1989**, *35*, 429–448. [\[CrossRef\]](#)
38. Alibo, D.S.; Nozaki, Y. Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. *Geochim. Cosmochim. Acta* **1999**, *63*, 363–372. [\[CrossRef\]](#)
39. Bau, M.; Dulski, P. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: Implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chem. Geol.* **1999**, *155*, 77–90. [\[CrossRef\]](#)
40. Shi, C.Y.; Yan, M.C.; Liu, C.M.; Chi, Q.H.; Hu, S.Q.; Gu, T.X.; Bu, W.; Yan, W.D. Abundances of chemical elements in granitoids of China and their characteristics. *Geochimica* **2005**, *5*, 470–482. (In Chinese with English Abstract)
41. Mogahed, M.; Abdelfadil, K.M. Constraints of Mantle and Crustal Sources Interaction during Orogenesis of Pre- and Post-Collision Granitoids from The Northern Arabian-Nubian Shield: A Case Study from Wadi El-Akhder Granitoids, Southern Sinai, Egypt. *Acta Geol. Sin.-Engl. Ed.* **2021**, *95*, 1527–1550. [\[CrossRef\]](#)
42. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution: An Examination of the Geochemical Record Preserved in Sedimentary Rocks*; Blackwell Science: Oxford, UK, 1985; pp. 1–312.

43. Hoskin, P.W.O.; Black, L.P. Metamorphic zircon formation by solid-state recrystallization of protolith igneous zircon. *Metamorph. Geol.* **2000**, *18*, 423–439. [\[CrossRef\]](#)
44. Vavra, G.; Gebauer, D.; Schmid, R.; Compston, W. Multiple zircon growth and recrystallization during polyphase Late Carboniferous to Triassic metamorphism in granulites of the Ivrea Zone (Southern Alps): An ion microprobe (SHRIMP) study. *Contrib. Miner. Pet.* **1996**, *122*, 337–358. [\[CrossRef\]](#)
45. Hoskin, P.W.O. Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. *Geochim. Cosmochim. Acta* **2005**, *69*, 637–648. [\[CrossRef\]](#)
46. Wu, Y.B.; Zheng, Y.F. Genetic mineralogy of zircons and its constraints on U–Pb age interpretation. *Chin. Sci. Bull.* **2004**, *49*, 1589–1604. (In Chinese with English Abstract) [\[CrossRef\]](#)
47. Pickard, A.L. SHRIMP U–Pb zircon ages for the Palaeoproterozoic Kuruman Iron Formation, northern Cape Province, South Africa: Evidence for simultaneous BIF deposition on Kaapvaal and Pilbara craton. *Precambrian Res.* **2003**, *125*, 275–315. [\[CrossRef\]](#)
48. Zhou, J.X.; Chen, Z.Y. *Study on Cathodoluminescence of Zircon under Electron Probe*; University of Electronic Science and Technology Press: Chengdu, China, 2007; pp. 1–104. (In Chinese)
49. Hinton, R.W.; Upton, B.G.J. The chemistry of zircon: Variations within and between large crystals from syenite and alkali basalt xenoliths. *Geochim. Cosmochim. Acta* **1991**, *55*, 3287–3302. [\[CrossRef\]](#)
50. Hanchar, J.M.; Miller, C.F. Zircon zonation patterns as revealed by cathodoluminescence and backscattered electron images: Implications for interpretation of complex crustal histories. *Chem. Geol.* **1993**, *110*, 1–13. [\[CrossRef\]](#)
51. Corfu, F.; Hanchar, J.M.; Hoskin, P.W.O.; Kinny, P. Atlas of zircon textures. *Rev. Mineral. Geochem.* **2003**, *53*, 469–500. [\[CrossRef\]](#)
52. Schaltegger, U.; Fanning, C.M.; Günther, D.; Maurin, J.C.; Schulmann, K.; Gebauer, D. Growth, annealing and recrystallization of zircon and preservation of monazite in high-grade metamorphism: Conventional and in-situ U–Pb isotope, cathodoluminescence and microchemical evidence. *Contrib. Miner. Pet.* **1999**, *134*, 186–201. [\[CrossRef\]](#)
53. Shen, Q.H.; Zhang, Z.Q.; Xia, M.X.; Wang, X.Y.; Lu, J.Y. Rb–Sr Age Determination on the Late Archean Ferrosiliceous Rock Series in Sijiaying, Luanxian, Hebei. *Geol. Rev.* **1981**, *27*, 207–212. (In Chinese with English Abstract)
54. Mahdy, N.M.; Ntafos, T.; Pease, V.; Sami, M.; Slobodnik, M.; Abu Steet, A.A.; Abdelfadil, K.M.; Fathy, D. Combined zircon U–Pb dating and chemical Th–U–total Pb chronology of monazite and thorite, Abu Diab A-type granite, Central Eastern Desert of Egypt: Constraints on the timing and magmatic-hydrothermal evolution of rare metal granitic magmatism in the Arabian Nubian Shield. *Geochemistry* **2020**, *80*, 125669.
55. Li, W.J.; Jin, X.D.; Cui, M.L.; Wang, C.L. Characteristics of rare earth elements, trace elements and geological significations of BIF from Sijiaying in eastern Hebei. *Acta Petrol. Sin.* **2012**, *28*, 3670–3678. (In Chinese with English Abstract)
56. Wang, R.M. *Graphic Discrimination of Metamorphic Rock*; Geological Publishing House: Beijing, China, 1981; pp. 1–199. (In Chinese)
57. Winchester, J.A.; Floyd, P.A. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chem. Geol.* **1977**, *20*, 325–343. [\[CrossRef\]](#)
58. Huston, D.L.; Logan, G.A. BIFs and bugs: Evidence for the evolution of the Earth’s early hydrosphere. *Earth Planet. Sci. Lett.* **2004**, *220*, 41–55. [\[CrossRef\]](#)
59. Planavsky, N.; Bekker, A.; Rouxel, O.J.; Kamber, B.; Hofmann, A.; Knudsen, A.; Timothy, W.L. Rare earth element and yttrium compositions of Archean and Paleoproterozoic Fe formations revisited: New perspectives on the significance and mechanisms of deposition. *Geochim. Cosmochim. Acta* **2010**, *74*, 6387–6405. [\[CrossRef\]](#)
60. Cox, G.M.; Halverson, G.P.; Minarik, W.G.; Heron, D.P.L.; Macdonald, F.A.; Bellefroid, E.J.; Strauss, J.V. Neoproterozoic iron formation: An evaluation of its temporal, environmental and tectonic significance. *Chem. Geol.* **2013**, *362*, 232–249. [\[CrossRef\]](#)
61. Pearce, J.A.; Harris, N.B.; Tindle, A.G. Trace element discrimination diagrams for the interpretation of granitic rocks. *J. Petrol.* **1984**, *25*, 957–983. [\[CrossRef\]](#)
62. Pearce, J.A. Trace Element Characteristics of Lavas from Destructive Plate Boundaries. In *Orogenic Andesites and Related Rocks*; Thorpe, R.S., Ed.; J. Wiley and Sons: Chichester, UK, 1982; pp. 525–547.
63. Zhang, L.C.; Zhai, M.G.; Zhang, X.J.; Xiang, P.; Dai, Y.P.; Wang, C.L.; Pirajno, F. Formation age and tectonic setting of the Shirengou Neoproterozoic banded iron deposit in eastern Hebei Province: Constraints from geochemistry and SIMS zircon U–Pb dating. *Precambrian Res.* **2012**, *222–223*, 325–338. [\[CrossRef\]](#)
64. Zhang, X.J.; Zhang, L.C.; Xiang, P.; Wan, B.; Pirajno, F. Zircon U–Pb age, Hf isotopes and geochemistry of Shuichang Algoma-type banded iron-formation, North China Craton: Constraints on the ore-forming age and tectonic setting. *Gondwana Res.* **2011**, *20*, 137–148. [\[CrossRef\]](#)
65. Li, Y.H.; Zhang, Z.J.; Wu, J.S.; Shang, L.P. Metamorphic chronology of the BIF in Malanzhuang of eastern Hebei Province and its geological implications. *Miner. Depos.* **2011**, *30*, 645–653. (In Chinese with English Abstract)
66. Dirks, P.; Hand, M. Structural and metamorphic controls on the distribution of zircon in an evolving quartzofeldspathic migmatite: An example from the Reynold Range, central Australia. *Metamorph. Geol.* **1991**, *9*, 191–201. [\[CrossRef\]](#)
67. Andersson, J.; Möller, C.; Johansson, L. Zircon geochronology of migmatite gneisses along the Mylonite Zone (S Sweden): A major Sveconorwegian terrane boundary in the Baltic Shield. *Precambrian Res.* **2002**, *114*, 121–147. [\[CrossRef\]](#)
68. Li, L.X.; Li, H.M.; Xu, Y.X.; Chen, J.; Yao, T.; Zhang, L.F.; Yang, X.Q.; Liu, M.J. Zircon growth and ages of migmatites in the Algoma-type BIF-hosted iron deposits in Qianxi Group from eastern Hebei Province, China: Timing of BIF deposition and anatexis. *J. Asian Earth Sci.* **2015**, *113*, 1017–1034. [\[CrossRef\]](#)

69. Bonatti, E. Metallogenesis at oceanic spreading centers. *Annu. Rev. Earth Planet. Sci.* **1975**, *3*, 401–433. [\[CrossRef\]](#)
70. Bolhar, R.; Kamber, B.S.; Moorbath, S.; Fedo, C.M.; Whitehouse, M.J. Characterisation of early Archaean chemical sediments by trace element signatures. *Earth Planet. Sci. Lett.* **2004**, *222*, 43–60. [\[CrossRef\]](#)
71. German, C.R.; Masuzawa, T.; Greaves, M.J.; Elderfield, H.; Edmond, J.M. Dissolved rare earth elements in the Southern Ocean: Cerium oxidation and the influence of hydrography. *Geochim. Cosmochim. Acta* **1995**, *59*, 1551–1558. [\[CrossRef\]](#)
72. Bau, M. Rare-earth element mobility during hydrothermal and metamorphic fluid rock interaction and the significance of the oxidation state of europium. *Chem. Geol.* **1991**, *93*, 219–230. [\[CrossRef\]](#)
73. Douville, E.; Bienvenu, P.; Charlou, J.L.; Donval, J.P.; Fouquet, Y.; Appriou, P.; Gamo, T. Yttrium and rare earth elements in fluids from various deep-sea hydrothermal systems. *Geochim. Cosmochim. Acta* **1999**, *63*, 627–643. [\[CrossRef\]](#)
74. Bekker, A.; Slack, J.F.; Planavsky, N.; Krapež, B.; Hofmann, A.; Konhauser, K.O.; Rouxel, O.J. Iron formation: The sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. *Econ. Geol.* **2010**, *105*, 467–508. [\[CrossRef\]](#)
75. Slack, J.F.; Grenne, T.; Bekker, A.; Rouxel, O.J.; Lindberg, P.A. Suboxic deep seawater in the late Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. *Earth Planet. Sci. Lett.* **2007**, *255*, 243–256. [\[CrossRef\]](#)
76. Wonder, J.; Spry, P.; Windom, K. Geochemistry and origin of manganese-rich rocks related to iron formation and sulfide deposits, western Georgia. *Econ. Geol.* **1988**, *83*, 1070–1081. [\[CrossRef\]](#)
77. Alexander, B.W.; Bau, M.; Andersson, P.; Dulski, P. Continently derived solutes in shallow Archean seawater: Rare earth element and Nd isotope evidence in iron formation from the 2.9 Ga Pongola Supergroup, South Africa. *Geochim. Cosmochim. Acta* **2008**, *72*, 378–394. [\[CrossRef\]](#)
78. Bau, M.; Dulski, P. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Res.* **1996**, *79*, 37–55. [\[CrossRef\]](#)
79. Kamber, B.S.; Webb, G.E. The geochemistry of late Archaean microbial carbonate: Implications for ocean chemistry and continental erosion history. *Geochim. Cosmochim. Acta* **2001**, *65*, 2509–2525. [\[CrossRef\]](#)
80. Gross, G.A. Tectonic systems and the deposition of iron formation. *Precambrian Res.* **1983**, *20*, 171–187. [\[CrossRef\]](#)
81. Li, S.G.; Hou, Z.H.; Yang, Y.C.; Sun, W.D.; Zhang, G.W.; Li, Q.L. Geochemical characteristics and formation age of Sanchazi paleo-magmatic arc in Mianle tectonic belt, South Qinling. *Sci. Sin.* **2003**, *33*, 1163–1173. (In Chinese)
82. Dai, Y.P.; Zhang, L.C.; Zhu, M.T.; Wang, C.L.; Liu, L.; Peng, X. The composition and genesis of the Mesoarchean Dagushan banded iron formation (BIF) in the Anshan area of the North China Craton. *Ore Geol. Rev.* **2014**, *63*, 353–373. [\[CrossRef\]](#)
83. Zhu, M.T.; Dai, Y.P.; Zhang, L.C.; Wang, C.L.; Liu, L. Geochronology and geochemistry of the Nanfen iron deposit in the Anshan-Benxi area, North China Craton: Implications for ~2.55 Ga crustal growth and the genesis of high-grade iron ores. *Precambrian Res.* **2015**, *260*, 23–38. [\[CrossRef\]](#)
84. Danielson, A.; Moller, P.; Dulski, P. The europium anomalies in banded iron formations and the thermal history of the oceanic crust. *Chem. Geol.* **1992**, *97*, 89–100. [\[CrossRef\]](#)
85. Frei, R.; Dahl, P.S.; Duke, E.F.; Frei, K.M.; Hansen, T.R.; Frandsson, M.M.; Jensen, L.A. Trace element and isotopic characterization of Neoarchaean and Paleo-proterozoic iron formations in the Black Hills (South Dakota, USA): Assessment of chemical change during 2.9–1.9 Ga deposition bracketing the 2.4–2.2 Ga first rise of atmospheric oxygen. *Precambrian Res.* **2008**, *162*, 441–474. [\[CrossRef\]](#)
86. Bau, M.; Möller, P. Rare earth element systematics of the chemically precipitated component in early Precambrian iron formations and the evolution of the terrestrial atmosphere–hydrosphere–lithosphere system. *Geochim. Cosmochim. Acta* **1993**, *57*, 2239–2249. [\[CrossRef\]](#)
87. Veizer, J.; Ala, D.; Azmy, K.; Bruckschen, P.; Buhl, D.; Bruhn, F.; Carden, G.A.F.; Diener, A.; Ebner, S.; Godderis, Y.; et al. $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater. *Chem. Geol.* **1999**, *161*, 59–88. [\[CrossRef\]](#)
88. Zhang, L.F.; Xu, Y.X.; Gao, X.M.; Li, H.M.; Jia, D.S.; Li, L.X.; Wang, Y.; Feng, H.Y. SHRIMP U–Pb Chronology of Zircon from Potassified Granite of Sijiaying Iron Mine in Eastern Hebei Province. *Miner. Depos.* **2012**, *31* (Suppl. 1), 163–164. (In Chinese)
89. Shen, Q.H.; Song, H.X. Progress, prospecting and key scientific problems in origin researches of high-grade iron ore of the banded iron formation (BIF) in the North China Craton. *Acta Petrol. Sin.* **2015**, *31*, 2795–2815. (In Chinese with English Abstract)
90. Zhai, M.G.; Guo, J.H.; Liu, W.J. Neoproterozoic to Paleoproterozoic continental evolution and tectonic history of the North China craton. *Asian Earth Sci.* **2005**, *24*, 547–561. [\[CrossRef\]](#)
91. Johnson, C.M.; Beard, B.L.; Beukes, N.J.; Klein, C.; O’Leary, J.M. Ancient geochemical cycling in the Earth as inferred from Fe isotope studies of banded iron formations from the Transvaal Craton. *Contrib. Mineral. Petrol.* **2003**, *144*, 523–547. [\[CrossRef\]](#)
92. Planavsky, N.J.; Rouxel, O.J.; Bekker, A.; Hoffmann, A.; Little, C.T.; Lyons, T.W. Iron isotope composition of some Archean and Proterozoic iron formations. *Geochim. Cosmochim. Acta* **2012**, *80*, 158–169. [\[CrossRef\]](#)
93. Zhang, Q.S. *Geology and Mineralization of Early Precambrian in China*; Jilin People’s Publishing House: Jilin, China, 1984; pp. 1–536. (In Chinese)
94. Li, Y.; Zou, H.; Said, N.; Liu, H. A new classification of barite deposits in China. *Ore Energy Resour. Geol.* **2023**, *14*, 100019. [\[CrossRef\]](#)

95. Cao, H.W.; Pei, Q.M.; Santosh, M.; Li, G.M.; Zhang, L.K.; Zhang, X.F.; Zhang, Y.H.; Zou, H.; Dai, Z.F.; Lin, B.; et al. Himalayan leucogranites: A review of geochemical and isotopic characteristics, timing of formation, genesis, and rare metal mineralization. *Earth-Sci. Rev.* **2022**, *234*, 104229. [[CrossRef](#)]
96. Cao, H.W.; Pei, Q.M.; Yu, X.; Cao, A.B.; Chen, Y.; Liu, H.; Zhang, K.; Liu, X.; Zhang, X.F. The long-lived partial melting of the Greater Himalayas in southern-Tibet, constraints from the Miocene Gyirong anatectic pegmatite and its prospecting potential for rare element minerals. *China Geol.* **2023**, *6*, 303–321.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.