Genesis of the Guangou karstic bauxite deposit in western Henan, China

Xuefei Liu a, Qingfei Wang a,*, Yuwen Feng a, Zhongming Li b, Shuhui Cai a

a State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, PR China
b Henan Institute of Geology Survey, Zhengzhou 450001, PR China

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A B S T R A C T
The Guangou bauxite deposit in western Henan, China, is located in the North China Block and to the north of the North Qinling orogenic belt. The orebody is hosted within the lower member of the Carboniferous Benxi Formation, which overlies unconformably upon the Ordovician Majiagou Formation. In the lower member of the Benxi Formation, the bauxite orebody (with a diaspor–illite–anatase mineral assemblage) is sandwiched between underlying ferric clay (illite–hematite–goethite) and overlying top clay (kaolinite–quartz–goethite). According to field observations and geochemical evidence including trace- and rare-earth-element (REE) compositions, especially Zr/Hf ratios, the ferric clays were weathered from the underlying argillaceous limestone in the Majiagou Formation. During this weathering process, trace elements S, Zn, Ni, Cr, V, Sc, F, Ba, and Be are depleted; Li, Rb, and B are enriched; and Zr, Hf, Bi, Ta, Ga, Nb, and Th are relatively immobile. REEs exhibit evident differentiation with enrichment of La, Ce, Pr, and Nd and depletion of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The bauxite formed in weak reducing, slightly basic water conditions according to the genese of coexisting diaspor and anatase, and it was altered during the epigenetic and second exposure periods, forming kaolinite and goethite, respectively. Inter-elemental relationship analyses of the ores suggest that the elemental behaviors of trace elements and REEs in the bauxitization process are mainly controlled by the mineral compositions in bauxite ore and chemical properties of the elements. For instance, zircon, rutile, and anatase contain Zr, Hf, Nb, Ta, W, and U. Based on geochemical evidence, together with age data and chemical compositions of the detrital minerals, both distant igneous rocks in the plate margin and Paleozoic carbonates and Precambrian rocks inside North China Block provide the miscellaneous material for the bauxite ore and the top clay.

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1. Introduction

Karstic-type bauxite, which is defined within the bedrock as carbonate (Bárdossy, 1982; Calagarí and Abedini, 2007; Deng et al., 2010), is widely distributed in the North China Block (NCB). The western Henan in the NCB contains approximately 1 billion tons of bauxite ore. Its geological, mineralogical, and geochemical features, as well as the ore-forming mechanism, have been studied since the 1950s (Liu et al., 2012a; Wu, 1996; Zhang, 1955). It is recognized that the bauxite orebodies occur as (semi-)stratiform, lenticular, and funnel shapes controlled by the paleokarstic topography (He, 2007). The ores are complex in composition, being composed of over 30 mineral species (Zhai et al., 2002). Despite numerous studies, the provenance rock, ore-forming environment, and elemental behaviors during weathering remain ambiguous or debatable. Most researchers have suggested that either the exposed Precambrian metamorphic rocks in the paleo-uplands developed in the NCB hinterland or that the underlying Ordovician carbonates or both are the major provenance rocks based on the geochemical studies of ores and their heavy-mineral contents (e.g., Feng, 1992; He et al., 2007; Meng et al., 1987; Wang et al., 2012a). Recently, based on the U–Pb ages of detrital zircons separated from the bauxite ore, the magmatic rocks in the Paleozoic arcs accreted to the NCB were considered to provide important source material (Y. Wang et al., 2010). In this study, we examined the geological, mineralogical, and geochemical characteristics in the Guangou bauxite deposit with the aim of gaining a better understanding of the bauxite genesis in western Henan.

2. Geological setting

2.1. Regional geology

Western Henan, in the NCB, is located north of the North Qinling orogenic belt (NQO) (Deng et al., 2011; Wang et al., 2012a) (Fig. 1). The Precambrian basement in the NCB is mainly composed of Archean to Paleoproterozoic metamorphic rocks overlying by (argillaceous-) carbonate and shale from the Cambrian to the Middle Ordovician (Deng et al., 2006, 2008). At the end of the Ordovician, the NQO and the NCB were both uplifted and then subjected to intense weathering over
150 Ma until the sedimentation of the Benxi Formation of the Late Carboniferous (Meng and Ge, 2002; Wang et al., 2012b). The lower member of the Benxi Formation is mainly composed of ferric clay (containing iron ore), bauxite ore, and top clay, which are overlain by the clastic rocks or carbonates in the upper member. The Benxi Formation was overlain by a coal-bearing formation and carbonates in the Taiyuan Formation and thousands of meters of terrestrial clastic rocks ranging from Permian to Triassic in age (Deng et al., 2003, 2009; Meng and Ge, 2002; Wang et al., 2012a). Subsequently, the bauxite horizon was uplifted and exposed to the surface again owing to tectonic movements during the Mesozoic and Cenozoic.

2.2. Deposit geology

In the Guangou bauxite deposit, three layers, i.e., ferric clay, bauxite ore, and top clay, were divided from bottom to top in the lower member of the Benxi Formation (Fig. 2). In some outcrops uncovered by mining, the underlying argillaceous limestone in the Majiagou Formation was observed to change into red-colored, relatively loose semi-weathered limestone (Fig. 3d), and the latter gradually converted into ferric clay upward. This suggests the possibility that the ferric clay is mostly sourced from the underlying argillaceous limestone (Fig. 3b).

The bauxite layer varies largely in thickness from several meters to tens of meters, which was mainly controlled by the karstic topography (Fig. 3a). The orebody thickness in the karstic sinkhole or depressions was greater than that in the highland. The bottom bauxite ore was occasionally penetrated by Fe-enriched veins (Fig. 3c). Cryptocrystalline, clastic, ooidic, and nodular textures dominate in the ores (Fig. 4).

3. Sampling and analytical methods

Six underlying argillaceous limestone, one semi-weathered limestone, two ferric clay, eleven bauxite ore, and two top clay samples were collected from the Guangou bauxite deposit, as illustrated in Fig. 2. The collected samples were cut for thin, polished sections in the laboratory of the China University of Geosciences (Beijing). Mineralogical and textural studies of selected samples were carried out using optical microscopy, X-ray diffraction (XRD), and electron probe X-ray microanalysis (EPMA). Major, trace, and rare-earth elements (REEs) of all samples were analyzed.

XRD analyses were carried out at the Petroleum Geology Research and Laboratory Center of Beijing using a Rigaku D/Mac-RC and CuKα1 radiation with a graphite monochromator and continuous scanning
under the following operating conditions: voltage of 40 kV, beam current of 80 mA, scanning speed of 8°/min, slit DS = SS = 1°, ambient temperature of 18 °C, and humidity of 30%. The contents (in mass %) of the main mineral phases identified by XRD were quantified by using an internal standard with corundum chosen as the reference material. The basic principles and procedure of quantitative analysis using the internal-standard method have been described in detail by Snyder and Bish (1989). Electron probe X-ray microanalyses were performed at the China University of Geosciences (Beijing) using a Hitachi S-3400N scanning electron microscope equipped

![Fig. 2. Cross section of the Guangou bauxite deposit showing the spatial relationships between the bauxite ore and its host rocks and sample locations.](image)

![Fig. 3. Field photographs illustrating the paleokarstic terrain and orebody features of the Guangou bauxite deposit: (a) paleokarstic terrain with alternating depressions and highlands in the Guangou pit; (b) contact between semi-weathered limestone and overlying ferric clay in the highland; (c) ferric clay and overlying bauxite ore; (d) semi-weathered limestone in the local highland area.](image)
Fig. 4. Photomicrographs of the bauxite ore: (a) kaolinite filling along the fracture in the diaspore ooid; (b) clastic texture; (c) pisolite, mainly composed of diaspore located in the illitic matrix; (d) pyrite in the ore. (Kao: kaolinite; Dsp: diaspore; Ilt: illite; Pyr: pyrite.)

Fig. 5. XRD patterns of four typical analyzed samples. (D: diaspore; H: hematite; Go: goethite; K: kaolinite; A: anatase; I: illite, V: volkonskoite; R: rutile.)
with a Link Analytical Oxford IE 350 ED X-ray spectrometer under the following operating conditions: accelerating voltage of 15 kV, beam current of $1 \times 10^{-8}$ A, beam lifetime of 50 s, and beam diameter of 1 μm.

Whole-rock chemical compositions were analyzed at the Analytical Laboratory of the Geological Survey of China in Langfang, Hebei Province. Major elements in whole rocks (except FeO, loss on ignition (LOI), H$_2$O$^+$, and CO$_2$) were determined by standard X-ray fluorescence (XRF) using a Philips Model 1480 spectrometer equipped with a Rh tube. The FeO contents were analyzed by using the volumetric method; the LOI and H$_2$O$^+$ contents were determined by using the gravimetric method; and the CO$_2$ contents were analyzed by using the potentiometry method. Trace element abundances (S, B, F, Li, Rb, Cs, Be, Sr, Ba, Cu, Zn, Ga, Ni, Cr, V, Sc, Zr, Hf, Nb, Ta, W, Th, and U) were analyzed by using a combination of emission spectrography (ES), inductively coupled plasma mass spectrometry (ICP-MS), and XRF. Detection limits were ≤0.1 wt.% for major elements and ≤2 ppm for most trace elements. The detection limits for Cr, Rb, Sr, and V are ~5 ppm, and those for F and S are 100 and 50 ppm, respectively.

### 4. Mineralogy

#### 4.1. Mineral composition

XRD analysis and EPMA revealed that the ferric clay is dominated by illite, hematite, goethite, anatase, and diaspore. Bauxite ore mainly comprises diaspore, anatase, illite, kaolinite, hematite, and goethite with minor amounts of rutile, zircon, and pyrite. The top clay consists of kaolinite, quartz, and goethite with small amounts of hematite, volkonskoite, illite, plagioclase, and rutile (Figs. 5 and 6 and Table 1).

#### 4.2. Occurrences of major minerals

Diaspore occurs as cryptocrystalline particles and is widely distributed in ooids, pisolites, and the matrix (Figs. 4 and 6). Anatase in the bauxite ore principally coexists with diaspore (Fig. 6a and b). In some case, diaspore was enwrapped by anatase aggregates (Fig. 6a), suggesting that diaspore and anatase formed synchronously. Illite mainly disperses in the matrix of the ore and in the ferric clay as scaly aggregates (Fig. 6g and h). Kaolinite mainly occurs as fine flakes within the diaspore aggregates.

### Table 1

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<th>Hematite (%)</th>
<th>Anatase (%)</th>
<th>Rutile (%)</th>
<th>Diaspore (%)</th>
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**Fig. 6.** Backscattered electron images showing the occurrences of major minerals: (a) diaspore being enwrapped by anatase aggregates and zircon dispersing in the diaspore matrix; (b) diaspore coexisting with anatase; (c) goethite coexisting with diaspore in a pisolite; (d) goethite with cubic shape occurring in the pisolite; (e) goethite and kaolinite aggregates dispersing in the illite matrix; (f) the goethite vein crosscutting the bauxite ore; (g) diaspore coexisting with illite in the matrix; (h) kaolinite filling in the void spaces and fractures within the diaspore aggregates.

**Fig. 7.** Binary diagrams showing the correlations between (a) Al$_2$O$_3$ and SiO$_2$ and between (b) Al$_2$O$_3$ and TiO$_2$ among the bauxite ore samples.

**Fig. 8.** Upper-crust-normalized trace-element graphs of argillaceous limestone, semi-weathered limestone, and ferric clay (a) and that of bauxite ore and top clay (b).
or aggregates in the top clay (Fig. 6e) and it principally fills in the void spaces within the diaspore aggregates in the ore, denoting an epigegetic origin (Figs. 4a and 6h). Three occurrences of goethite were identified in the backscattered electron images, including fine grains or aggregates in the top clay (Fig. 6e), fine cubic crystals in the episolite (Fig. 6c and d), and veins in the bauxite bottom (Fig. 6f). Zircons are mainly scattered in the ore as single crystals (Fig. 6a).

5. Geochemistry

5.1. Major elements

Low Si, Al, Fe, Mg, and K contents in the underlying argillaceous limestone indicate that it contains minor argillite components. Compared to the limestone, both semi-weathered limestone and ferric clay have elevated levels of SiO₂ (25.45–33.55 wt.%), Fe₂O₃ (16.85–20.97 wt.%), and Na₂O (10.50–11.55 wt.%).

Figs. 4a and 6h). Three occurrences of goethite were identified in the backscattered electron images, including fine grains or aggregates in the top clay (Fig. 6e), fine cubic crystals in the episolite (Fig. 6c and d), and veins in the bauxite bottom (Fig. 6f). Zircons are mainly scattered in the ore as single crystals (Fig. 6a).

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Table 2
Major-, trace-, and rare-earth-element compositions of analyzed samples.

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The bauxite ore is characterized by enriched Al₂O₃ (62.61–81.76 wt.%), erratic amounts of SiO₂ (0.45–16.49 wt.%), and small amounts of Fe₂O₃ (0.20–4.91 wt.%), K₂O (0.03–3.50 wt.%), and TiO₂ (2.86–4.67 wt.%). The high negative correlation between Al₂O₃ and SiO₂ in the bauxite ore (Fig. 7a) suggests that SiO₂ was depleted as the Al₂O₃ concentrated in the bauxitization process. However, a lack of correlation between Al₂O₃ and TiO₂ in bauxite ore samples reveals that Al₂O₃ and TiO₂ are not the immobile element pairs in the bauxitization process at Guangou (Fig. 7b). The top clay shows high SiO₂ contents resulting from the presence of abundant kaolinite. Additionally, the TiO₂ (1.27–1.66 wt.%) in the top clay is low, suggesting a low degree of weathering compared to that of the bauxite ore.

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28.39 wt.%), Al₂O₃ (31.30–34.97 wt.%), and K₂O (5.31–6.32 wt.%). The bauxite ore is characterized by enriched Al₂O₃ (62.61–81.76 wt.%), erratic amounts of SiO₂ (0.45–16.49 wt.%), and small amounts of Fe₂O₃ (0.20–4.91 wt.%), K₂O (0.03–3.50 wt.%), and TiO₂ (2.86–4.67 wt.%). The high negative correlation between Al₂O₃ and SiO₂ in the bauxite ore (Fig. 7a) suggests that SiO₂ was depleted as the Al₂O₃ concentrated in the bauxitization process. However, a lack of correlation between Al₂O₃ and TiO₂ in bauxite ore samples reveals that Al₂O₃ and TiO₂ are not the immobile element pairs in the bauxitization process at Guangou (Fig. 7b). The top clay shows high SiO₂ contents resulting from the presence of abundant kaolinite. Additionally, the TiO₂ (1.27–1.66 wt.%) in the top clay is low, suggesting a low degree of weathering compared to that of the bauxite ore.
Fig. 9. Binary diagrams showing the correlations between (a) TiO$_2$ and Zr, (b) TiO$_2$ and Hf, (c) TiO$_2$ and Nb, (d) TiO$_2$ and Ta, (e) Zr and Hf, and (f) Nb and Ta in the bauxite ore samples and (g) Zr and Hf variations among the underlying argillaceous limestone, semi-weathered limestone, ferric clay, bauxite ore, and top clay.

Fig. 10. Chondrite-normalized REE patterns of the underlying argillaceous limestone, semi-weathered limestone, and ferric clay (a) and those of bauxite ore and top clay (b).
5.2. Trace elements

The underlying argillaceous limestone is characterized by low contents of trace elements, mostly less than tens of parts per million except for S (the contents of which are > 1500 ppm). Both semi-weathered limestone and ferric clay have similar trace-element compositions with S, B, F, Li, Rb, Ba, and Zr being higher than 100 ppm and others ranging from several to tens of parts per million. Similar upper-crust-normalized trace-element patterns between semi-weathered limestone and ferric clay indicate that the ferric clay is most likely to derive from the underlying argillaceous limestone, as is consistent with the field observation (Fig. 8a).

The bauxite ores have high contents of Zr, B, F, S, Sr, Cr, and V at the level of hundreds of parts per million; other trace elements mainly range from several to tens of parts per million (Table 2). The top clay contains more than 100 ppm contents of Zr, F, Li, Ba, S, Sr, Cr,

Fig. 11. Mass changes for major, trace, and rare-earth elements with Zr as the immobile element during the weathering process from the underlying argillaceous limestone to ferric clay at the Guangou bauxite deposit.

Fig. 12. Cluster diagram from bauxite ore samples in the Guangou bauxite deposit, western Henan.
and V and the contents of other trace elements vary from several to tens of parts per million. The top clay has spidergram patterns roughly similar to those of bauxite ore, with differences in several alkaline elements (Li, Rb, Cs, and Be) (Fig. 8b). These differences mainly result from the higher abundance of clay minerals, which are the main carrier for alkaline elements, in the top clay.

Correlation analyses revealed that TiO₂ and high field strength elements (Zr, Hf, Nb, and Ta) exhibit a weak positive correlation in the bauxite ore samples, whereas Zr versus Hf and Nb versus Ta exhibit highly positive correlation, with correlation coefficients ($R^2$) of 0.99 and 0.81, respectively (Fig. 9). The similar behaviors of Zr and Hf indicate their immobility during bauxitization, and thus their ratio can serve as an index for ore provenance identification. Similar Zr/Hf ratios in the underlying argillaceous limestone, semi-weathered limestone, and ferric clay support their inheritance relationships (Fig. 9g).

5.3. Rare-earth elements

The underlying argillaceous limestone is characterized by low contents of ΣREE (9.99–44.00 ppm), moderately varied ratios of light to heavy REEs ($\Sigma$LREE/$\Sigma$HREE = 0.48–2.86), and nearly flat REE patterns with (La/Yb)N ranging from 0.38 to 3.78, negative Eu anomalies (0.57–0.64), and weak Ce anomalies (0.76–1.01). The semi-weathered limestone contains 677.16 ppm ΣREE and exhibits a right-dipping REE pattern with negative Eu (0.67) and Ce anomalies (0.83). The ferric clay has variable ΣREE contents (692.27–1056.14 ppm), nearly constant $\Sigma$LREE/$\Sigma$HREE ratios (9.08–9.53), negative Eu anomalies (0.63–0.64), and positive Ce anomalies (1.12–1.36) (Table 2 and Fig. 10a). The similar REE patterns of semi-weathered limestone and ferric clay likely imply that they came from the same provenance rocks.

The bauxite ores have highly varied ΣREE contents (83.59–1306.85 ppm) and $\Sigma$LREE/$\Sigma$HREE ratios (3.35–25.84), relatively stable negative Eu anomalies (0.51–0.63), and erratic Ce anomalies (0.5–1.58) (Fig. 10b). The top clay has 434.74–644.79 ppm ΣREE, high $\Sigma$LREE/$\Sigma$HREE ratios (14.72–15.81), visible Eu anomalies (0.55–0.70), and varied Ce anomalies (0.94–2.04). The roughly similar REE patterns of the bauxite ore and the top clay also indicate that they are possibly from the same source rocks.

5.4. Mass change

According to field observations and the geochemical evidence analyzed above, the argillaceous limestone is considered to be the precursor of the ferric clay. The mass change during the transition between the two was calculated by using the immobile element method (MacLean and Kranidiotis, 1987). The change of all elements was calculated against Zr, which is deemed as the most immobile element. Details of the principle and calculation procedure of this method have been given by MacLean et al. (1997) and the calculated mass changes of the major, trace, and rare-earth elements are illustrated in Fig. 11. It shows that CaO, LOI, SiO₂, Fe₂O₃, MgO, MnO, and FeO are depleted, with CaO and LOI being almost completely lost. Trace elements S, Zn, Ni, Cr, V, Sc, F, Ba, and Be are depleted; Li, Rb, and B are enriched; and Hf, Bi, Ta, Ga, Nb, and Th are relatively immobile. REEs are evidently differentiated in the weathering process; e.g., elements La, Ce, Pr, and Nd are enriched, whereas Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu show depletion with different degrees.

![Fig. 13. Eh–pH diagram showing the overall formation environment of karstic bauxite (area A) and that in the Masatdag bauxite deposit in Turkey with gibbsite (initial bauxite mineral), diaspore, goethite, hematite, and chamosite (area B); the Manaf and Dehnow bauxite deposits with boehmite, kaolinite, and hematite in Iran (area C); the Guangxi Permian diaspore–chamosite bauxite deposits in China (area D); and the Guangou diaspore–illite bauxite deposit in China (area E) according to ore mineral formation conditions. (The base diagram was revised from Garrels and Christ (1965).)](image)

![Fig. 14. Eu-anomaly variations in each layer from the underlying argillaceous carbonate to the overlying top clay in the Guangou deposit.](image)
5.5. Cluster analysis

Cluster analysis was employed to evaluate the element associations in the bauxite ores. CaO, MnO, MgO, and FeO were excluded from the cluster analysis owing to their low contents. Seven main clusters with correlation coefficients greater than 0.7 in each cluster were distinguished: (1) SiO₂–K₂O–Rb–Cs–Li–B, (2) Dy–Ho–Er–Tm–Yb–Lu–Na₂O–Ba–Fe₂O₃, (3) La–Pr–Nd–Sm–Eu–Gd–Th–Ce–P₂O₅–Be–F, (4) Nb–Ta–W–U, (5) Bi–Zn, (6) Zr–Hf–Th–Ga–Sr, and (7) Al₂O₃–H₂O⁺ (Fig. 12). Each cluster represents a group of elements with similar geochemical behavior during bauxitization (Mutakbayhwa et al., 2003).

6. Discussion

6.1. Mineral genesis and ore-forming environment

Diaspore could form under diverse environments, e.g., metamorphic, hydrothermal, or supergene, according to both field observations and experimental studies (Dangić, 1988, and references therein; Liu et al., 2012b). Supergene diaspore is formed in reducing, alkaline conditions (D’Argenio and Mindszenty, 1995). Anatase in karstic bauxite generally precipitates under reducing conditions (Özlü, 1983; Zarasvandi et al., 2008). The coexistence of diaspore and anatase and their enwrapping at Guangou indicate that both are supergene and formed during a syngenetic stage. These characteristics further reveal that the depression in the paleokarstic terrain, which is favorable for bauxite accumulation, has a reducing, alkaline condition.

The illite in weathered rocks could have derived from mica (Meunier and Velde, 2004, and references therein) or reprecipitate via feldspar dissolution (Bétard et al., 2009; Jiménez-Espinosa et al., 2007). The fine scaly aggregates of illites that developed in both bauxite ore and ferric clay are possibly mainly weathered from mica in the protoliths. Kaolinite in bauxite may be residual, syngenetic, or epigenetic in origin (Dangić, 1985; Karadağ et al., 2009). The occurrences of kaolinite in the Guangou bauxite deposit imply complex origins. The kaolinite in the ore coexisting with diaspore should be an epigenetic product induced by diaspore silicification (Dangić, 1985), whereas the kaolinite in the top clay could be a Paleozoic weathered product (Wang et al., 2012b).

The goethite occurrences imply diverse origins. The fine goethite in the top clay is considered to be a Paleozoic weathered product. The cubic goethite in pisolith is transformed from pyrite in situ after the bauxite horizon was uplifted and exposed to oxidizing surface conditions. The goethite veins penetrating the ore are formed via flow of Fe-bearing solutions resulting from dissolution of pyrites under these oxidizing conditions (Wang et al., 2011).

The ore-forming environment of karstic bauxite determines the types of aluminum hydroxides, i.e., diaspore, boehmite, or gibbsite, and also controls their paragenetic minerals to some extent (D’Argenio and Mindszenty, 1995; Liu et al., 2012b; Temur and Kansun, 2006; Zarasvandi et al., 2012). Based on the formation conditions of the major minerals in karstic bauxite presented by D’Argenio and Mindszenty (1995), Temur and Kansun (2006), Liu et al. (2012b) and Zarasvandi et al. (2012), the Guangou bauxite formed in slightly reducing and basic water conditions (Fig. 13). According to the same principle, we summarize the inferred formation conditions of several other karstic deposits based on their mineral compositions in Fig. 13. The Masatdağ bauxite in Turkey with gibbsite as the initial bauxite mineral (Temur and Kansun, 2006) formed approximately under Eh −0.1 to 0.5 and pH 5–9 water conditions (area B), the Mandan and Dhenow boehmite bauxites (Zarasvandi et al., 2012) in Iran formed under approximately Eh −0.1 to 0.4 and pH 6–7 water conditions (area C), and the Permian diaspore bauxites in South China (Liu et al., 2012b) formed under reducing (−0.5 < Eh < −0.1) and basic (7 < pH < 9) water conditions (area D). Area A in Fig. 13 roughly outlines the range of overall conditions for bauxite formation in the paleokarstic environment.

The bauxites generally experienced alteration and reworking after their formation during the epigenetic or second exposure periods, as evidenced by many case studies (Dangić, 1985; Karadağ et al., 2009; Liu et al., 2010; Wang et al., 2011). In the Guangou bauxite, diaspore was partially altered to kaolinite during the epigenetic stage, and nearly all pyrites in the bauxite ore were dissolved or transformed into goethite during the second exposure period.

6.2. Elemental behaviors

In the weathering process from argillaceous limestone to ferric clay, loss of SiO₂, MgO, and FeO suggest that some argillic components are dissolved. The large loss of S is mainly related to the dissolution of sulfides, which is also responsible for the loss of Zn, Ni, Cr, V, and Sc. Losses of F, Ba, and Be possibly result from dissolution of argillic components. The evident enrichments of Li, Rb, and B are related to the formation of illite (Wang et al., 2012a). Elements Hf, Bi, Ta, Ga, Nb, and Th exhibit little change, suggesting relatively immobile features. The evident differentiation of REEs during the weathering process mainly results from the distinct REE chemical properties under surface conditions.

Although the mass change from provenance rocks to bauxite cannot be estimated at Guangou because of its polygenetic features, the elemental occurrences and behaviors during bauxitization can be qualitatively analyzed. Based on the mineralogical and chemical compositions and the cluster analysis, the behaviors of elements in the bauxite ore at Guangou can be discussed.

Accessory minerals inherited from the provenance rocks control most of the trace- and rare-earth-element behaviors. The elemental assemblage Nb–Ta–W–U in cluster 4 should be mainly related to the existence of rutile, and the cluster of Zr and Hf is controlled by zircon. Na₂O, Ba, Dy, Ho, Er, and Th exhibit little change, suggesting relatively immobile features. The high correlation coefficient between P₂O₅ and Ce in cluster 3 would indicate that the minor monazites are residual.

Secondary minerals formed during the Paleozoic weathering process still play an important role in the trace-element behaviors. Alkali elements are the mobile elements in weathering; however, the illite present contains small amounts of K, Li, Rb, and Cs, as indicated by cluster 1. Boron appears in clusters 1, showing that the element is mainly absorbed by illite (Wang et al., 2012a). Fe₂O₃, Dy, Ho, Er, and Th exhibit little change, suggesting relatively immobile features. The high correlation coefficient between P₂O₅ and Ce in cluster 3 would indicate that the minor monazites are residual.

Neoformations in these reducing and basic ore-forming conditions also result in accumulation of special trace elements. Although Zr, Hf, Nb, Ta, W, Th, and U are mainly contained by zircon and rutile, abundant anatases formed under reducing conditions could also absorb some Zr, Hf, Nb, Ta, W, Th, and U dispersing in the solution (Mordberg et al., 2001). The high correlation between Sr and Th in cluster 6 might relate to minor amounts of svanbergite (Liu et al., 2012a). Both Bi and Zn are mobile elements (Mordberg, 1996); the weak positive correlations between S and Bi and between S and Zn indicate that they are enriched in sulfides formed during the Paleozoic.

Additionally, the chemical properties of elements influence the behaviors of trace elements during the whole ore-forming process. For instance, element Ga, concentrated in nearly all karstic bauxite, is commonly considered to be enriched in diaspore and boehmite (Bárdossy and Aleva, 1990); however, the weak correlation between Al₂O₃ and Ga at Guangou barely supports this view. The highly positive correlations between Ga and Zr and between Ga and Hf indicate that the enriched Ga was possibly jointly absorbed by the diaspore, anatase, and detrital minerals.
6.3. Provenance analysis and ore-forming process

The trace- and rare-earth-element compositions, immobile-element ratios, and field observations all support the ferric clay being mainly weathered from underlying argillaceous limestone, with the bauxite ore and top clay being allochthonous. The Eu anomaly was considered to be retained during intense weathering and was utilized for identifying the provenance rocks of the bauxite (Mameli et al., 2007; Mongelli, 1993). Within the Guanqou deposit, the Eu anomaly increases with weathering from the underlying argillaceous limestone to semi-weathered limestone and then decreases from semi-weathered limestone to ferric clay (Fig. 14). Yet the lower Eu anomaly in the bauxite ores at Guanqou compared with the underlying argillaceous limestone still implies that the bauxite ores were not directly weathered from the underlying argillaceous limestone. Information obtained from detrital zircon dating (Y. Wang et al., 2010) combined with detrital tourmaline analyses in the bauxite ore (Wang et al., 2012a) suggests that distant igneous rocks in the NQO and the regional metamorphic rocks and the underlying argillaceous limestone within the NCB, jointly provide the source materials for the bauxite ore and the top clay in western Henan.

From the Late Ordovician to the Middle Carboniferous, the NQO and the NCB were exposed and suffered intense weathering, forming abundant Al-enriched soils. In the Late Carboniferous, under the prevalent warm and wet conditions, ions, including those of Al, Si, Fe, Ti, etc., were released from the Al-enriched soils under extremely acidic conditions contributed from distant orogenic belt along plate margins and Paleozoic carbonates and Precambrian rocks inside NCB. The ferric clay suffered epigenetic alteration and second exposure reworking. D’Argenio and Mindszenty, 1995. Bauxites and related paleokarst: tectonic and climatic event markers at regional unconformities. Eclogae Geol. Helv. 88 (3), 451–469.


References


