

Article

Metallogenic Process of Forming the Large Xiangcaowa Karstic Bauxite Deposit from the Southern Margin of the North China Craton

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Abstract: North China Craton (NCC) formed the world's largest karstic bauxite belt in the Late Carboniferous, with significant variations in metallogenic sources and conditions, which affect the overall understanding of karstic bauxite genesis. The Xiangcaowa bauxite deposit in the southern NCC is a large deposit of uncertain provenance and genesis. This study employed geological, mineralogical, and chronology analysis to investigate the sources and genesis of Xiangcaowa bauxite, further contributing to a full understanding of the origin of bauxite throughout the NCC. Xiangcaowa ore-bearing rock series is composed of bauxite and claystone layers. The composition of bauxite ore encompasses diasporite, kaolinite, anatase, pyrite, zircon, and rutile. Widely developed mineral assemblages, such as diasporite–anatase–pyrite, indicate that bauxite is mainly formed in reducing and alkaline karstic depressions. Detrital zircons, aged ~450, ~520, ~950, and ~1100 Ma, predominantly originate from igneous rocks in the North Qinling Orogenic Belt (NQOB), and the ~1650 and ~2400 Ma zircon age populations are primarily from the southern margin of the NCC. Detrital rutiles, which are concentrated in 800–510 Ma, are primarily from the metamorphic rocks of the South Qinling Orogenic Belt (SQOB); rutiles aged ~1500–910 Ma are primarily from metamorphic rocks in the NQOB. These results confirm that the principal sources of the bauxite are the igneous and metamorphic rocks within the NQOB, along with the metamorphic rocks of the SQOB, while the basement rocks of the NCC contribute only minorly to its formation. A large karstic bauxite deposit was formed by the transport of large amounts of weathered material into extensive karstic depressions where reducing and alkaline conditions favoured diasporite deposition.



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Keywords: karstic bauxite; bauxite provenance; North Qinling Orogenic Belt; detrital rutile; detrital zircon

1. Introduction

The classification of bauxite deposits depends on the lithology of the bedrock, with two main types being distinguished: karstic and lateritic [1,2]. The lateritic bauxite is used to refer to bauxite that is found overlying aluminosilicate rocks, while karstic bauxite denotes bauxite that is found overlying karstic carbonate rocks [3]. Over 95% of bauxites in China are karstic, which are concentrated in Henan, Shanxi, Guangxi, and Guizhou provinces, while a small amount of lateritic bauxite is mostly distributed in Hainan and Fujian provinces [4].

Despite fruitful studies on the source and depositional conditions of bauxite in the North China Craton (NCC), the complex formation process and variable provenance make it still ambiguous [5,6]. Previous studies on the mineralogy and sulfur isotopic composition in the southern margin of the NCC (S-NCC) reveal bauxite was formed under reducing and alkaline conditions [7], whereas bauxite in Shanxi was precipitated in an alkaline suboxidized to alkaline subreduced environment [8]. Karstic bauxite is rich in detrital minerals, indicating complex sources [6]. Bainaimiao Arc Terrane are the main provenance of bauxite in the northern portion of the NCC, while North Qinling Orogenic Belt (NQOB) is the main source in the southern boundary. The central portion of NCC is a mixed source. Volcanic activity is also involved in bauxitization [6,9,10]. Given the complexity of the bauxite metallogenic environment and the diversity of sources, the study of typical large deposits is very important for understanding bauxite in the NCC.

Xiangcaowa bauxite is a large deposit located in S-NCC, and its provenance and genesis are still unclear. By means of X-ray diffraction (XRD), scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS), and U-Pb dating of detrital zircon and rutile, this study aims to investigate the provenance and genesis of Xiangcaowa bauxite deposit. This study further pinpoints the source of karstic bauxite within S-NCC, detailing the mineralization process of karstic bauxite deposits and highlighting their importance for metallogenesis throughout the NCC.

2. Geological Setting

2.1. Geological Evolution of the NCC and Bauxitization

NCC is comprised of several different tectonic units: the Eastern Block, Western Block, and Central Orogenic Belt (COB) [11,12]. Its northern boundary is the Central Asian Orogenic Belt, while its southern part is adjacent to the NQOB (Figure 1a,b) [9,13,14]. The Eastern Block contains a tonalite–trondhjemite–granodiorite belt from the Eo-Archean to Neo-Archean, and the greenschist belt from Neo-Archean [15–17]. The COB is subdivided further into Archean–Paleoproterozoic complexes [17]. These complexes represent widely exposed parts of the COB, which underwent a variety of metamorphism from greenschist to granulite during Archean and Paleoproterozoic tectono-thermal events [18,19]. Granulite facies metamorphism took place across the entire NCC between 1.9 and 1.8 Ga [20]. Since then, the interior of the NCC has continued to expand, forming Meso-Neoproterozoic strata and magmatic rocks [21–23]. During the Paleozoic, NCC gradually migrated along the northern margin of Gondwana [24]. From ~445 to 310 Ma, NCC was entirely uplifted and underwent strong weathering and karstification, forming widespread paleo-karstic topography dominated by a large range of karstic depressions [4]. Weathered crust and iron-bearing claystone overlying the karstic surface [7]. During the Late Carboniferous period, the NQOB uplift and Bainaimiao Arc Terrane formed, and NCC evolved into a marginal-walled basin, which allowed ore-forming materials to be transported to the karstic depression [5,7,10]. Subsequently, large-scale bauxites were formed by rapid weathering under favourable climatic conditions close to the equator [10]. After the Late Carboniferous, NCC was submerged by seawater and the ore-bearing rock series was further overlain by clastic and carbonate rocks [9].

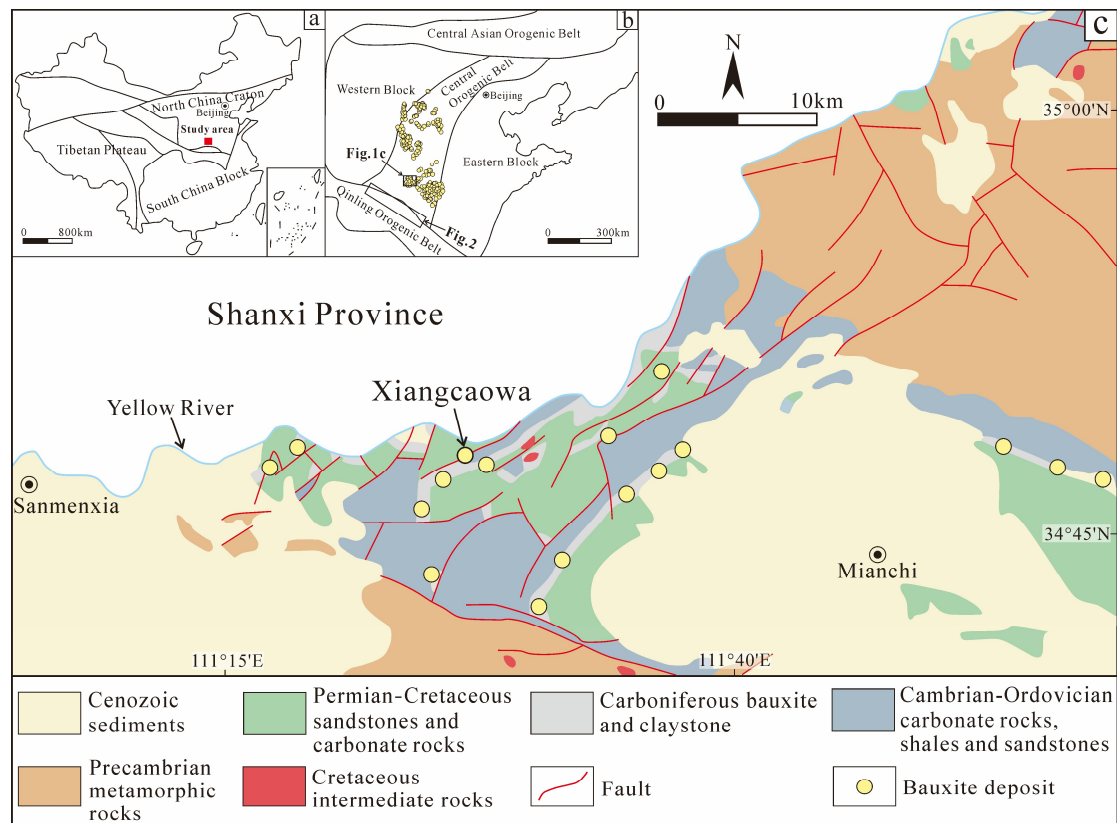


Figure 1. (a) Location of the study area in geological map of China (modified after [13]); (b) karstic bauxite distribution map in North China Craton (modified after [7]); (c) simplified geological map of the Sanmenxia area (modified after [7]).

2.2. Geological Features of the NQOB

The southern margin of NQOB is the Shangdan fault, and the northern margin is Luonan–Luanchuan fault (Figure 2) [25,26]. The primary constituents of the NQOB are the Kuanping, Erlangping, and Qinling Groups [27]. The zircon age in the metabasalt of the Kuanping Group is 943 Ma [27,28], while the zircon ages in the metasandstone are ~450 and ~950 Ma [29]. The main metamorphic grade is greenschist facies, which can reach amphibolite facies. The Ar–Ar dating of the amphibole is 435 ± 2 Ma, and the zircon ages in the amphibolite are 442 ± 6 and 415 ± 5 Ma [30]. The Erlangping Group exhibits a lens distribution [31,32]. Numerous early Paleozoic granite plutons have developed in the Erlangping Group, mainly formed between 480–460 Ma and 440–420 Ma [33]. The Erlangping Group has experienced greenschist and amphibolite facies metamorphism, which is characterized by superposition metamorphism [34]. Liu et al. [34] gained metamorphic age of amphibolite from 440 to 400 Ma. The Qinling Group mainly amphibolite facies metamorphism, locally reaching ultra-high-pressure eclogite facies, accompanied by multi-stage magmatism and metamorphism [35,36]. Neoproterozoic and Paleozoic granites are abundant within the Qinling Group [35,37]. The Neoproterozoic granites are predominantly represented by S-type and I-type granitoids, with the former being emplaced between 960 and 890 Ma, and the latter being emplaced <890 Ma [38]. The Paleozoic granites are mainly I-type granitoids with a small amount of S-type granitoids, of which the I-type granitoids formed at around 470 Ma, and the remaining granites were mainly concentrated at around 450–410 Ma [39,40]. The Qinling Group experienced metamorphism of amphibolite facies at ~1.0 Ga [41], and there are also high-pressure (HP) and ultra-high-pressure (UHP) metamorphic rocks with ages mainly concentrated in the 520–480 Ma range [33,42,43]. According to Cheng et al. [44], Lu–Hf isochron dating of garnet is 494 ± 3 and 516 ± 6 Ma.

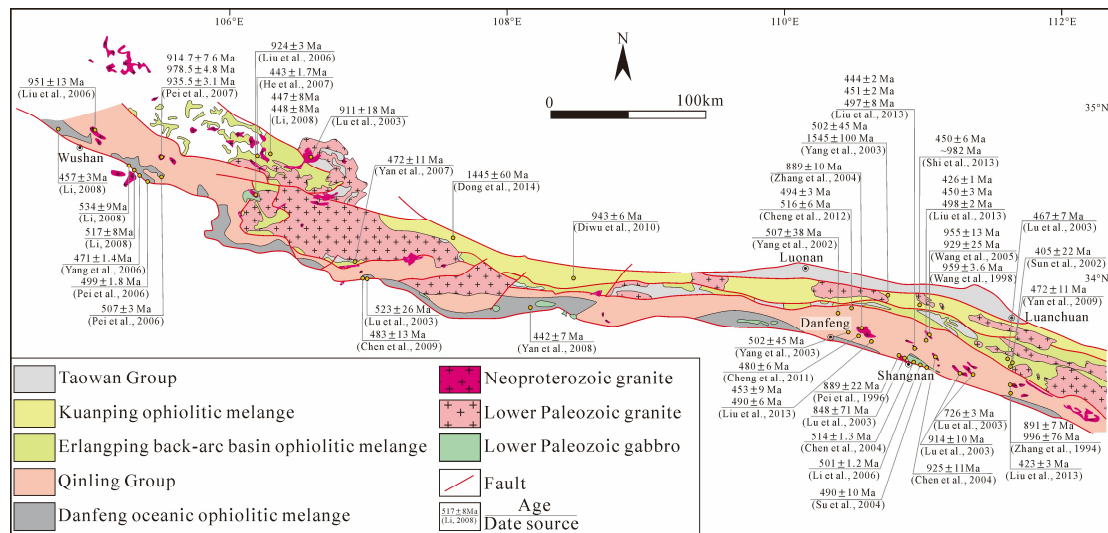


Figure 2. Geological map of the North Qinling Orogenic Belt and their published ages (modified after [13,45]). Dating data are from [29,41,44–67].

2.3. The Geology of Xiangcaowa Karstic Bauxite Deposit

Bauxite deposits within the NCC are concentrated primarily in Henan and Shanxi provinces (Figure 1b) [10,68]. The Xiangcaowa bauxite deposit is located in the Sanmenxia area of S-NCC (Figure 1b); the outcropping strata consist mainly of Precambrian metamorphic rocks, Cambrian–Ordovician carbonate rocks, shales and sandstones, Carboniferous bauxite and claystone, Permian–Cretaceous sandstones and carbonate rocks, and Cenozoic sediments (Figure 1c). The study area lacks significant structural development and magmatic rocks (Figure 1c).

The Xiangcaowa ore-bearing rock series is comprised of the top claystone layer and the bottom bauxite layer, which is covered by carbonate rocks (Figure 3). Iron-bearing claystone underlying the bauxite occurs locally [4]. The paleo-karstic topography determines the thickness and shape of bauxite; thick, high-quality bauxite is generally formed in karstic depressions, and bauxite is thin or absent in karstic uplifted areas [7,10]. The Xiangcaowa bauxite is mainly layered and stratoid and is approximately 3 to 5 metres thick. The ore is light gray (Figure 3), with oolitic, clastic, and cryptocrystalline textures (Figure 4a–d).

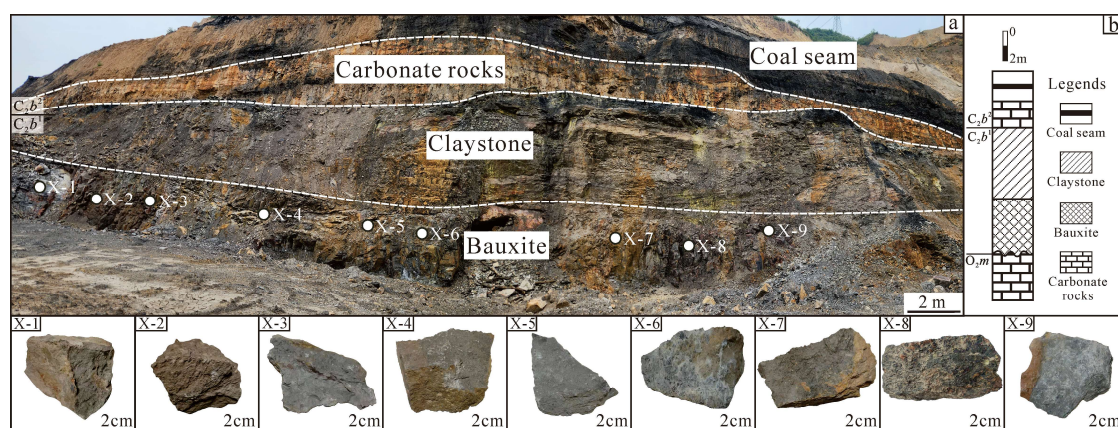


Figure 3. (a) The outcrop photo in Xiangcaowa bauxite deposit illustrates the sequence composition and sample location; (b) the drill core profile of bauxite; and samples X-1~X-9 are bauxite ores, showing the structural characteristics of the ores.

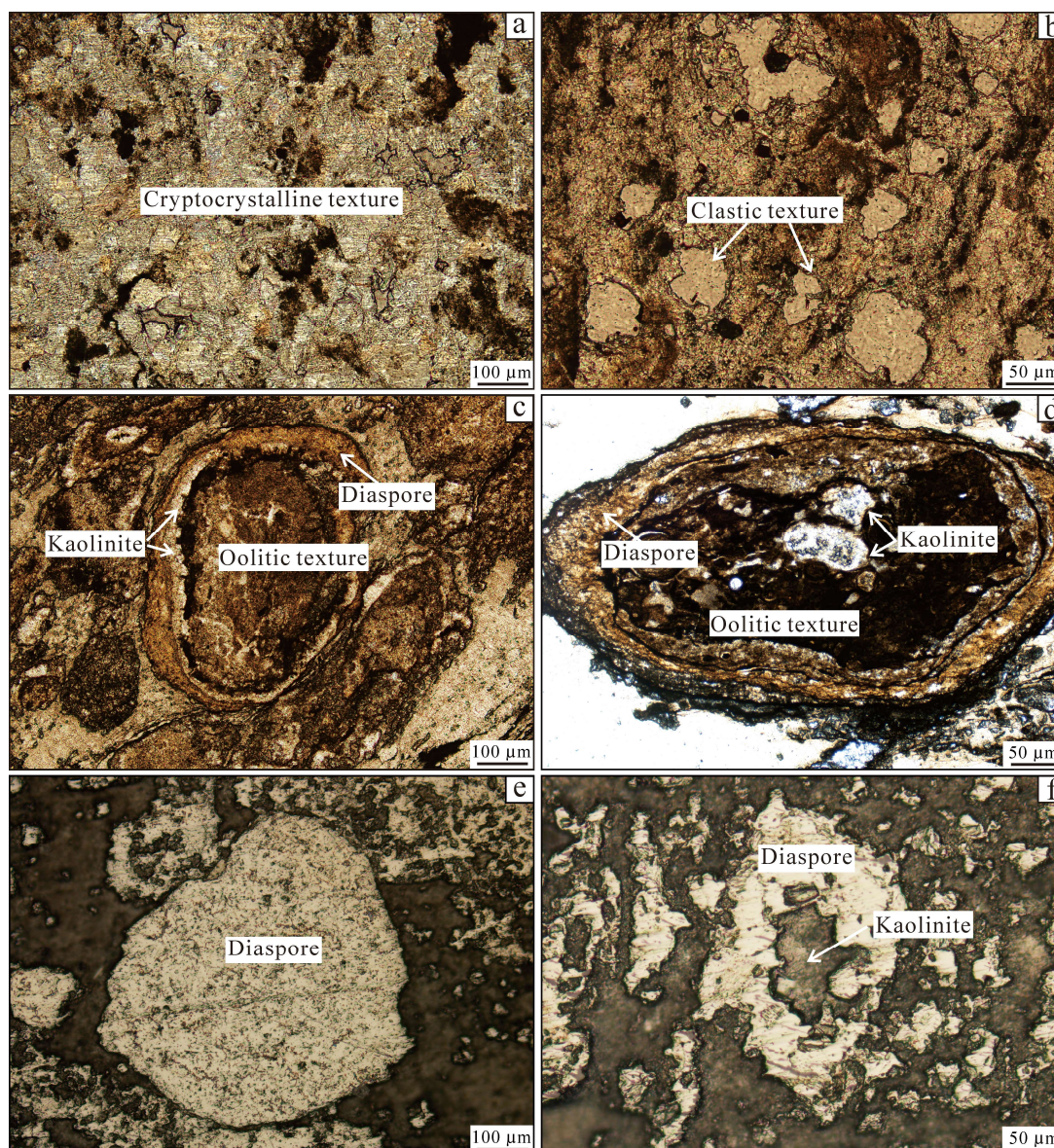


Figure 4. Photomicrograph of Carboniferous Xiangcaowa bauxite. (a) Cryptocrystalline texture; (b) clastic texture; (c,d) an ooid composed of diaspore and kaolinite; (e) cryptocrystalline diaspore aggregates in ore matrix; and (f) ore matrix composed of diaspore and kaolinite.

3. Sampling and Analytical Methods

Nine samples (X-1 to X-9), all weighing over 3 kg, were collected from Xiangcaowa bauxite (geographical coordinates: 111°27′21″ E, 34°48′11″ N). Mineralogical and chronological analyses of the samples were performed.

XRD and SEM-EDS analyses were performed at the China University of Geosciences in Beijing, China. Among them, XRD graphite-monochromatized CuKα1 radiation under controlled laboratory conditions (18 °C, 30% humidity). The instrument was Rigaku D/Max-RC, and parameters included continuous scanning mode with 40 kV voltage, 80 mA beam current, 8°/min scanning speed, and slit DS = SS = 1°. The relative intensity ratio (*RIR*) method was used to estimate the mineral concentration of the sample. The *RIR* value is calculated as follows [69]:

$$RIR_{i,s} = \left(\frac{X_s}{X_i} \right) * \left(\frac{I_{(hkl)i}}{I_{(hkl)s}} \right) * \left(\frac{I_{(jkl)s}^{rel}}{I_{(hkl)i}^{rel}} \right) \quad (1)$$

X is the weight fraction of the sample, I is the reflection intensity, I^{rel} is the relative reflection intensity, and i and s are the clay mineral sample and internal standard phase.

Corundum ($\alpha\text{-Al}_2\text{O}_3$) was selected as the standard to compare the diffraction strength of powder materials. The RIR_{cor} value is determined by the mass ratio of corundum to clay minerals 1:1. In a sample containing a known amount of corundum, the concentration of any phase i is provided by [69]:

$$X_i = \left(\frac{X_{cor}}{RIR_{cor}} \right) * \left(\frac{I_{(hkl)^i}}{I(113)_{cor}} \right) \quad (2)$$

A HITACHI S-450 equipment was used to perform SEM-EDS analysis. The operational pressure was maintained at 1 bar, with an ambient temperature of $21\text{ }^\circ\text{C} \pm 0.5\text{ }^\circ\text{C}$ and a humidity level of $46\% \pm 1\%$.

The zircon and rutile grains were separated through the process of grinding the samples to $420\text{ }\mu\text{m}$, subsequently employing traditional heavy liquid and magnetic techniques, and ultimately undergoing manual extraction under a binocular microscope. Zircon and rutile grains were selected based on a comprehensive evaluation of cathode luminescence, transmission, and reflection images to ensure that the selected grains avoid inclusions and cracks [5]. The U-Pb dating analysis was conducted by Beijing Zhongkekuangyan Geological Analysis Laboratory Co., Ltd, Beijing, China. The laser ablation system utilized was the ESI NWR 193 nm (Electro Scientific Industries, Beaverton, OR, USA), while the ICP-MS equipment employed was the Agilent 7500 (Agilent Tech, Santa Clara, CA, USA). During laser ablation, helium was utilized as the carrier gas, while argon was the compensating gas. These gases were mixed through a Y-connector prior to their introduction into the ICP. Every zircon and rutile analysis includes a sample signal of 45 s and a blank signal of roughly 15–20 s [70]. In zircon U-Pb dating, GJ-1 served as the external standard, every five to ten sample points, GJ-1 was examined twice. For rutile U-Pb dating, DXK was employed as the external standard. Every 5–10 sample points were interspersed with two DXK standards and one monitoring standard JDX [70]. Concordia ages and diagrams for the zircon and rutile grains were produced using the Isoplot software (version 3.0) [71].

4. Results

4.1. Mineral Composition and Their Occurrence

The light gray bauxite ore of Xiangcaowa predominantly consists of diaspore, kaolinite, and anatase, along with minor quantities of pyrite, zircon, and rutile (Figures 4–6, Table S1). The SEM photos of the bauxite show that diaspore is closely related to pyrite and anatase (Figure 6). Diaspore commonly occurs in the form of cryptocrystalline aggregates, which together with kaolinite form the ore matrix (Figure 4c–f). Diaspore and anatase encased each other (Figure 6a,b). Anatase also occurs in pyrite aggregates as inclusions within the diaspore–kaolinite matrix (Figure 6c). In the bauxite, framboidal pyrite is extensively produced (Figure 6d). Kaolinite generally occurs as fine scaly aggregates or cryptocrystalline in the internal fractures of the diaspore aggregates, and there is a clear tendency for the edges of the diaspore to transition to scaly kaolinite (Figures 4f and 6e). In addition, kaolinite also forms ooids with diaspore (Figure 4c,d). Round-shaped zircon and rutile grains occur in ores (Figure 6f–h).

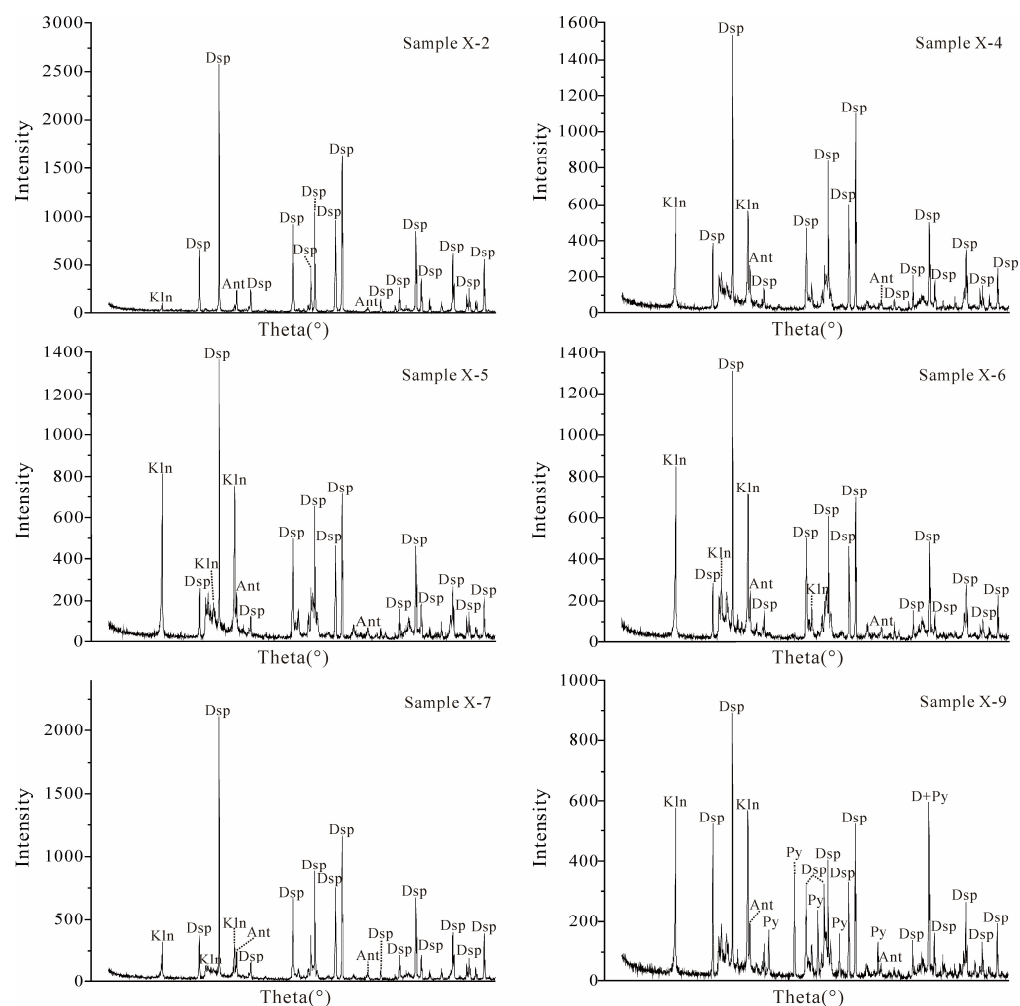


Figure 5. XRD spectra of Xiangcaowa bauxite deposit. (Mineral abbreviations [72]: Dsp—diaspore; Kln—kaolinite; Ant—anatase; Py—pyrite).

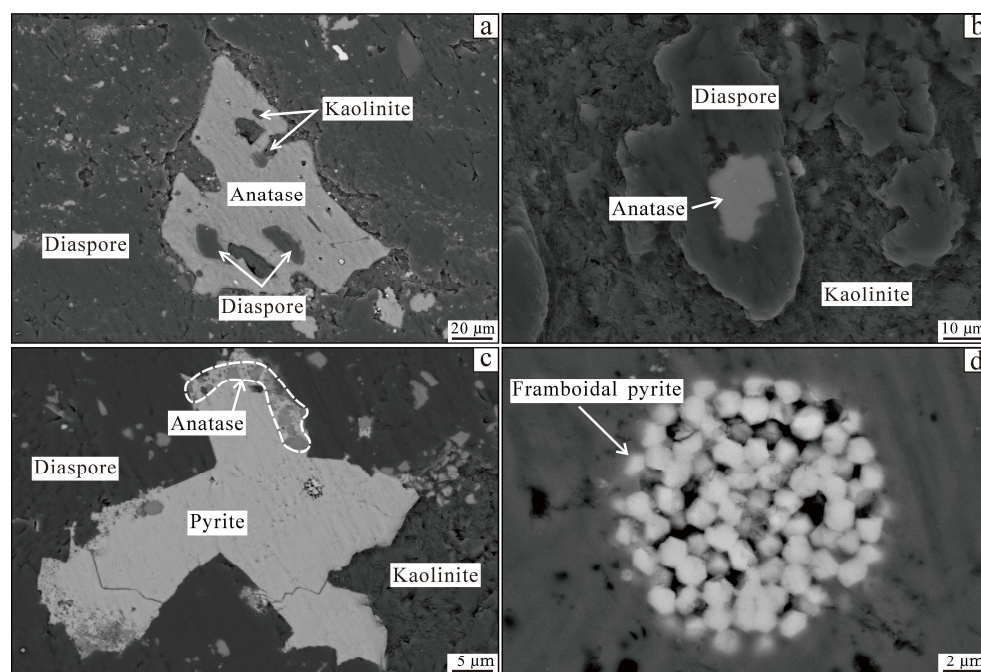


Figure 6. Cont.

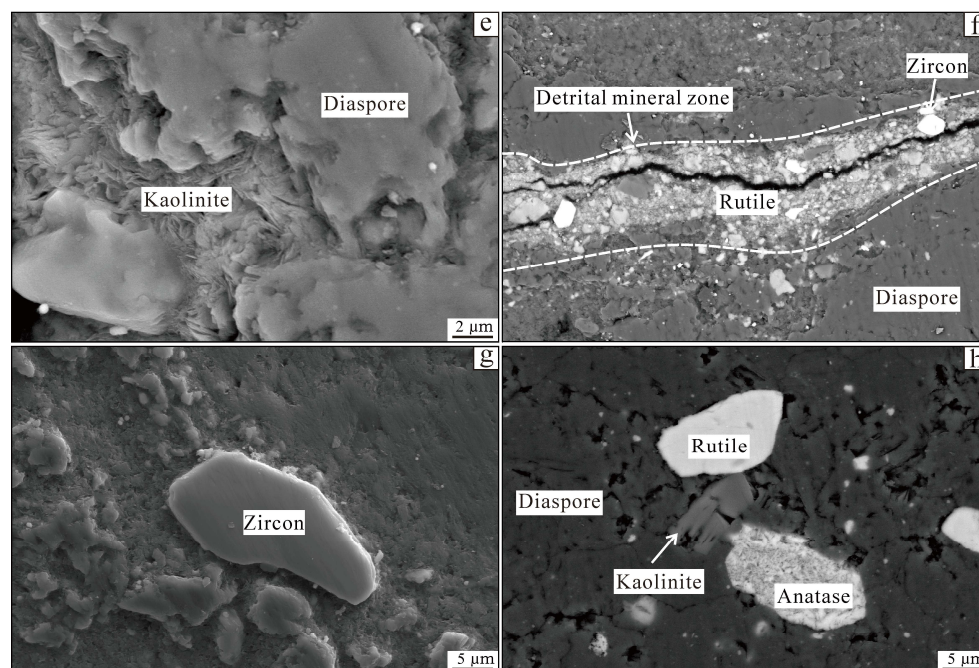


Figure 6. Backscattered SEM photos of Xiangcaowa bauxite. (a) several diaspore inclusions within anatase aggregates; (b) anatase is encased in diaspore aggregates; (c) pyrite and anatase aggregates located in the diaspore–kaolinite matrix; (d) extensive development of framboidal pyrite in the diaspore–kaolinite matrix; (e) scaly kaolinite is located at the boundary of the diaspore; (f) detrital mineral zone in the matrix; and (g,h) round detrital zircon and rutile grains distributed in the matrix.

4.2. Zircon Trace Element Composition

135 detrital zircons were analyzed, with crystal lengths ranging from 60 to 150 μm (Figure 7a). The majority of zircons display oscillatory zoning, which is compatible with their high Th/U ratios (0.1–3.7), indicating magmatic origin (Figures 7a and 8). A few zircons have irregular secular zoning and low Th/U ratios (Figure 8), which are typical of metamorphic zircons.

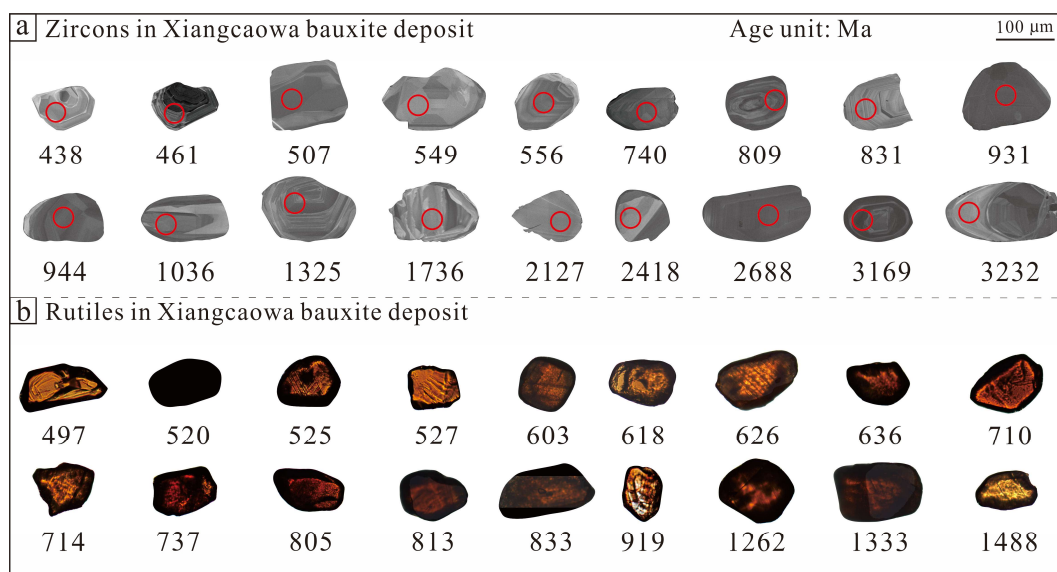


Figure 7. (a) Representative cathode luminescence images of detrital zircons separated from bauxite ore, and red circles indicating the location of U–Pb analysis; (b) morphology of detrital rutiles in Xiangcaowa bauxite.

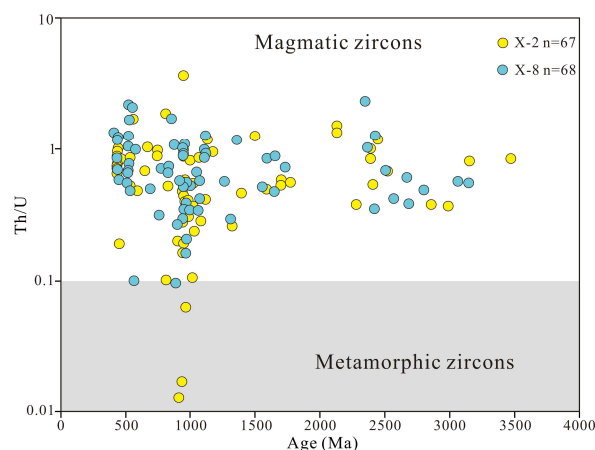


Figure 8. U-Pb age variation and Th/U ratio of zircons in Xiangcaowa bauxite (The fields were established by [73]).

Table S2 shows the trace element data for detrital zircons. Zircon grains in sample X-2 have Hf contents of 6158–12,861 ppm, Th contents of 11–489 ppm, Y contents of 151–3556 ppm, U contents of 62–858 ppm, Ta contents of 0.2–15 ppm, and Nb contents of 0.4–45 ppm. The content of Σ REE is 386–6277 ppm, and the heavy rare earth element content (380–3580 ppm) is much higher than the light rare earth element (2–85 ppm). Zircon grains in sample X-8 have Hf contents of 5574–12,313 ppm, Th contents of 42–1203 ppm, Y contents of 34–3438 ppm, U contents of 68–725 ppm, Ta contents of 0.3–15 ppm, and Nb contents of 0.2–30 ppm. The content of Σ REE is 99–6334 ppm, and the heavy rare earth element content (89–6266 ppm) is much higher than the light rare earth element (4–450 ppm).

4.3. Zircon U-Pb Age

Two samples of Xiangcaowa bauxite deposit yielded 135 zircon age data, with the results shown in Table S3 and the concordia diagram displayed in Figure S1. Detrital zircons in sample X-2 have an age range of 3467–430 Ma that form larger age populations at ~450 and ~950 Ma, three smaller age populations at ~530, ~810, and ~1100 Ma, and several zircon grains are aged ~1700, ~2400, ~2850, and ~3450 Ma (Figure 9a). Detrital zircons in sample X-8 have an age range of 3145–406 Ma that form a larger age population at ~520 Ma, two smaller age populations at ~450 and ~950 Ma, and several zircon grains are aged ~400, ~1100, ~1400, ~1650, ~2350, ~2700, and ~3150 Ma (Figure 9b).

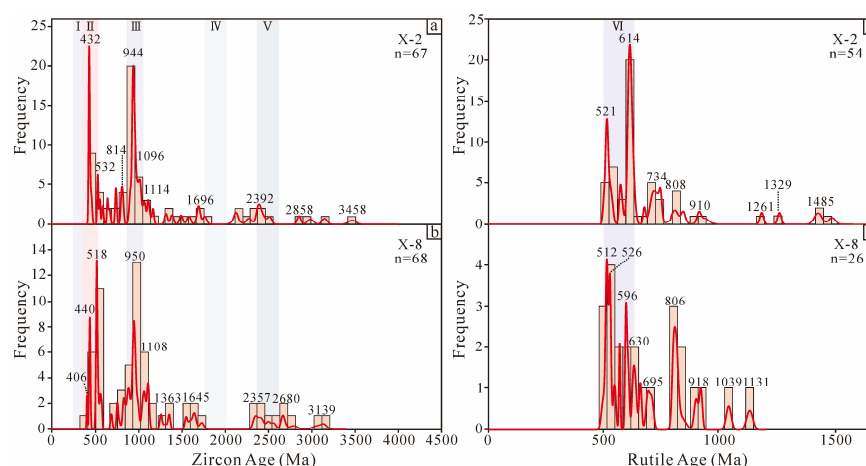


Figure 9. Histograms of U-Pb ages of detrital zircon and rutile grains in Xiangcaowa bauxite. (a,b) U-Pb ages of detrital zircons from samples X-2 and X-8; (c,d) U-Pb ages of detrital rutiles from samples X-2

and X-8. I: magmatic intrusion and volcanism in the northern margin of the NCC during the period of 310–300 Ma; II: magma intrusion of NQOB or Bainaimiao Arc Terrane during ~450 Ma; III: ~970 Ma, NQOB magma intrusion occurred; IV: magmatism and metamorphism of NCC during ~1900–1800 Ma; V: during ~2500 Ma, NCC subducted along the COB and magmatic activity occurred; and VI: during ~650–500 Ma, the convergence of South China Block and East Gondwana. Background data for detrital zircon and rutile are from [5,74–80].

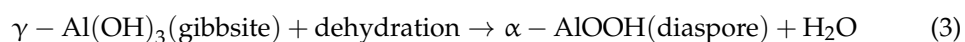
4.4. Rutile U-Pb Age

The detrital rutile grains range in length from 60 to 130 μm , the shape is round and reddish-brown to yellow-brown in color (Figure 7b). Two samples of the Xiangcaowa bauxite deposit yielded 80 rutiles' age data, and the corresponding results are provided in Table S4. Detrital rutiles in sample X-2 have an age range of 1545–509 Ma that form a larger age population at ~610 Ma, two smaller age populations at ~520 and ~730 Ma, and several rutile grains aged ~800, ~910, ~1250, ~1300, and ~1500 Ma (Figure 9c). Detrital rutiles in sample X-8 have an age range of 1131–497 Ma, which form two larger age populations at ~510 and ~520 Ma, two smaller age populations at ~600 and ~800 Ma, and several rutile grains aged ~630, ~700, ~920, ~1030, and ~1130 Ma (Figure 9d).

5. Discussions

5.1. Mineral Genesis and Ore-Forming Environment

Scholars have two views on the origin of diaspore: metamorphic origin and supergene crystallization origin [3,81]. Previous studies generally assumed that the formation of gibbsite in the weathering stage is unstable, usually through the following reaction into diaspore [82]:



However, based on the mineral paragenetic assemblage, current studies on karstic bauxite have pointed to a supergene precipitation [83]. In this study, diaspore mainly has a cryptocrystalline structure and low crystallinity, indicating that it is caused by supergene precipitation. In addition, diaspore is closely associated with anatase and pyrite (Figure 6a–c). These characteristics prove that diaspore is a supergene origin.

Pyrite is generally associated with diaspore and anatase, indicating that pyrite precipitated in the metallogenic stage (Figure 6c). Framboidal pyrite originates from the bacterial reduction of sulfate (Figure 6d) [84] and its presence indicates microorganism involvement in the bauxite mineralization process [10]. Kaolinite can be of residual, syngeneic, or epigenetic origin [85,86]. Cryptocrystalline kaolinite distributed in the ore matrix is a residual product of the weathering of primary minerals during the early stage of mineralization. Ooids composed of diaspore and kaolinite indicate that kaolinite is formed during the diagenetic period (Figure 4c,d). Kaolinite occurs as fine scaly aggregates around the diaspore with erosion at the boundary, indicating that the kaolinite must be a post-diagenetic product induced by silicification of the diaspore (Figures 4f and 6e) [86]. Anatase and diaspore are closely associated in the ore matrix suggesting that abundant anatase is formed during the diagenetic stage (Figure 6a,b). The detrital minerals in bauxite, rutile and zircon, contain crucial information about the source region (Figure 6f–h) [83].

The formation of karstic bauxite has been significantly influenced by karstic topography. The ferric mineral-bearing claystones are usually formed in the uplifted area, where goethite and hematite are the main iron minerals, and the uplifted area is an acidic oxidizing environment [7]. The ferrous mineral-bearing claystones are usually formed in karstic depressions, where siderite and pyrite are the main iron minerals, and the depression is an alkaline-reducing environment [87]. The mineral composition and assemblages in karstic

bauxite strictly recorded the metallogenic conditions of bauxite (Figure 10) [81]. The mineral paragenetic assemblages in Xiangcaowa bauxite show that diasporite is predominantly associated with anatase and pyrite (Figure 6a–d). Anatase is generally precipitated under weak alkaline conditions in karstic bauxite [88]. Pyrite is formed under reducing conditions. Based on the formation conditions of these paragenetic minerals, the metallogenic environment of Xiangcaowa bauxite is reducing and alkaline (Figure 10).

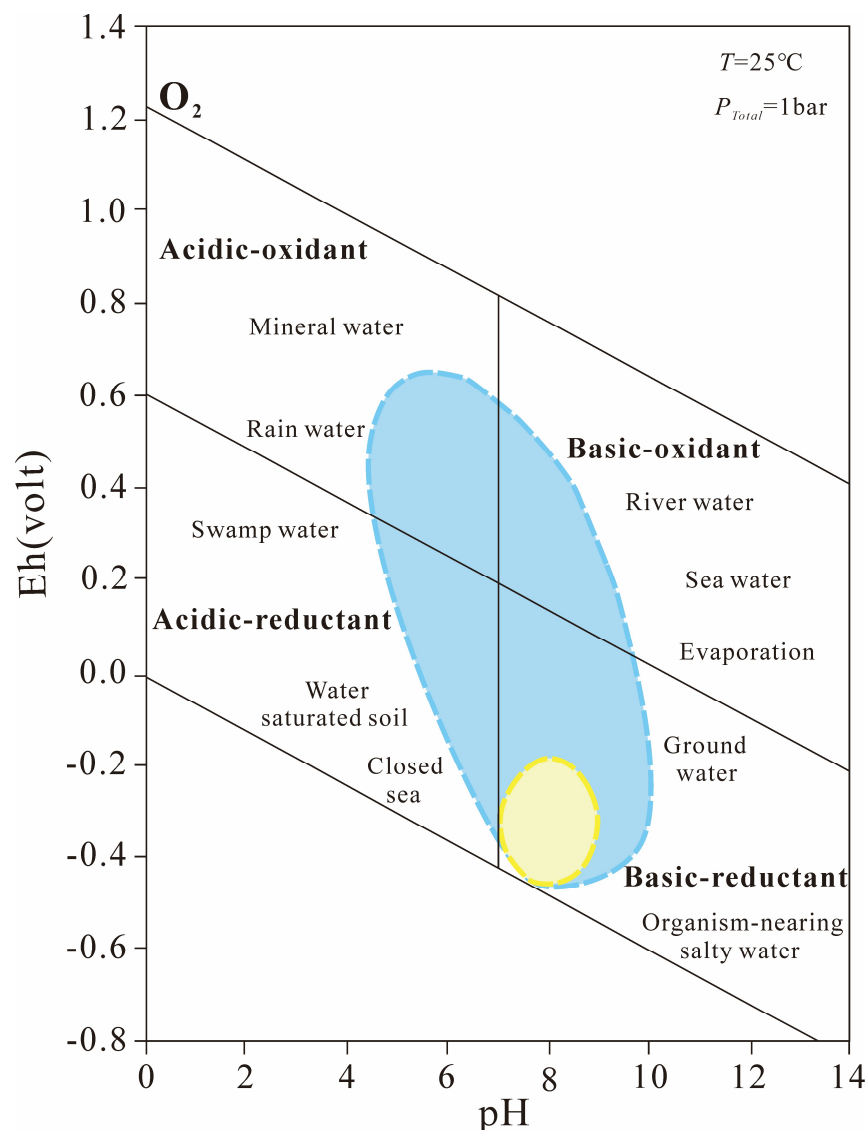


Figure 10. The Eh–pH diagram of metallogenic conditions. “Blue area” represents the integral formation environment of karstic bauxite; “yellow area” represents the metallogenic environment of Xiangcaowa bauxite (modified after [89]).

5.2. Source of Detrital Zircons

Detrital zircons of samples X-2 and X-8 have $\text{Th}/\text{U} > 0.1$, indicating that they were formed mainly in magmatic processes (Figure 8). The trace element contents of magmatic zircons show high sensitivity in distinguishing source rock types and their crystallization conditions [90]. Therefore, the composition of trace elements in zircon has become an effective indicator for identifying zircons from different sources [90–93]. In this study, the distribution characteristics of the detrital zircon grains on Y vs. U/Yb and Hf vs. U/Yb diagrams mainly indicate continental origin (Figure 11a,b). U and Y concentrations of detrital zircons were positively correlated, and most of the data fell in the granitoid and larvikite

regions, indicating that they are mainly derived from felsic igneous rocks (Figure 11c). The concentrations of Ta and Nb in zircons are positively correlated (Figure 11d), suggesting that they may originate from different rock types. The Y concentration of zircons is positively correlated with its Yb/Sm and Nb/Ta (Figure 11e,f), again indicating that most of the zircon is derived from felsic igneous rocks. The trace element composition of most detrital zircons indicates that they originate from felsic igneous rocks.

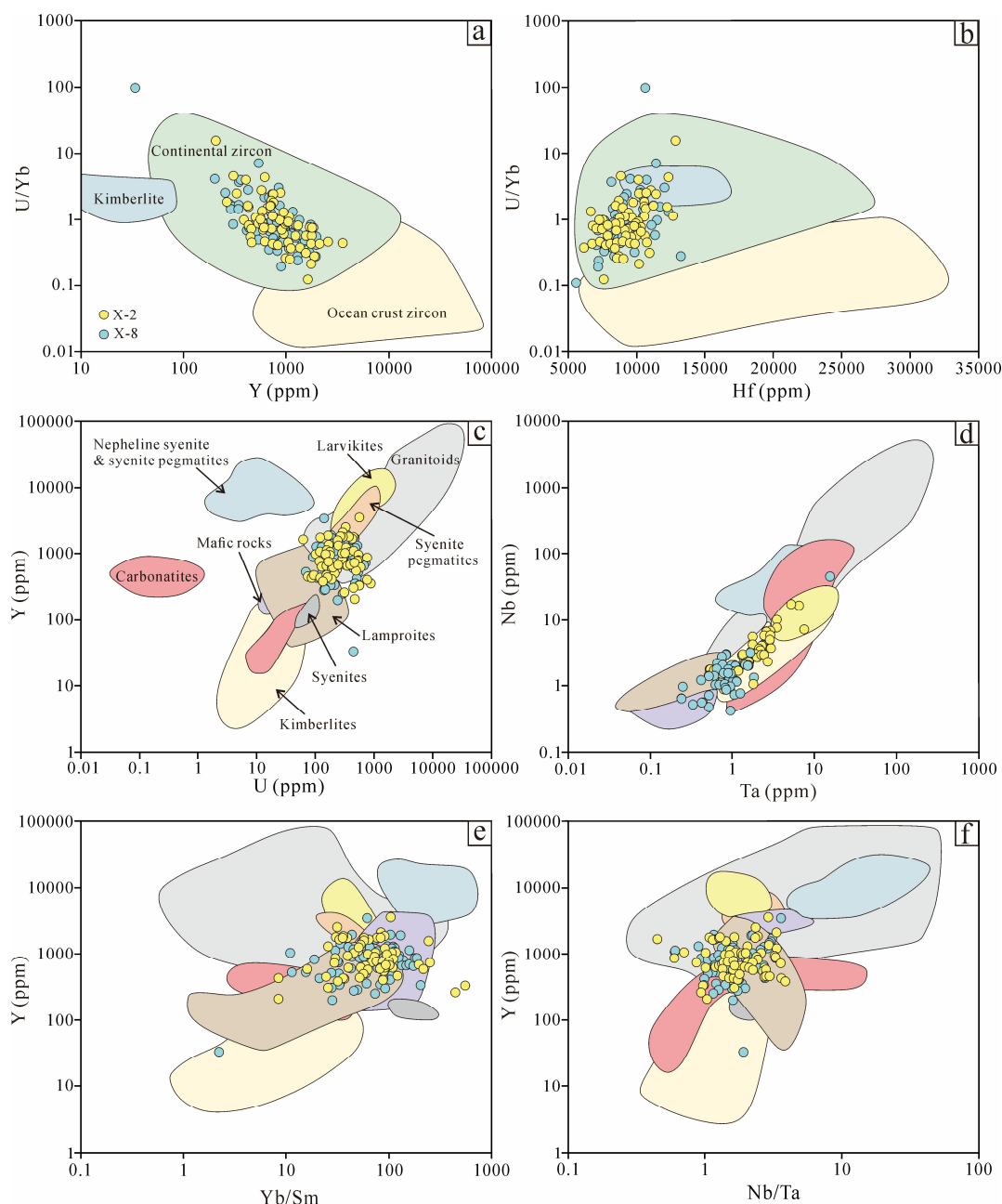


Figure 11. Binary diagrams of U/Yb vs. Y (a), U/Yb vs. Hf (b), Y vs. U (c), Nb vs. Ta (d), Y vs. Yb/Sm (e) and Y vs. Nb/Ta (f) for the detrital zircon grains in samples X-2 and X-8 (the fields were established by [90]).

The detrital zircons' U-Pb ages reveal three major age populations at ~450, ~520, and ~950 Ma, secondary age populations extending from 2400 to 1100 Ma, and minor ages spanning from 3450 to 2700 Ma (Figure 9a,b).

During the Early Paleozoic (460–420 Ma), extensive magmatic activity occurred throughout the NQOB, resulting in strong crust-mantle interaction and re-cycling of an-

cient crust materials [27]. Therefore, it is reasonable to propose that the ~450 Ma zircons originated from the NQOB (Figure 9). Cao et al. [94] reported the zircon age in the metamorphic quartz sandstone of the Kuanping Group was 515–513 Ma, and the zircons are of magmatic origin. Shi et al. [29] dated the zircons in the mica schist of the Kuanping Group at 506 Ma, and the trace element composition of metamorphic rock indicates that it may have originated from Neoproterozoic magma, which is consistent with the result of zircons from felsic igneous rocks in this study. Thus, we conclude that Kuanping Group was the provenance of detrital zircons aged ~520 Ma. Around 950 Ma, magmatic activity was prevalent at the S-NCC and NQOB [28]. The zircon grains' rounded shape, as shown in Figure 7a, suggests they have undergone long-term transport, so it is assumed that the ~950 Ma zircons originated from the NQOB (Figure 9).

The zircon grains are aged 2400–1100 Ma, with several minor age populations at ~1100, ~1400, ~1650, and ~2400 Ma. The zircon age of the Taihua complex was 2.4 Ga [95], and its trace element characteristics are similar to those in this study, all of which are of continental origin. Multi-stage magmatic events occurred in the NCC during the Mesoproterozoic, including a phase of magmatic activity in the Longwangzhuang alkaline pluton [96]. According to Lu et al. [97], Longwangzhuang granite was formed around 1400–1650 Ma, and the trace element composition of the whole rock shows that the granite was formed in the continental environment, which is consistent with the results of this study. Furthermore, the zircon grains within the Kuanping mica schist were 1100 Ma in age, and the trace element composition indicates that they were of felsic origin [98], which is similar to this study. These characteristics demonstrate that zircons aged 2400–1100 Ma were derived from the Taihua complex and Longwangzhuang alkaline pluton in S-NCC, and the Kuanping Group from NQOB. Another group of zircons in bauxite is 3450–2700 Ma. The 3.0–2.6 Ga magmatic activities were prevalent throughout the NCC [99]. Detrital zircon grains, aged between 3.4 and 2.5 Ga, also exist in the NQOB [29], and their trace element characteristics exhibit similarities to those in this study, indicating the source of felsic igneous rocks. Since the round shape of detrital zircons and the characteristics of long-term transport (Figure 7a), we believe that zircons from ~3450–2700 Ma are mainly from NQOB.

5.3. Source of Detrital Rutiles

Rutiles typically originate under metamorphic conditions, whereas the zircons in metamorphic rocks are limited, so the abundance of rutiles in metamorphic rocks is relatively high [100,101]. In this study, we can further explore the role of metamorphic rocks in the mineralization process. The detrital rutiles in Xiangcaowa bauxite are mainly formed at 800–510 Ma, with five age populations of ~510, ~520, ~600, ~630, and 800 Ma, and minor ages varying from 1500 to 910 Ma (Figure 9c,d). The round crystal morphology of these rutiles is evidence of their long-term transport (Figure 7b).

The geochronology of gneiss, plagioclase amphibolite, and eclogite in the Qinling Group has been thoroughly studied by numerous scholars, and the results show that HP-UHP metamorphic events occurred in 520–480 Ma [42,43]. Thus, it can be concluded that the rutiles with an age of ~510 Ma were from the Qinling Group. The entire NQOB and NCC lacked metamorphic events of ~800–520 Ma [27,29,102], so these rutile grains were likely to have originated elsewhere. The three age populations of ~520, ~600, and ~630 Ma are similar to the ages of Gondwana-related metamorphic rocks (Figure 9) [103]. Combined with previous research, during the Cambrian, the South China Block (SCB) gathered in Eastern Gondwana [104]. Therefore, detrital rutiles of the Xiangcaowa bauxite (aged 630 to 520 Ma) originated from the SCB receiving Gondwana metamorphic rocks. Since the South Qinling Orogenic Belt (SQOB) has not yet separated from the SCB during this period, and the SCB has not collided with SQOB during the bauxite mineralization

period (~320 Ma), rutiles between 630 and 520 Ma originate from the SQOB. In addition, Hu et al. [105] determined that the metamorphic age of diorite gneiss in the Douling complex is 818 ± 10 Ma. The Douling complex is a crystalline basement of the SQOB developed in Neoproterozoic–Paleozoic strata, and the complex has only experienced amphibolite facies metamorphism, but not HP/UHP metamorphic events [106,107]. The above evidence indicates that ~800–520 Ma of detrital rutiles were derived from the SQOB.

Another group of rutiles with ages of 1500–910 Ma. The amphibolite facies metamorphism took place in the Qinling Group at ~1.0 Ga [27], and the age spectrum of rutiles in this group exhibits similarity to that of gneiss within the Qinling Group. Zhang et al. [41] obtained Rb–Sr isochron ages of gneiss are 986 ± 169 and 1142 ± 18 Ma from the Qinling Group. In addition, Shi et al. [29] obtained zircons from felsic gneiss in the NQOB with an age range of ~1600–1000 Ma. Therefore, these rutiles with ages of 1500–910 Ma were derived from the metamorphic rocks of the NQOB. We proposed that the source of detrital rutile grains in Xiangcaowa bauxite may be metamorphic rocks of the NQOB and SQOB according to the above research results.

5.4. Provenance and Genesis of Bauxite Deposit

As a sedimentary deposit, bauxite, is considered to have multiple aluminum sources, which can be derived from igneous rocks, metamorphic rocks, volcanic ash, and other aluminum-bearing protoliths [4,10]. Consequently, the source of karstic bauxite is typically allochthonous and multi-sourced [108]. Combining this study with previous research results [5,6], we can establish a possible provenance model of karstic bauxite in the S-NCC (Figure 12). The basement of the NQOB is predominantly comprised of the Qinling Group, characterized by rocks that have undergone significant deformation and metamorphism. These rocks have undergone amphibolite facies metamorphism at ~1.0 Ga [27,45]. In the subduction of Shangdan and Kuanping Ocean, granite intrusion was formed (Figure 12a) [35,65]. During ~950–850 Ma, the NQOB and NCC collided due to the Kuanping Ocean crust's fatigue, forming granite with an age of ~889–844 Ma (Figure 12b) [35]. At about 540 Ma, the Shangdan Ocean subducted under the NQOB, forming the Erlangping back-arc basin; around 520 Ma, the continuous subduction of the Shangdan Ocean crust led to the intrusion of a large amount of granite into the NQOB [13]. Meanwhile, the Erlangping back-arc basin subducted southward, forming ~500 Ma HP-UHP metamorphic rocks [109]. The Erlangping back-arc basin closed at ~450 Ma. At the same time, the Shangdan Ocean probably existed and continued to subduct at ~460–422 Ma [107,110]. During 450–420 Ma, the Shangdan Ocean crust subducted northward and formed granite [102]. Meanwhile, the expansion of the Mianlue Ocean led to the separation of SQOB from SCB (Figure 12c); until 400 Ma, the Shangdan Ocean was closed, ultimately leading to the collision between the SQOB and NQOB [13]. During 445–310 Ma, the NCC underwent uplift and strong karstification, forming a wide range of paleo-karstic topography, with iron-bearing claystone overlying the karstic surface [9]. At the same time, NQOB also experienced long-term weathering and formed rich weathering materials [5]. At ~340 Ma, the NCC was close to the equator, and the clay minerals in the iron-bearing claystone further dissociated into various ions, which encountered the carbonate barrier and formed diasporite under alkaline and reducing conditions [87]. During ~320 Ma, uplift of NQOB resulted in an overall north-dipping topography of NCC; at the same time, large-scale volcanic activity occurred on the northern margin of NCC [111]. The igneous and metamorphic rocks of the NQOB, metamorphic rocks of the SQOB, along with the Precambrian metamorphic basement of the NCC, were transported into karstic depressions. The warm and humid tropical climate and the greenhouse effect caused by volcanic eruptions accelerate the dissolution of weathering materials to form large karstic bauxite deposits (Figure 12d) [5].

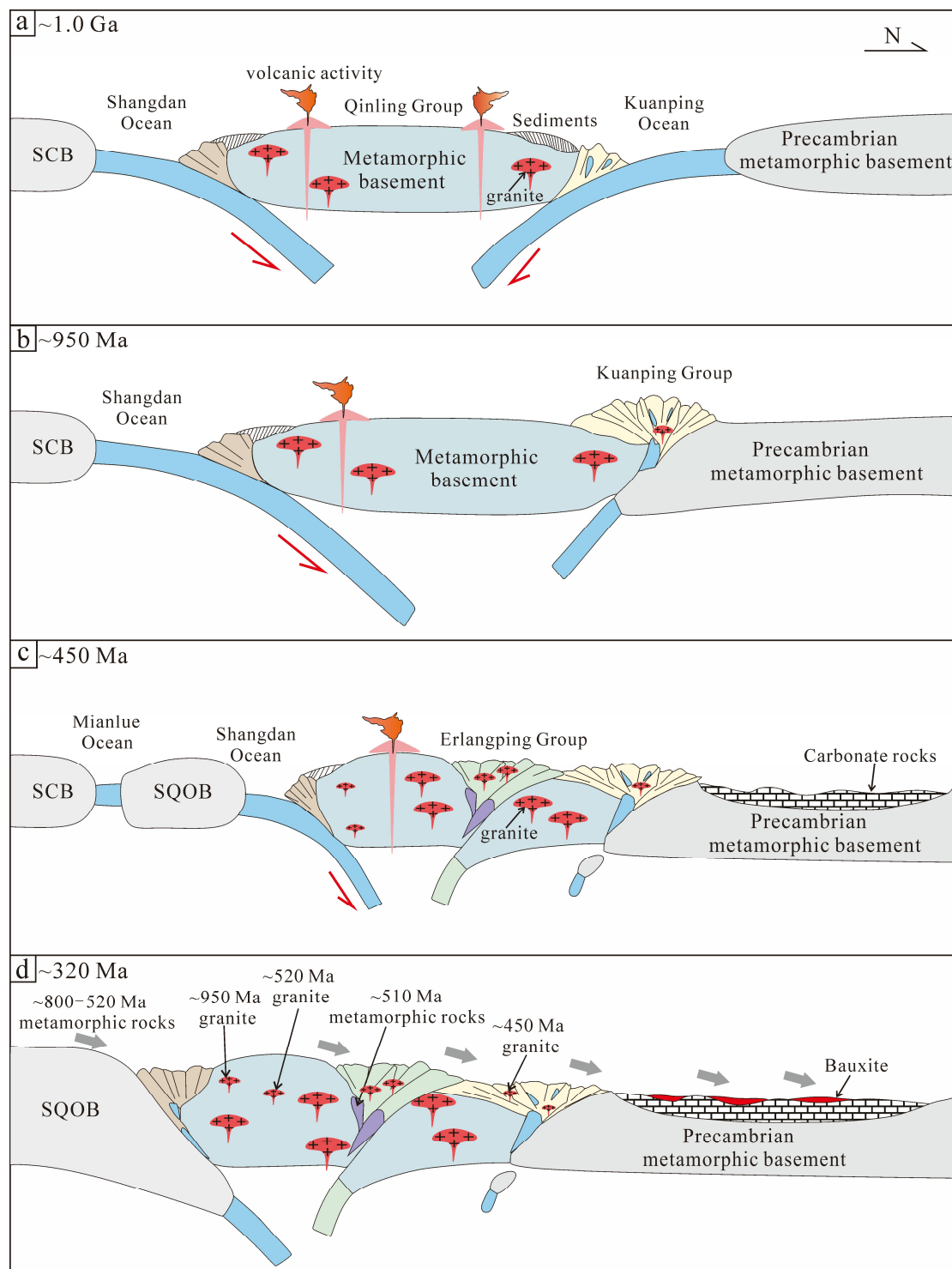


Figure 12. A possible provenance model for Late Carboniferous karstic bauxite deposits. (a) during ~1.0 Ga, the Kuanping Ocean subducted southward, resulting in a large amount of granite intrusion; (b) illustrates the granite plutons that were formed due to the tectonic collision between the NQOB and NCC at ~950 Ma; (c) illustrates that the Shangdan Ocean continues to subduct at ~450 Ma, at this time, the Mianlue Ocean expanded, resulting in the separation of the SQOB from SCB; and (d) illustrates that the north-dipping topography of the NQOB and SQOB leads to ore-forming materials being transported to NCC (modified after [13]). SCB: South China Block; SQOB: South Qinling Orogenic Belt.

6. Conclusions

The ore-bearing rock series of the Xiangcaowa bauxite consists of two layers, the bauxite and claystone layers. The mineral composition of bauxite is predominantly comprised of diaspore, anatase, and kaolinite, with minor pyrite, detrital rutile, and zircon. The mineral paragenetic assemblages (diaspore–anatase–pyrite) indicate that the metallogenic environment of Xiangcaowa bauxite is reducing and alkaline. Detrital zircon and rutile U–Pb dating indicate that Xiangcaowa karstic bauxite is an allochthonous and multi-source deposit. Various U–Pb age spectra of detrital zircons and rutiles suggest that the igneous and metamorphic rocks of the NQOB and metamorphic rocks of the SQOB are the main sources of bauxite. In addition, the widespread Precambrian basement rocks within the NCC also contribute to the formation of bauxite. A large amount of allochthonous material was transported to a wide karstic depression and deposited in a large bauxite deposit under alkaline reducing conditions. This study further reveals the complexity of bauxite sources and genesis in the NCC, and the regional variation is significant, so further research is needed on typical deposits in different zones.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15030310/s1>, Figure S1: U–Pb concordia for the detrital zircons; Table S1: Semiquantitative analysis results (wt.%) of Xiangcaowa karstic bauxite samples; Table S2: Trace elements compositions (ppm) of detrital zircons in samples X-2 and X-8; Table S3: U–Pb dating results of zircons from the samples X-2 and X-8; Table S4: U–Pb dating results of rutiles from the samples X-2 and X-8.

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