Provenance of Lower Carboniferous Bauxite Deposits in Northern Guizhou, China: Constraints from Geochemistry and Detrital Zircon U-Pb Ages

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ABSTRACT: The Lower Carboniferous Jiujialu Formation bauxite deposits of northern Guizhou Province, China, are a Kazakhstan subtype of karst bauxite deposits. The provenance of the Jiujialu Formation has long been debated, with uncertainty about the formation of the bauxite deposits. Here we report new geochemical data that indicate the affinity between the Lower–Middle Ordovician clastic rocks and argillaceous dolostones and the overlying Carboniferous bauxite deposits, all of which are characterized by high Al2O3, K2O, and SrREE contents, flat post-Archean Australian shale (PAAS)-normalized REE patterns, and uniform immobile element ratios (TiO2/Al2O3, Nb/TiO2, and Zr/TiO2). Their similar detrital zircon age distributions further indicate the link between the bauxite deposits and the clastic rocks and argillaceous dolostones. Zircon age spectra of clastic rocks of the Lower Silurian Hanchiatien Formation in northern Guizhou match those of the bauxite deposits, with a maximum age peak at ~980 Ma and other secondary age peaks, suggesting these clastic rocks may represent the provenance of the bauxite deposits. The youngest detrital zircons (~445 Ma) occur only in the bauxite deposits and are probably sourced from K-bentonite beds of the Ordovician–Silurian transition. Our analyses indicate that the source materials of the bauxite deposits in the Jiujialu Formation are of mixed provenance: Lower–Middle Ordovician aluminosilicate rocks and argillaceous dolostones of the underlying strata, and Lower Silurian clastic rocks and K-bentonite from adjacent areas. A comparison of Early Carboniferous bauxite provenances in northern and central Guizhou indicates that paleotopography was the major factor controlling the provenance of these bauxite deposits.

KEY WORDS: weathering, bauxitization, karstification, chemical weathering, Jiujialu Formation.

0 INTRODUCTION

Bauxite is generally considered a chemical residuum produced by intense subaerial weathering in humid tropical to subtropical regions, and comprises aluminum hydroxides and smaller quantities of iron oxyhydroxides and clay minerals (Yu et al., 2019; D’Argenio and Mindszenty, 1995; Bárdoassy, 1994, 1982). Apart from the economic value of bauxite deposits, their geological history is of interest in that it indicates a long-term sedimentation hiatus, a warm and humid paleoclimate, and a stable tectonic background (Combes and Bárdoassy, 1995).

D’Argenio and Mindszenty (1995). The global distribution of post-Quaternary bauxite deposits indicates their concentration in the intertropical convergence zone (Price et al., 1997), implying that the modern tropical climate provides favorable conditions for bauxitization. It is, therefore, not surprising that bauxitization declined globally during the ice ages as, for example, in the Late Paleozoic Ice Age (LP1A) (Yu et al., 2019; Bogatyrev et al., 2009; Bárdoassy, 1994); however, the Late Paleozoic was the most favorable period for bauxite formation in China due to its unique paleoclimate and paleohydrology (Yu et al., 2019). The unique characteristics of Chinese bauxite deposits thus provide an opportunity to enhance our understanding of the coupling between the generation of large karst bauxite deposits and their provenance, tectonic background, paleoclimate, and paleohydrology.

Based on bedrock lithology, bauxite deposits are classified into three categories (Bárdoassy, 1982): (1) karst-type deposits.
covering carbonate rocks, (2) laterite-type deposits formed by in-situ laterization of underlying aluminosilicate rocks, and (3) Tikhvin-type (sedimentary) deposits overlying aluminosilicate rocks and produced by transportation and redeposition of lateritic bauxite deposits. The Kazakhstan subtype of karst-type bauxite deposits is characterized by abrupt changes in deposit thickness, cyclic bauxite-claystone alternation, and basalts of both aluminosilicate and carbonate rocks. The bauxite deposits of Guizhou Province are karst- and sedimentary-type deposits, and are divided into four deposit belts from south to north: the Qingzhen-Xiuwen, Kaili-Huangping, Zunyi-Xifeng, and Wuchuan-Zheng’an-Daozhen (WZD) belts (Zhou and Liu, 2016; Liu, 1987). The Early Carboniferous and Early Permian were the main bauxitization periods in Guizhou, with deposits in the Qingzhen-Xiuwen and Zunyi-Xifeng regions being formed during Early Carboniferous (Liao and Liang, 1991). The mineralogical, geochemical, and petrological characteristics of the bauxite deposits in the Zunyi area have previously been studied (Weng et al., 2019; Liao and Liang, 1991; Liu, 1991).

The provenance of bauxite in the Zunyi-Xifeng area is still debated, with two main perspectives arising in previous studies: (1) stratigraphic contact relationships imply that the underlying Cambrian Loushanguan Group dolostone may be the main source of the Jiujialu Formation bauxite (Ling et al., 2017; Liu, 1987), and (2) geochemical analyses indicate that the Lower Carboniferous bauxite has an affinity with the aluminosilicate rocks of the underlying Lower–Middle Ordovician strata (Weng et al., 2019; Liu, 1999, 1991; Liao and Liang, 1991; Wang, 1988). Both perspectives are based on petrographic and geochemical evidence for the provenance of bauxite deposits, however, these existing evidences are not strong, for petrographic and geochemical features are usually strongly compromised by intense weathering and diagenesis (Bárdossy, 1982; Comer et al., 1980). However, zircon is a common accessory mineral in bauxite, and is resistant to physical and chemical weathering, so detrital zircon U-Pb age spectra provide unambiguous information concerning deposit provenance. Recently, detrital zircon geochronology has become a more powerful tool in the determination of bauxite provenance (Wang R X et al., 2018; Yang et al., 2018; Hou et al., 2017; Mongelli et al., 2016; Wang Q F et al., 2016; Yu et al., 2016, 2014; Boni et al., 2012).

This study investigates bauxite provenance using whole-rock geochemical and zircon U-Pb geochronological data from both Carboniferous bauxite deposits and underlying Ordovician strata in the Zunyi-Xifeng area. We also discuss possible links between bauxite deposit provenance and paleotopography.

1 GEOLOGICAL SETTING

The study area lies in the central part of the South China Block, near the northern boundary of the E-W trending Qianzhong uplift (Fig. 1a), an important geological unit in Guizhou, the formation of which was initiated during the Cambrian Fu-rongian (Fig. 1a; Deng et al., 2010). The evolution of the Qianzhong uplift included a critical transformation from an underwater uplift to an island during the closing stages of the Late Ordovician, under the control of the Guangxi Orogeny (also known as the Duyun Orogeny; Deng et al., 2010), leading to exposure of the Qianzhong area and formation of the Qianzhong anticline between the Xiuwen and Xifeng areas (Rong et al., 2011; Niu et al., 2007). During the Silurian, the topography sloped downwards from central to northern Guizhou. Ordovician strata were denuded in central Guizhou, while northern Guizhou continued to receive sediment (Zhao et al., 1989). During the Late Silurian, the Qianzhong uplift expanded northward, connecting with the Upper Yangtze Platform after the end of the Guangxi Orogeny (He et al., 2005), causing the absence of Devonian strata in study area (Fig. 2). In a reversal of the Silurian topography, during the Carboniferous the topography in Guizhou sloped upwards from south to north (Fig. 1b; Yu et al., 2019; Deng et al., 2010). Southern Guizhou was then situated within a relatively stable shallow marine environment, and accumulated marine carbonate deposits. The Qingzhen-Xiuwen area in central Guizhou was a coastal karstic peneplain, and the Zunyi-Xifeng area in northern Guizhou included karstic highlands with large sinkholes and dolines. The Qingzhen-Xiuwen and Zunyi-Xifeng bauxite belts were separated by a zone of relatively high elevation (Fig. 1b; BGMRGZP, 2017; Ling et al., 2017; Liu, 1987).

Palynological records preserved within bauxite orebodies indicate that the Jiujialu Formation bauxite deposits were formed during the Early–Middle Viséan (Middle Mississippian) in the Zunyi area (Fig. 2; Liu and Liao, 2012). Devonian strata are absent in the study area, and Paleozoic strata change from E-trending to NE- or NNE-trending due to a series of folds and faults (Fig. 3). The thicknesses of the bauxite deposits range from ~3 to ~110 m (mean=8–20 m), and they are strongly controlled by the karstic landforms (Weng et al., 2019, 2011). The bauxite-bearing series of the Jiujialu Formation exhibit an ‘iron-bauxite’ structure from bottom to top, with cyclic alternation of bauxite ore and bauxitic claystone layers caused by glacio-eustatic fluctuations during the LPIA (Weng et al., 2019; Yu et al., 2019). The bedrock underlying the bauxite deposits gradually becomes younger from central to northern Guizhou, from the Cambrian Loushanguan Group to the Silurian Hanchatien Formation, and contains more terrigenous clastic sediment, under the influence of the Qianzhong uplift (Fig. 2; Zhou and Liu, 2016). The Zunyi-Xifeng area lies in the petrographic transitional zone of the basement, with the southern and northern parts of the bauxite deposits unconformably in mainly contact with the Cambrian Loushanguan Group dolostone and the Lower Ordovician Tongzi Formation argillaceous dolostone, respectively (Figs. 1b, 2). The units overlying the bauxite deposits are black shales of the Lower Permian Liangshan Formation or limestone of the Lower Permian Qixia Formation. The bauxite deposits comprise aluminum (mainly diaspore), iron (hematite or pyrite), and clay (kaolinite, illite, and chlorite) minerals and accessory minerals including zircon, anatase, and rutile, with Al₂O₃, Fe₂O₃, and SiO₂ contents of 17.99 wt.%–77.71 wt.% (mean=59.67 wt.%), 0.45 wt.%–35.47 wt.% (5.38 wt.%), and 1.44 wt.%–46.55 wt.% (14.59 wt.%), respectively (Weng et al., 2019). These characteristics indicate that bauxite deposits in the Zunyi area are Kazakhstan-subtype karst bauxite deposits (Weng et al., 2019).
2 SAMPLING

Samples for geochemical analysis and detrital zircon U-Pb dating were collected from the Tuanxi stratigraphic section (27°27′59.70″N, 107°9′46.43″E; Fig. 3) in the Zunyi area of northern Guizhou. Bauxite samples for U-Pb dating were collected from the Xianrenyan section (27°25′58.23″N, 107°7′20.36″E; Fig. 3). The Tuanxi section comprises mainly Cambrian Furongian–Lower Permian carbonates and shales (Fig. 4). The Cambrian Loushanguan Group comprises mainly pure dolostone with a thickness of 500–1 300 m. The overlying Lower Ordovician Tongzi Formation includes three members of ~60 m in thickness, with one containing argillaceous dolostones with interbedded shales and the other two consisting of dolostone. Three argillaceous dolostone samples (XWO1T-2–4), one dolostone sample (XWO1T-1), and one shale sample (XWO1T-5) were collected at equally spaced intervals from the upper part of the formation (Figs. 4, 5a). The formation changes upward into bioclastic limestone of the Lower Ordovician Honghuayuan Formation. The overlying Lower–Middle Ordovician Meitan Formation comprises shale, fine-grained sandstone, and interbedded limestone. Four shale samples (XWO1M-1, 2, 4, 6), one fine-grained sandstone sample (XWO1M-5), and one limestone sample (XWO1M-3) were collected at equally spaced intervals from the formation, which is unconformably overlain by limestone of the Lower Permian Qixia Formation (Figs. 4, 5b–5d). A detrital zircon sample (XWO1M-Z) was collected from yellow-grey fine-grained sandstone interlayers of the Meitan Formation (Fig. 5d). In the Xianrenyan Section, the Jiujialu Formation bauxite deposits are unconformably in contact with argillaceous dolostone of the Lower Ordovician Tongzi Formation, and are unconformably overlain by limestone of the Lower Permian Qixia Formation (Fig. 4). An ‘iron-bauxite’ structure is distinguishable in the bauxite deposits, and the high-grade bauxite ores include

Figure 1. (a) Paleogeographic map of the South China Block during the Early Carboniferous, after Liu and Xu (1994). The purple rectangle indicates the Zunyi-Xifeng area of northern Guizhou. (b) Paleogeographic reconstruction of bauxite deposits of the Jiujialu Formation and their underlying strata during the Early Carboniferous in central to northern Guizhou, based on cross-section X–X′ in (a).
porous, clastic, and oolitic types of mineralization (Figs. 5e, 5f). The four bauxitic samples for U-Pb dating (ZNKG-3, 7, 9, 11) were collected from different bauxite ore layers. Logging data from drill core ZK5600 with exceptional orebody thicknesses of up to 110 m and seven bauxite-claystone cycle reflect the geochemical characteristics of the Jiujialu Formation bauxite deposits in the Zunyi area (Fig. 4, Weng et al., 2019). Ninety-three major-elements and rare earth elements (REEs) analyses were undertaken for the bauxite orebody (Al$_2$O$_3$>55 wt.%) and bauxitic claystone (Al$_2$O$_3$<55 wt.%) from drill core ZK5600.

3 ANALYTICAL METHODS

Geochemical analyses were undertaken at the ALS Chemex Laboratory, Guangzhou, China, for 11 whole-rock bedrock samples collected from outcropping bauxite deposits. Samples were coarsely crushed in a corundum jaw device, then powdered in an agate ring mill to a grain size of <200 mesh. Sample major-element compositions were determined by X-ray fluorescence using a Shimadzu XRF-1800. The relative standard deviation (RSD) and relative error (RE) in major-element contents were <5% and <2%, respectively. Trace-element and REE compositions were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Powdered samples were dissolved in HF+HNO$_3$ in Teflon bombs, after which the solution was evaporated to dryness. The evaporation step was repeated with dilute HNO$_3$ before the residue was finally dissolved in HNO$_3$ and an internal standard was added, with the solution then being diluted with ultrapure water for analysis. Trace-element RSD and RE values were <10%.

Zircons from five samples (XWO,M-Z; ZNKG-3, 7, 9, 11) were separated by standard heavy-liquid and magnetic separation techniques, selected by hand-picking, set in epoxy mounts, and polished to reveal their cores. Backscattered-electron and cathodoluminescence (CL) images were obtained to reveal internal zircon structures and to position in-situ analyses. To reduce experimental errors and enhance data reproducibility, four bauxitic samples and the basement samples were analyzed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) using GeoLas 2005 LA and Agilent 7500a ICP-MS systems at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, and an Agilent 7700e ICP-MS system.
equipped with a GeoLasPro LA system at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Analytic results for the four bauxite samples are highly consistent, indicating the data are reliable. Zircon 91500 was used as an external standard for isotopic fractionation correction, and was analyzed twice for every eight sample analyses. The Excel-based ICPMSDataCal was used for off-line signal analysis, time-drift corrections, and U-Pb dating calculations (Liu et al., 2008). Concordia diagrams and weighted means were produced using Isoplot/Ex version 4 (Ludwig, 2008). In order to visualize the frequency of zircon ages, Kernel density estimation (KDE) plots and histograms are plotted using densityplotter (Vermeesch, 2012).

4 RESULTS
4.1 Major-Element Compositions
Shale and sandstone samples from the Meitan and Tongzi Formations have similar major-element compositions (Table 1) and are aluminosilicate rocks, with SiO$_2$ (48.28 wt.%–55.50 wt.%; mean=53.00 wt.%) and Al$_2$O$_3$ (16.55 wt.%–21.75 wt.%; mean=19.53 wt.%) contents. They have TFe$_2$O$_3$ (6.01 wt.%–10.66 wt.%; mean=7.28 wt.%), K$_2$O (6.77 wt.%–8.95 wt.%; mean=7.46 wt.%), MgO (2.06 wt.%–3.67 wt.%; mean=2.75 wt.%), CaO (0.03 wt.%–3.23 wt.%; mean=1.46 wt.%), Na$_2$O (0.08 wt.%–0.12 wt.%; mean=0.11 wt.%), and TiO$_2$ (0.58 wt.%–0.76 wt.%; mean=0.71 wt.%) contents. The argillaceous dolostone samples from the Tongzi Formation have CaO and MgO contents of 13.7 wt.%–18.6 wt.% (mean=16.87 wt.%) and 10.20 wt.%–12.95 wt.% (mean=12.10 wt.%), respectively, higher than those of the aluminosilicate rocks. Their SiO$_2$ (26.11 wt.%–33.69 wt.%; mean=29.50 wt.%), Al$_2$O$_3$ (4.51 wt.%–9.29 wt.%; mean=6.78 wt.%), K$_2$O (2.42 wt.%–5.04 wt.%; mean=3.67 wt.%), Fe$_2$O$_3$ (2.23 wt.%–3.70 wt.%; mean=2.77 wt.%), TiO$_2$ (0.14 wt.%–0.35 wt.%; mean=0.25 wt.%), and Na$_2$O (0.05 wt.%–0.07 wt.%; mean=0.06 wt.%) contents are lower than those of aluminosilicate rocks. One limestone sample from the Meitan Formation and one dolostone sample from the Tongzi Formation have very high CaO and MgO contents and extremely low Al$_2$O$_3$ contents (Table 1).

Data for bauxitic claystone and bauxite ore of the Jiujialu Formation, collected from the ZK5600 drill core, were compared with those of the bedrock (Weng et al., 2019). The bauxite orebody (bauxitic claystone and ore) and underlying Ordovician sediments (shales, fine-grained sandstones, and argillaceous dolostones) exhibit a strong negative correlation between Al$_2$O$_3$ and SiO$_2$ contents ($r$=-0.81; $P(\alpha)=0.01$; $n=102$; Fig. 6a), and Al$_2$O$_3$ and Fe$_2$O$_3$ contents are negatively correlated in the bauxite orebody ($r$=-0.72; $P(\alpha)<0.01$; $n=93$; Fig. 6b). Average Fe$_2$O$_3$ contents are highest in bauxitic claystone, especially at the bottom of the bauxite deposits (Weng et al., 2019; Fig. 6b). Some alkaline earth element (e.g., Ca and Mg) contents are considerably lower in the bauxite orebody than in underlying Ordovician sediments (Figs. 6c, 6d), and Al$_2$O$_3$ and K$_2$O contents are strongly positively correlated in bauxitic claystone and
underlying Ordovician sediments (Al_2O_3 < 35 wt.%; \( r = 0.91; P(\alpha) < 0.01; n = 21 \); Fig. 6e). In contrast, Al_2O_3 and K_2O are negatively correlated in bauxite orebody (\( r = -0.75; P(\alpha) < 0.01; n = 93 \); Fig. 6e), indicating that the clay minerals were converted gradually to aluminum hydroxides during intense chemical weathering, with leaching of K. Al_2O_3 and TiO_2 contents are strongly positively correlated (\( r = 0.93; P(\alpha) < 0.01; n = 104 \); Fig. 6f), indicating the immobility of Ti during chemical weathering.

### 4.2 Trace-Element Compositions

Shale samples from the Meitan Formation have high total REE (ΣREE) contents (219.0 ppm–277.1 ppm; mean=239.0 ppm), weak negative Ce anomalies (Eu/Eu*=0.90–0.94; mean=0.92), and almost flat post-Archean Australian shale (PAAS)-normalized REE patterns ([(La/Yb)_N]=0.95–1.61; mean=1.38; Fig. 7a; Table 1). The ΣREE content (183.8 ppm) of fine-grained sandstone sample XWO1M-5 is lower than those of the shale samples, and its REE pattern shows enrichment in light REEs (LREEs) (Fig. 7a). Limestone sample XWO1M-3 has a high ΣREE content of 198.1 ppm and pronounced middle-REE enrichment (Fig. 7a). One shale and three argillaceous dolostone samples from the Tongzi Formation have relatively low ΣREE contents (48.9 ppm–71.6 ppm; mean=58.5 ppm) and flat PAAS-normalized REE patterns ([(La/Yb)_N]=0.85–1.22; mean=1.00; Fig. 7b). Dolostone sample XWO1T-1 from the Tongzi Formation has an extremely low ΣREE content of 29.37 ppm (Fig. 7b). Aluminosilicate and argillaceous dolostone samples from the Meitan and Tongzi formations have weak Eu anomalies (Eu/Eu*=0.95–1.12; mean=0.99) and weak negative Ce anomalies (Ce/Ce*=0.91–0.99; mean=0.94). Clastic rocks and carbonates of the Meitan and Tongzi Formations rocks have variable trace element contents with, for example, Nb and Zr contents of 0.8 ppm–16.4 ppm and 10.0 ppm–125.0 ppm, respectively (Table 1). There are pronounced positive correlations among high field strength elements (Ti, Zr, and Nb; Figs. 6g, 6h).

### 4.3 Zircon Morphology

The internal structure of detrital zircon grains is revealed in CL images (Fig. 8). Based on size, morphology, and internal structure, the detrital zircon grains can be divided into three groups: (1) euhedral-subhedral zircon grains with clear oscillatory zonation and lengths of 65–178 μm, indicating a magmatic origin (Figs. 8d, 8f, 8h, 8m, 8q); (2) grains with...
multistage growth indicated by homogeneous dark cores surrounded by bright rims (Figs. 8g, 8r), and (3) grains with sub-rounded and rounded structures and homogeneous bright or dark zones, indicating recrystallization (Figs. 8a–8c, 8e, 8i–8l, 8n–8p, 8s, 8t).

4.4 Zircon Geochronology

A total of 357 analyses of zircon grains from five samples (XWO3M-Z, ZNKG-3, 9, 7, 11) were carried out; U-Pb isotopic compositions are listed in Supplementary Table S1, and concordia diagrams are shown in Fig. 9. 314 analyses were <10% discordant and are presented as KDE plots in Fig. 10. Ages of <1 500 Ma are 206Pb/238U ages, and those of older grains (>1 500 Ma) are 207Pb/206Pb ages (Spencer et al., 2016). Uncertainties for individual analyses in the concordia diagrams and Table S1 are 1 SD. The Th/U ratios of zircon are generally considered useful indicators of their origin, with low (<0.1) and high (>0.4) Th/U ratios indicating metamorphic and magmatic origins, respectively (Hoskin and Schaltegger, 2003; Rubatto, 2002). Here, 243 grains have Th/U ratios of >0.4, and 13 of <0.1, indicating that most zircon grains were derived from the weathering and recycling of igneous rocks.

4.4.1 Sample ZNKG-3

The 67 concordant U-Pb analyses from sample ZNKG-3 yield zircon ages of 2 864–427 Ma (Fig. 10a), with an age spectrum comprising six groups: a main age peak at 1 006–967 Ma (weighted mean=991±8 Ma; MSWD=1.9; n=10; MSWD=mean square weighted deviation) and subordinate peaks at 922±14 Ma (MSWD=3.3; n=7), 792±13 Ma (MSWD=3.2; n=7), 648±16 Ma (MSWD=2.5; n=4), 448±19 Ma (MSWD=2.1; n=3), and 21 analyses yield scattered ages of 2 864–1 020 Ma, with a small peak at 2 631±54 Ma (MSWD=1.3; n=4).

4.4.2 Sample ZNKG-7

The KDE plot for 64 analyses of sample ZNKG-7 yields zircon ages of 2 681–444 Ma (Fig. 10b) with three age clusters, including a major peak at 998–970 Ma with a weighted mean age of 982±6 Ma (MSWD=1.3; n=13), and other age peaks at 844±14 Ma (MSWD=1.7; n=5) and 718±16 Ma (MSWD=1.8; n=4). One analysis yielded the youngest age of 444±4 Ma, and 21 ages are scattered from the Mesoproterozoic to Paleoproterozoic.
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Notes: Ce/Ce*=2CeN/(LaN + PrN); Eu/Eu*=2EuN/(SmN+GdN); shale. XWO1M-1, 2, 4, 6 and XWO1T-5; fine-grained sandstone. XWO1M-5; limestone. XWO1M-3; dolostone. XWO1T-1; argillaceous dolostone. XWO1T-2, 3, 4.
Provenance of Lower Carboniferous Bauxite Deposits in Northern Guizhou, China

4.4.3 Sample ZNKG-9

The 61 concordant zircon ages for sample ZNKG-9 include an oldest age of 2,821±34 Ma and youngest of 460±5 Ma (Fig. 10c). Two zircon grains yielded Archean ages of 2,821±34 and 2,817±32 Ma. Twenty-three zircon grains have ages of 2,478–1,101 Ma, with a cluster at 2,455±28 Ma (MSWD=0.7; n=5). Eighteen analyses yields aged ages of 1,066–978 Ma, with a main peak at 992±8 Ma (MSWD=1.2; n=9). Ages between 914 and 572 Ma display two clusters, one at 820–798 Ma (weighted mean=808±18 Ma; MSWD=1.3; n=4) and one at 642–630 Ma (635±6.0 Ma; MSWD=0.7; n=4).

4.4.4 Sample ZNKG-11

The 59 concordant U-Pb ages for sample ZNKG-11 zircons include an oldest age of 2,668±38 Ma (Fig. 10d). Twelve grains have Paleoproterozoic ages with a distinct peak at 2,436±41 Ma (MSWD=1.6; n=7), 14 have Mesoproterozoic ages, and 19 have ages of 1,089–910 Ma (mean=1,065±10 Ma; MSWD=1.8; n=9). Zircons with ages of 838–529 Ma include two groups at 831±11 Ma (MSWD=0.6; n=3) and 541±27 Ma (MSWD=3.3; n=3). The youngest age in the sample is 460±5 Ma.

Representative samples of the bauxite of the Lower Carboniferous Jiujialu Formation (ZNKG-3, 7, 9, 11) are considered individually in the subsections 4.4.1–4, and those of the fine-grained sandstone of the Lower–Middle Ordovician Mei- tan Formation (XWO1M-Z) in subsection 4.4.5 below.

4.4.5 Sample XWO1M-Z

The 63 concordant U-Pb ages for sample XWO1M-Z (Fig. 10e) include an oldest age of 3,385±35 Ma. The age spectrum includes five groups with 12 Paleoproterozoic ages with a peak at 1,813±32 Ma (MSWD=0.5; n=7); 11 of 1,544–997 Ma with a peak at 1,066±16 Ma (MSWD=2.4, n=7), a predominant age peak at 956–922 Ma (weighted mean=943±11 Ma; MSWD=2.1, n=8), and a range of 883–590 Ma, with distinct clusters at 883–851 Ma (weighted mean=867±12 Ma; MSWD=1.3; n=6) and 769–710 Ma (weighted mean=602±18 Ma; MSWD=2.1; n=4). The dominant peak at 536–515 Ma yielded a weighted mean age of 527±7 Ma (MSWD=2.0; n=7). The youngest age was 486±6 Ma.
5 DISCUSSION

5.1 Provenance of the Lower–Middle Ordovician Strata in Northern Guizhou

The provenance of Lower–Middle Ordovician strata in northern Guizhou is constrained by the contemporary paleogeographic setting of the South China Block. During the Early–Middle Ordovician, the western margin of the Yangtze Block was an exposed continent, and the siliciclastic-dominated units in the northwest of the block gradually changed towards the southeast into carbonate-dominated successions (Zhang et al., 2002; Liu and Xu, 1994). The northern Guizhou lies in the center of the Yangtze Block, and was dominated by open and restricted carbonate platform facies during the Early Ordovician and shore and shallow-sea facies in the Middle Ordovician (BGMRGZP, 2017). The gradual decrease in paleo-elevation from the west to the east of the Yangtze Block favored the transport of siliciclastic sediments to the northern Guizhou. The contemporary Cathaysia Block was largely covered by seawater at that time, and clastic materials from it were blocked by a wide, deep basin and could not reach the Zunyi-Xiřeng area by fluvial transport (Liu and Xu, 1994).

The younger (~527, 600, and 867–723 Ma) and older (940–930 and 1 810 Ma) peaks in the detrital zircon age spectrum of fine-grained sandstone of the Meitan Formation from northern Guizhou are similar to the ages of Cambrian and pre-Cambrian strata on the western margin of the Yangtze Block, further implicating the Early–Middle Ordovician aluminosilicate rocks derived from the western margin of the block (Figs. 11a–11d). The dominant age peaks at 860–750 and ~940 Ma in Cambrian and pre-Cambrian strata match well the ages of widespread Neoproterozoic volcano-sedimentary strata, and of felsic intrusions and mafic-ultramafic plutons (1 000–740 Ma) associated with continuous Neoproterozoic subduction on the western margin of the Yangtze Block (Sun et al., 2009, 2008; Zhou et al., 2006, 2002; Li et al., 2003). The youngest age peak of Cambrian strata on the western margin of Yangtze Block, at ~527 Ma, corresponds to the contemporary wide-scale volcanic event in the Yangtze Block, was probably derived from volcanic tuffs (Lan et al., 2017; Okada et al., 2014; Jiang et al., 2009). During the Early Paleozoic, Archean and Paleoproterozoic basement rocks were sparsely exposed in the northern part of the Yangtze Block (including the Koulging Complex, Huangtuling granulites, and Houhe Complex) and on the western margin of the Yangtze Block (Dahongshan and Dongchuan Groups; Zhao and Cawood, 2012; Zhao et al., 2010; Greentree and Li, 2008; Zheng et al., 2007), indicating that the age peaks at ~1 800 and 2 500 Ma in Cambrian and pre-Cambrian strata were derived from the reworking of basement

Figure 7. Post-Archean Australian shale (PAAS)-normalized REE patterns for (a) shale, fine-grained sandstone, and limestone of the Lower–Middle Ordovician Meitan Formation; (b) shale, argillaceous dolostone, and dolostone in the Lower Ordovician Tongzi Formation; (c) bauxite ore of the Lower Carboniferous Jiujialu Formation, modified after Weng et al. (2019), the blue area represents ranges of normalized REE patterns in Jiujialu Fm. bauxite ore; (d) bauxitic claystone of the Lower Carboniferous Jiujialu Formation, modified after Weng et al. (2019), the yellow area shows ranges of normalized REE patterns in Jiujialu Fm. bauxitic claystone. Normalization values are from McLennan (1989).
rocks in the Yangtze Block. Zircons in youngest age group (~458 Ma) in northeastern Guizhou almost belong to hydrothermal origin, which is probably attributed to the Qianzhong tectonic regimes transformed from extension to compression, Qianzhong uplift are thus considered as another source area for Lower–Middle Ordovician strata in northern Guizhou (Fig. 11b; He et al., 2020).

5.2 Provenance of the Lower Carboniferous Bauxite Deposits in Zunyi

The following lines of evidence indicate that the provenance of the Lower Carboniferous bauxite deposits in the Zunyi area is closely associated with underlying aluminosilicate rocks and argillaceous dolostones of Lower–Middle Ordovician strata.

1) The Al_2O_3 contents of aluminosilicate rocks (16.55 wt.%–21.75 wt.%) and argillaceous dolostones (4.51 wt.%–9.29 wt.%) in Ordovician sedimentary units indicate that underlying Ordovician strata may have been the main Al source for bauxite deposits during bauxitization. The strong negative correlation between Al_2O_3 and SiO_2 contents and the relative depletion in alkaline-earth elements in bauxite deposits compared to underlying Ordovician sediments further indicate an affinity between bauxite orebodies and underlying sediments (Figs. 6a, 6c, 6d). The mean K_2O content of bauxite (2.0 wt.%) in the Zunyi area is higher than that of other bauxites (1.19 wt.%) in central Guizhou-southern Sichuan, consistent with the high K_2O contents of the underlying sediments (Fig. 6c; Weng et al., 2019; Liu, 1999). Fe_2O_3 and K_2O contents are the highest in the bauxitic claystone, and are likely associated with the generation of massive hematite and illite in the bauxitic claystone (Figs. 6b; Weng et al., 2019). Furthermore, the vertical geochemical profile reflects element gradually change from bedrock to bauxite deposits (Liao and Liang, 1991; Wang, 1988). Weathering residues of shale and argillaceous dolostones in the Tongzi Formation occur between the bottom of bauxite deposits and the basement surface. The Al_2O_3 and Fe_2O_3 contents gradually increase while SiO_2 and K_2O contents decrease upward in the weathering residues zone.

2) Ratios of immobile elements (e.g., Nb/TiO_2 and Zr/TiO_2) are stable during bauxitization and can be used to constrain the precursor rocks of bauxite deposits (Ling et al., 2018; Ahmadnejad et al., 2017; Zamanian et al., 2016; Liu et al., 2013). The TiO_2-Al_2O_3, Nb-TiO_2, and Zr-TiO_2 plots for samples of Cambrian Furongian pure carbonate, Ordovician bedrock, and Carboniferous bauxite exhibit pronounced linear correlations (r≥0.95), indicating the bedrocks can be regarded as the precursor rocks of bauxite deposits (Figs. 6f, 6g, 6h; MacLean et al., 1997; MacLean and Barrett, 1993; MacLean, 1990; MacLean and Kranidiotis, 1987). The Cambrian Furongian pure carbonates may have provided less source material for bauxite deposits than Lower–Middle Ordovician aluminosilicate rocks, with these carbonates having very low Al contents (Al_2O_3=0.25 wt.%–1.5 wt%; Weng et al., 2019; Ling et al., 2017). Besides, the residual Ordovician strata in the Zunyi area indicate that the Cambrian Furongian sedimentary units were only slightly denuded.
(3) REE contents and patterns are another geochemical fingerprint of potential source materials (Ahmadnejad et al., 2017; Ling et al., 2017; Liu et al., 2013; Esmaeily et al., 2010). The ΣREE contents of Lower–Middle Ordovician aluminosilicate and argillaceous dolostones are similar to those of the bauxite deposits (Figs. 7a–7d), implying that the bedrocks were a major source of REEs in bauxite deposits. The mobilization of REEs is controlled mainly by leaching during subaerial weathering (Braun et al., 1993; Nesbitt, 1979). The bauxitic claystone has higher K and Fe contents than the bedrock (Figs. 6b, 6e), and its REE contents and patterns are quite consistent among different samples, implying that it underwent only slight leaching (Fig. 7d). The degree of fractionation of REEs is largely determined by the mineralogy (Nesbitt, 1979). Bauxitization probably generates accessory weathering minerals (e.g., florencite, rhabdophane, and parisite) enriched in LREEs, which cause more pronounced fractionation than HREEs in bauxite ore of the Jiujialu Formation (Figs. 7c; Wang X M et al., 2013; Wang Q F et al., 2010; Mameli et al., 2007; Braun et al., 1993). These considerations suggest that the REE patterns of the bauxite claystone and HREE patterns of bauxite ore changed only slightly during subaerial weathering and can be tracers of provenance. The REE patterns of shales and argillaceous dolostones of the Ordovician Meit an and Tongzi Formations are characterized by almost flat plots, similar to the REE patterns of the bauxitic claystone and the HREE patterns of the bauxite ore in the Lower Carboniferous Jiujialu Formation (Figs. 7a–7d). Previous studies have indicated that Eu anomalies are retained in intense weathering profiles (Mongelli et al., 2014; Liu et al., 2013; Wang et al., 2010; Mameli et al., 2007; Mongelli, 1997). The Eu/Eu* ratios (0.94–1.12; mean=0.99) of Ordovician aluminosilicate rocks and argillaceous dolostones are similar to those of the bauxite orebody (0.8–1.4; mean=1.04), indicating their affinity.

The four samples (ZNKG-3, 7, 9, 11) from the Lower Carboniferous Jiujialu Formation for which zircon ages were determined yielded consistent detrital zircon age spectra, with ages ranging from Neoarchean (~2 864 Ma) to Silurian (~427
Ma), indicating that the parent material for different bauxite ore layers may have been the same (Figs. 10a–10d). The detrital zircon age spectra of the Lower Carboniferous Jiujialu Formation can be divided into six clusters, with a main peak at ~982 Ma, subordinate peaks at 1 135–1 029 Ma, and minor peaks at the early of the Paleoproterozoic (~2 443 Ma), Early Neoproterozoic (~927 and 833 Ma), Late Neoproterozoic (640–572 Ma), and Early Paleozoic (445 Ma) (Fig. 11e). The Jiujialu Formation bauxite and Meitan Formation fine-grained sandstone display roughly similar detrital zircon age distributions (Figs. 11a, 11e), with corresponding peaks in the Early (~943 and 867 Ma) and Late Neoproterozoic (~600 Ma) in the Meitan Formation. Based on the geochemical, geochronological, and petrographic evidence, we therefore suggest that the Lower–Middle Ordovician aluminosilicate and argillaceous dolostones in the Zunyi area provided significant weathering material for the Lower Carboniferous bauxite deposits; however, the most prominent age peak (~980 Ma) and the youngest age peak (~445 Ma) in the bauxite deposits are different from the largest cluster (~527 Ma) and youngest age (~486 Ma) in fine-grained sandstone of the Meitan Formation (Figs. 11a, 11e), indicating that the bauxite deposits have provenances apart from Ordovician bedrock.

This new result implies that the Lower Silurian siliciclastic rocks in the more northern Zunyi area may also have provided weathering material for the bauxite deposits of the Jiujialu Formation. The siliciclastic rocks of the Lower Silurian Hanchiatien Formation are widely exposed in the WZD belt of northern Guizhou (BGMRGBZP, 2017; Yu et al., 2014; Gu et al., 2013). Our data is very similar to previously published geochronological data for the Hanchiatien Formation (Figs. 11e, 11f; Yu et al., 2015). The major age peak at ~980 Ma and subordinate peak at 1 030–1 100 Ma occur in both sediment units, with other consistent age peaks at 2 500–2 400, 830–800, and ~600 Ma. The consistent immobile-element ratios (TiO₂/Al₂O₃, Nb/TiO₂, and Zr/TiO₂) of Lower Silurian Hanchiatien siliciclastic rocks and the bauxite deposits also indicate their affinity (Figs. 6f, 6g, 6h). This link is further supported by the Early Carboniferous petrography and paleotopography of northern Guizhou. The Hanchiatien Formation, with a thickness of ~600 m in northern Guizhou, comprises mainly clastic rocks, which could have provided sufficient aluminosilicate weathering material for the bauxite deposits (Fig. 2; BGMRGBZP, 2017). Furthermore, the topography of Guizhou gradually rose to the north during the Early Carboniferous (Fig 1b), allowing material eroded from Lower Silurian siliciclastic rocks to be transported southward over the short distance from the relatively high erosional regions to depressions (sinkholes and dolines) near the Zunyi-Xifeng area.

Figure 10. Kernel density estimation plots and histogram of detrital zircon U-Pb ages from ZNKG-3, 7, 9, 11 and XWO1M-Z.
Figure 11. Kernel density estimation plots for detrital zircon U-Pb ages in the South China Block, including: (a) fine-grained sandstone of the Lower–Middle Ordovician Meitan Formation in Zunyi (this study); (b) fine-grained sandstone of the Lower–Middle Ordovician Meitan Formation in northeastern Guizhou, after He et al. (2020); (c) Cambrian strata on the western margin of the Yangtze Block, after Hofmann et al. (2016) and Xia et al. (2016); (d) Pre-Cambrian strata of the western Yangtze Block, after Zhou et al. (2006) and Sun et al. (2009); (e) bauxite of the Lower Carboniferous Jiujialu Formation in the Zunyi area (present study); (f) fine-grained sandstone of the Lower Silurian Hanchiatien Formation near northern Guizhou, after Yu et al. (2015); (g) bauxite of the Lower Carboniferous Jiujialu Formation near Guiyang, after Wang et al. (2018); (h) Cathaysia Pre-Ordovician strata, after Yu et al. (2010, 2008, 2007), Wang et al. (2008), Wu et al. (2010), and Xiong et al. (2018).

K-bentonite is a potential source of the Jiujialu Formation. A noticeable age peak at 445±5 Ma (MSWD=0.71; n=3) was yielded by the youngest of the four bauxite samples, which cannot be sourced from the clastic rocks of the Lower Silurian Hanchiatien Formation or Lower–Middle Ordovician basement (Figs. 11a, 11e, 11f). Most of the ~445 Ma zircon are euhedral crystals with clear oscillatory zonation, lengths of 135–178 μm, and aspect ratios of 3:1 (Figs. 8h, 8m), implying a magmatic origin without significant erosion during transportation. Volcanic ash is generally considered a good source for bauxite deposits (Hou et al., 2017; Yu et al., 2016). It can be transported long distances by wind, and weathers rapidly in warm and humid climates (Yu et al., 2016). Even after long-range transport, the pristine morphologies of zircon crystals are preserved, with zircon being resistant to weathering and with aeolian transportation causing little grain erosion (Brimhall et al., 1988). It follows that the most likely source of the ~445 Ma zircons is the K-bentonite layers of the Ordovician–Silurian transition in South China. K-bentonite ~445 Ma in age is distributed widely in the Uppermost Ordovician Wufeng Formation and the Lower Silurian Longmaxi Formation in the Yangtze Block (Fig. 2; Du et al., 2020; Yang et al., 2019; Su et
2019; Su et al., 2009). The K_2O content of the K-bentonite of Cathaysia blocks during the Guangxi Orogeny (Yang et al., 2019; Su et al., 2009). The K_2O content of the K-bentonite in South China is commonly thought to be derived from volcanic ash produced during collision of the Yangtze and Cathaysia blocks during the Guangxi Orogeny (Yang et al., 2019; Su et al., 2009). The K_2O content of the K-bentonite layers in the Tongzi Section is 3.10 wt.%–7.27 wt.% (mean= 5.45 wt.%; Su et al., 2009), similar to the K_2O content of the bauxitic claystone of the Jiujialu Formation bauxite deposits (0.26 wt.%–9.78 wt.%; mean=5.81 wt.%; Weng et al., 2019).

5.3 Paleogeographic Controls on the Provenance of the Early Carboniferous Bauxite in Guizhou

Lower Carboniferous bauxites in Qingzhen-Xiwen areas are derived from chemical-weathering products of Paleozoic sedimentary units on the western margin of the Yangtze Block according to U-Pb geochronological analyses of detrital zircon (Wang et al., 2018) and are significantly different in provenance with the contemporary bauxite in Zunyi-Xifeng areas. Zircon age spectra in two areas are characterized by the largest age peaks at 900–800 and ~980 Ma, respectively (Figs. 11e, 11g). Large age peaks at 900–800 Ma are common in Cambrian–Devonian sedimentary rocks derived from Neoproterozoic volcanic and intrusive rocks along the western margin of the Yangtze Block (Fig. 11c; Wang et al., 2018; Hofmann et al., 2016; Xia et al., 2016), whereas dominant age peaks at ~980 Ma are prevalent in Pre-Ordovician strata in the Cathaysia Block (Fig. 11h). The different provenances of two contemporary and adjacent bauxite belts were controlled mainly by the paleotopography of the South China Block.

The transport distance and direction of precursor material are constrained by lateral changes of paleotopography during the formation of bauxite (Li et al., 2020; Bárdossy and Combes, 1999; D’Argenio and Mindszenty, 1995; Bárdossy, 1982), with previous studies showing the significance of paleotopography during bauxite formation. Different origins (autochthonous or allochthonous) of Karst bauxite can indicate the distance between provenance and deposit sites (Combes and Bárdossy, 1995; D’Argenio and Mindszenty, 1995). In the Tethyan realm, autochthonous and paraautochthonous bauxite deposits generally appear in intracontinental high-elevation areas and overlies aluminosilicate-bearing carbonate rocks, while allochthonous deposits commonly accumulated in precontinental low-elevation regions (Bárdossy and Combes, 1999; Combes and Bárdossy, 1995; D’Argenio and Mindszenty, 1995). The Lower Carboniferous bauxite deposits in the North China Block (NCB) provide further evidence of the influence of paleotopography on provenance (Zhao and Liu, 2019; Wang et al., 2016). The provenances of bauxite deposits in the southern and central NCB were mainly in the rapidly uplifting North Qinling Belt, while those of deposits in the northern NCB included both the North Qinling Belt and the northern margin of the NCB. The accelerated uplift of the northern margin of the NCB at ~310 Ma converted paleotopography of the NCB from north- to south-dipping, promoting southward transport of clastic sediments (Zhao and Liu, 2019; Wang et al., 2016). Similarly, apatite fission-track dating indicates that the accelerated uplift around the bauxite deposits in the Yongjiang Basin during the Miocene increased the rate of erosion in the highlands, and contributed younger source material to the bauxite deposits through river and sheet flow (Yang et al., 2018).

The topography of the Yangtze Block facilitated eastward transport of weathering material from the western margin of the Yangtze Block to the low-elevation coastal karstic plain of the Qingzhen-Xiwen area (Fig. 1a). In contrast, during the Early Carboniferous the Zunyi-Xifeng area lay in intracontinental karstic highlands (paleo-altitude >100 m) with deep depressions (Weng et al., 2019), with weathering material being derived from the basement and surrounding higher erosional regions. Precursor material was thus either accumulated in-situ or transported over short distances, accompanied by sheet flow and soil creep (D’Argenio and Mindszenty, 1995; Liao and Liang, 1991). The gap in bauxite deposits between the Zunyi-Xifeng and Qingzhen-Xiwen areas thus probably represents an erosion zone (Fig. 1b; Liu et al., 2017; Liu, 1987). This highland blocked transportation of weathering material from northern Guizhou to the Qingzhen-Xiwen area in central Guizhou. Our results thus indicate that it was paleotopography that caused the difference in provenance between the Jiujialu Formation bauxite deposits in northern and central Guizhou.

6 CONCLUSION

Whole-rock geochemical and U-Pb geochronological analyses of detrital zircon samples from the Lower Carboniferous Jiujialu Formation bauxite deposits and underlying Ordovician strata indicate mixed provenances for the deposits. Source material was derived from the aluminosilicate rocks and argillaceous dolostones of the Lower–Middle Ordovician bedrock, siliciclastic rocks of Lower Silurian strata, and K-bentonite layers in the Ordovician–Silurian transition units in adjacent areas. The Lower–Middle Ordovician strata in northern Guizhou were mainly sourced from the western margin of the Yangtze Block. The different provenances in the Zunyi-Xifeng and Qingzhen-Xiwen areas were controlled mainly by paleotopography.

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