

Metallogenic Model of Bauxite in Central Guizhou Province: an Example of Lindai Deposit

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Abstract: The bauxites in central Guizhou are hosted by the Lower Carboniferous Jiujiayu Formation. Geochemical characteristics of the Lindai bauxite deposit indicate that the underlying Shilengshui Formation dolomite is the precursor rock of mineral resources. Weathering simulation experiments show that Si is most likely to migrate with groundwater, the migration rate of which is several magnitude higher than Al and Fe under nature conditions (pH=3–9). The neutral and acid non-reducing condition is the most conducive to the Al rich and Si removal, while the acid reducing conditions is the most conducive to the Al rich and Fe removal. In the process of bauxite formation, coal beds overlying the Al-bearing rock series or other rock formation rich in organic materials can produce acid reducing groundwater, which are important for the bauxite formation. Finally, propose the metallogenic model of the bauxite in central Guizhou Province and put forward three new words which are “original bauxite material”, “bauxite material” and “original bauxite”.

Key words: bauxite, groundwater, geochemical characteristics, weathering simulation experiments, Central Guizhou Province

1 Introduction

China is one of the most important countries in the world for her abundant bauxite resources, where there are more than 300 mineral origin places distributed in 19 provinces (regions). And Guizhou is one of the four biggest bauxite resources provinces in China. With its reserves and basic reserves in 155.23 and 216.25 million tons by the end of 2008, Guizhou ranks the first among the four, followed with Henan, Guangxi and Shanxi provinces (Liu et al., 2009; USGS, 2009; Wu et al., 2006). Guizhou bauxite deposits are divided into five bauxite deposit belts, namely, Xiuwen, Xifeng, Zhunyi, Zhengan and Daozhen from south to north. Lindai bauxite, laying in the NWW 32km from the Guiyang city, belongs to Xiuwen bauxite deposit belt. Domestic and foreign scholars have done a lot of researches on bauxite mineralogy and geochemistry and claimed various insights on the genesis of bauxite deposits (Liu et al., 2010; Mongelli, 1997; MacLean et al., 1997; Öztürk et al., 2002; Calagari and Abedini, 2007; Ye et al., 2007; Zhang et al., 2013). Moreover, many

researches on the utilization of bauxite associated rare elements have been done as well in recent years and bauxite associated rare elements such as Ga, Li, Sc, Ti and V has achieved industrial grade in many regions and major industrial exploitation value (Tang et al., 2001, 2002; Liu, 2007). But articles in the experimental methods to study the genesis of bauxite deposits are rare, except Valetton (1972) and Chen (1991, 1996) who have done some related experiments and pointed out that the acidic condition is conducive to silicon, aluminum fractionation and that humic acid can enhance the ability of SiO₂, Fe₂O₃ and Al₂O₃ migration as colloidal state in water (Valetton, 1972; Chen, 1991, 1996). By setting the Lindai bauxite deposit in Qingzhen district, Guizhou Province as an example, soaking and leaching the suspected precursor rocks—Shilengshui Formation dolomite and its weathered laterite of the Lindai bauxite by the method of weathering simulation experiments, then contrasting with the different migration relationship of Al, Si, Fe, Ca and Mg. This article will design different pHs as well as a variety of acidic and alkaline conditions to find out the most suitable aqueous conditions for Si and Fe migration but the enrichment of Al. Therefore, we can know the

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groundwater conditions to form the bauxite deposits under natural conditions in theory and draw out of the metallogenic model diagram of bauxite in central Guizhou, which can develop basic theory of the bauxite mineralization as well as provide adequate theoretical basis for actual prospecting exploration.

2 Geological Setting and Geological Features

The research area is located at Guiyang complex tectonic deformation zone, north Guizhou anticline, Yangtze paraplatform (Guizhou Provincial Bureau of Geology and Mineral Resources, 1987). In early Paleozoic, most part of Guizhou was in a marine sedimentary environment, and by the end of early Paleozoic, the Caledonian movement has led to central and north Guizhou uplift, forming the central Guizhou doming. It is the large scale ancient complex anticlinal structure which extends northeast, with its structural highs

in Zhuzang, Zhijin county, and it is one part of the upper Yangtze ancient land. After nearly 100 million years of weathering and erosion, the central Guizhou has become penplain landform in Devonian, constituting a favorable basis of geological conditions for the formation of karst type bauxite. At early carboniferous the South China Sea water transgressed from south to north when Lindai area was the karst depression and shallow lake facies, then sedimentation occurred to form the Jiujialu Formation Al-bearing rock series. Moreover, the transgression at Permian extends, and then completely turns central Guizhou into the carbonate deposition at the mid of Qixia epoch (Gao, 1992; Guizhou Provincial Bureau of Geology and Mineral Resources, 1987). Rock units in this region are exposed, including Upper Proterozoic, Sinian, Mid to Upper Cambrian, Lower Carboniferous, Permian and Triassic (Figs. 1a, 1b).

The bauxite is hosted by the Lower Carboniferous Jiujialu Formation, and parallel unconformity with the

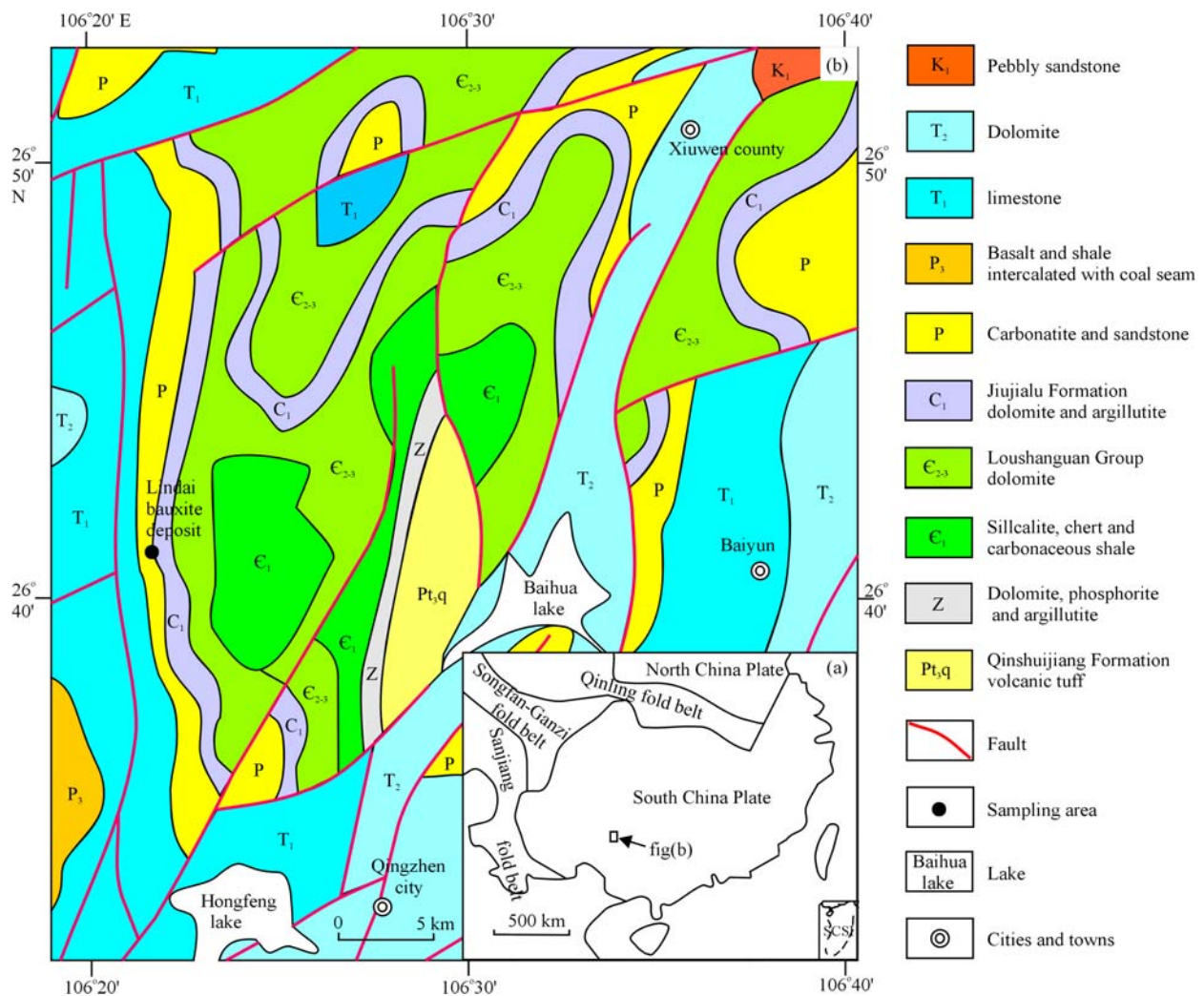


Fig. 1. (a), an index map of South China Plate showing the location of the Lindai bauxite deposit; (b), Geologic map illustrating the geological features of the Lindai bauxite deposit, Guiyang, China.

overlying and underlying strata. The underlying stratum is the Middle Cambrian Shilengshui Formation dolomite while the overlying stratum is the Lower Carboniferous Baizuo Formation dolomite. The geological structure of Qinzhen region is complicated with faults staggered distribution and sequence of strata hybrid. The faults can be divided into two groups, namely, NE and NNE. Ore bearing strata Jiujiayu Formation are inverted bedding nearly south-north strike, inclining to NNE with dip angle of 70°–80°. Ore-bearing rock series Jiujiayu Formation (C_{ij}) is divided into three layers: the upper layer (C_{ij}^3) is coal beds, composed of black carbonaceous shale intercalated with coal seams, in its thickness of 3–4 m; the middle layer (C_{ij}^2) is bauxite beds, in its thickness of 1–12 m, and 5–6 m in general, consisting of compact bauxite, clastic bauxite and high iron bauxite; the lower layer (C_{ij}^1) is ferruginous beds, mainly ferruginous clay shale and iron ore body, with ferruginous rock composed of red, steel gray or dark clumps of siderites, star dot pyrites and lenses of hematite, in its thickness of 2–10 m (Fig. 2).

3 Sampling and Experimental Methods

3.1 Sampling

The samples to research were collected from Muzhuchong open pit and outcrop in Lindai bauxite, Qingzhen city. We selected three representative bauxite samples (compact bauxite, clastic bauxite and high iron bauxite) as well as the underlying Shilengshui Formation dolomite and its weathered laterite (Fig. 3). The major element abundances were determined by X-ray fluorescence (XRF) from a panalytical company (formerly Philips Analytical Instruments Division) Model Axios (PW4400) spectrometer. The trace element and rare earth element abundances were analyzed through inductively coupled plasma mass spectrometry (ICP-MS) from a Finnigan MAT company Model ELEMENT. The ICP-OES (Model Vista MPX produced by Varian company) analyses

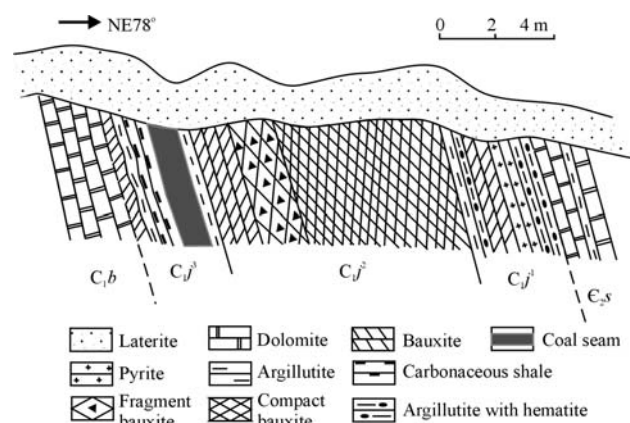


Fig. 2. Geological section of Lindai bauxite deposit.

were utilized for determining the composition of soaking and leaching solution. All of analyses above were determined in Institute of Geochemistry, Chinese Academy of Sciences. The detailed analytical procedures were described by Franzini et al. (1972) and Qi et al. (2000), and the analysis results are summarized in Table 1, 2, 3. The pH values of the solutions were determined by LIDA PHS-3C laboratory pH meter with a rechargeable composite electrode Model E-201-C-9.

3.2 Conditional experiments

3.2.1 Soaking experiments

We used the weathering simulation experiment method to soaking the suspected precursor rocks—Middle Cambrian Shilengshui Formation dolomite and its weathered massive laterite of the Lindai bauxite (Fig. 3). Firstly, in the method of tube immersion, with 22 colorimetric tubes of 50 mL for 20–60 mesh samples each in 5 g, add them into the 50 mL prepared solution containing inorganic acid (HCl), organic acid (citric acid) and reducing acid (oxalic acid) for each. Secondly, before closing colorimetric tubes with glass covers, use HCl and NaOH to adjust solution pH to specified values. 30 days later, sampled the solutions with 12 mL. Then, centrifuge and filter the solutions by pinhole filter membrane. Thirdly, before sending these solutions to ICP-OES to be determined, add 0.5 mL of HNO_3 to acidify them. Analysis results are summarized in Table 2.

3.2.2 Leaching experiments

Leaching experiments were done with the automatic cycle leaching device (Fig. 4) that is composed of the gas generating device and the automatic cycle leaching device. The latter is composed of three parts, namely, the weathering and leaching, the evaporation cycle as well as the rainwater synthesis. The specific procedures of the experiments are show as follows: (1) Mash the massive laterite and select some 8–20 mesh samples by standard sieve. Before placing them in a 60°C oven thermostat to dry for 8 hours, use running water and then ultrapure water to wash the samples three times respectively. Then weight 130 g laterite samples in three copies by the balance and load them into the glass column at the weathering and leaching part. (2) The CO_2 -containing gas, HCl-containing gas and air gas produced by generation device goes into the automatic cycle leaching device on the right. (3) Control the power of electric stove to sustain the evaporation at the same level. So water vapor rises up to the rainwater synthesis, mixing with the CO_2 -containing gas, the HCl-containing gas and the air respectively, and then condensation of three rainwaters with different pH value leaches the sample column at weathering and

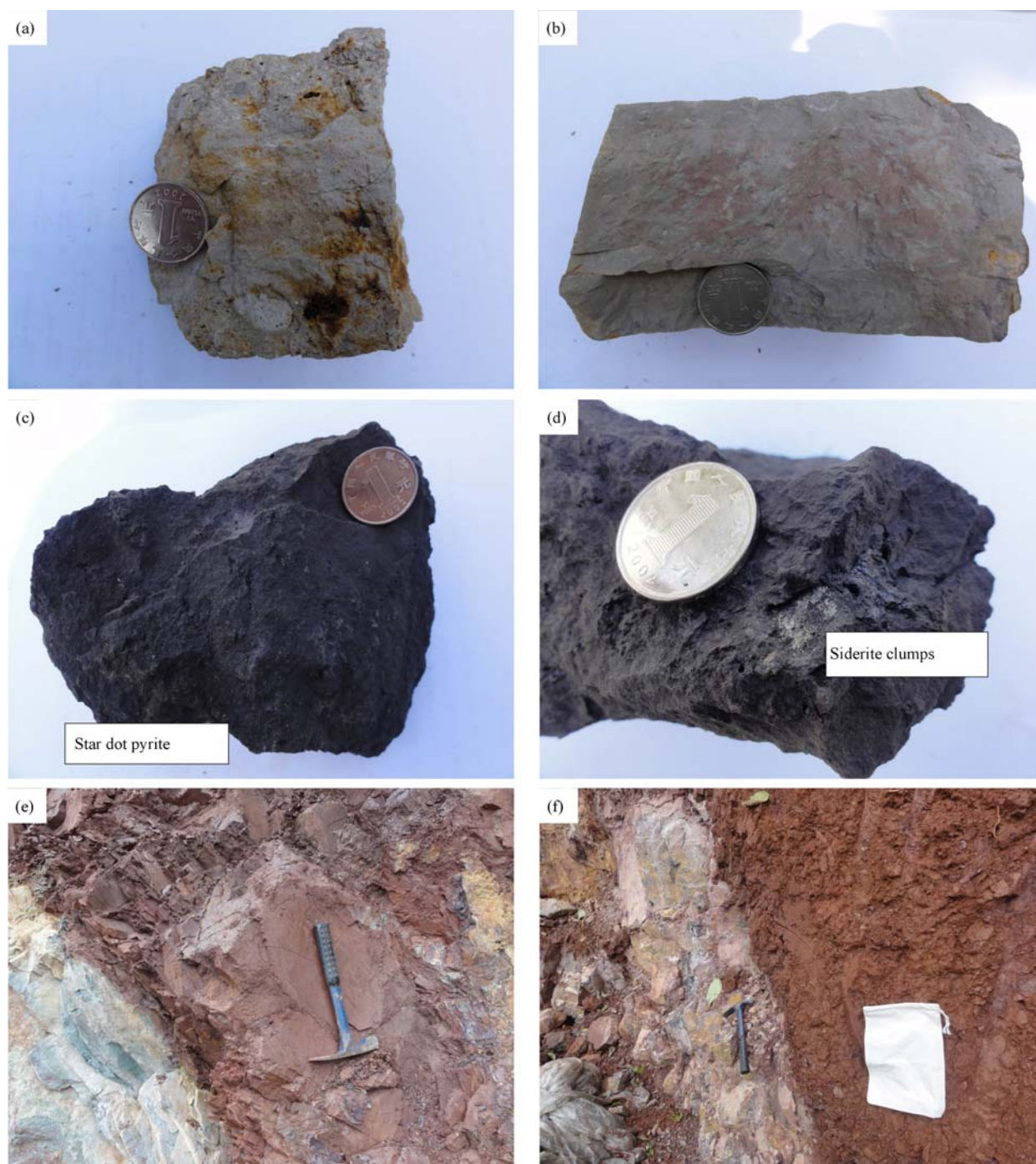


Fig. 3. The sample structures in the Lindai bauxite deposit.

(a), Clastic bauxite; (b), compact bauxite; (c), high iron bauxite with star dot pyrite; (d), high iron bauxite with siderite clumps; (e), dolomite and its weathered massive laterite; (f), dolomite and its weathered loose laterite.

leaching part. (4) Leaching experiment continues for 15 days with 8 hours a day, about 7 mL leaching solution a minutes. Control the leaching solution to about 2200–2800 mm (divided the total volume of leaching solution by cross-sectional area of sample column), about twice of the annual average rainfall in Guiyang city (1200–1500 mm) (compilation of the annual average rainfall in china with 30 years), which shows that the one day experiments

nearly equals to two years weathering and leaching in nature. (5) Sampling the leaching solution 12 mL from the flask every two or three days before constant solution volume to 400 mL. Centrifuge and filter the solutions by Pinhole filter membrane. Before sending these solutions to ICP-OES to be determined, add 0.5 mL of 1:1 HNO_3 to acidify. Analysis results are summarized in Table 3.

Table 1 Major (%), trace and REE (ppm) element compositions of bauxite samples from the Lindai bauxite

Sample no	LD-07	LD-08	LD-10	LD-11	LD-12	LD-13	Sample no	LD-07	LD-08	LD-10	LD-11	LD-12	LD-13
Lithology	Clastic bauxite	Compact bauxite	High iron bauxite	Loose laterite	Massive laterite	Dolomite	Lithology	Clastic bauxite	Compact bauxite	High iron bauxite	Loose laterite	Massive laterite	Dolomite
SiO ₂	1.20	34.49	1.53	36.29	40.26	2.13	Sb	3.66	2.04	11.7	5.37	3.09	3.97
Al ₂ O ₃	76.84	44.89	70.92	21.53	21.59	1.50	Cs	0.07	2.60	0.07	18.2	28.6	0.5
Fe ₂ O ₃	2.18	2.20	6.29	14.02	15.69	0.74	Ba	8.06	33.8	8.73	258	237	25.6
MgO	0.15	0.51	0.21	4.26	4.20	19.36	Hf	51.9	32.3	33.8	6.42	14.2	0.52
CaO	-	-	-	2.62	0.68	29.68	Ta	5.19	4.81	3.76	1.56	1.76	0.28
Na ₂ O	0.74	0.06	1.22	0.20	0.72	0.89	W	8.64	13.1	13.2	5.54	7.06	2.90
K ₂ O	0.14	1.23	0.19	5.13	6.33	0.33	Tl	0.03	0.09	1.15	0.80	0.67	0.05
MnO	-	0.02	-	0.18	0.05	0.04	Pb	158	32.6	87.8	122	67.2	18.0
P ₂ O ₅	0.23	0.07	0.13	0.10	0.27	0.03	Bi	8.01	3.17	2.70	0.76	0.94	0.07
TiO ₂	5.12	3.58	2.55	0.86	1.20	0.07	Th	44.3	71.6	23.1	36	32	1.65
L.O.I.	14.31	13.46	16.97	13.73	8.03	45.24	U	48.1	14.3	54.3	7.10	6.03	0.89
Total	100.91	100.51	100.01	98.92	99.03	100.01	La	39.1	82.8	43.5	81.0	93.3	4.64
ClA	98.87	97.22	98.05	73.03	73.62	4.63	Ce	85.4	140	44.7	164	203	8.60
Li	2.63	799	1.11	104	94.2	6.31	Pr	8.98	15.4	9.03	19.0	21.0	1.13
Be	6.18	3.00	5.87	8.53	5.19	0.50	Nd	37.8	55.3	33.1	72.0	76.6	4.55
Sc	6.68	14.7	4.64	22.7	22.7	0.77	Sm	11.8	11.8	7.83	16.1	15.2	1.03
V	138	260	206	129	99.0	9.91	Eu	1.91	2.19	1.39	3.04	3.03	0.19
Cr	106.14	96.28	60.61	122.09	162.4	181.25	Gd	13.82	11.5	17.69	15.45	14.79	1.12
Co	3.75	14.5	87.8	34.0	54.0	4.01	Tb	2.6	1.95	3.81	2.54	2.24	0.17
Ni	210.45	103.39	144.9	170.2	297.85	225.4	Dy	14.1	11.8	22.2	14.8	12.1	0.99
Cu	288	61.7	932	36.5	20.6	32.2	Ho	2.58	2.49	4.10	2.86	2.41	0.18
Zn	63.7	61.3	39.6	88.7	93.1	48.4	Er	6.99	7.74	10.5	8.46	7.12	0.49
Ga	13.9	27.3	17.2	27.1	22.5	1.37	Tm	0.95	1.15	1.32	1.20	0.96	0.06
Ge	1.77	1.09	3.21	2.09	2.30	0.12	Yb	5.96	7.95	7.67	8.26	6.44	0.38
As	43.0	34.8	89.0	44.9	63.3	31.1	Lu	0.83	1.18	0.98	1.17	0.93	0.06
Rb	1.57	14.2	2.46	171	153	7.38	ΣREE	230.2	353.26	207.82	409.89	459.12	23.58
Sr	206	118	52.9	68.6	85.9	85.4	LREE	182.37	307.49	139.55	355.14	412.13	20.14
Y	71.7	56.6	116	72.9	64.4	5.35	HREE	47.83	45.76	68.27	54.74	46.99	3.44
Zr	1890	1180	1240	222	512	19.3	LR/HR	3.81	6.72	2.04	6.49	8.77	5.85
Nb	117	89.0	66.9	22.0	29.4	1.89	(La/Yb) _N	4.33	6.88	3.74	6.48	9.57	8.13
Mo	6.69	1.50	13.3	4.14	11.9	4.86	(La/Sm) _N	2.61	4.30	3.40	3.08	3.76	2.76
Ag	1.65	1.19	6.07	0.27	0.37	-	(Gd/Lu) _N	2.08	1.22	2.25	1.65	1.99	2.40
Cd	0.63	0.63	0.38	0.74	0.76	0.22	Ce/Ce*	1.07	0.92	0.53	0.98	1.07	0.88
In	0.32	0.37	0.18	0.13	0.15	0.01	Eu/Eu*	0.52	0.58	0.37	0.60	0.63	0.54
Sn	15.9	18.2	9.44	5.05	5.33	0.51	La/Y	0.55	1.46	0.38			

Note: Ce/Ce*=Ce_N/(La_N • Pr_N)^{1/2}; Eu/Eu*=Eu_N/(Sm_N • Gd_N)^{1/2}

Table 2 Concentration of soaking solution for dolomite and laterite in the Lindai bauxite (Experiment for 30 days)

Sample number	Characteristic of solution	pH value	Al (ppm)	SiO ₂ (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Si/Al	Fe/Al	Ca/Al	Mg/Al	Migration rate of Al (mg/g)	Migration rate of Si (mg/g)	Migration rate of Fe (mg/g)	Migration rate of Ca (mg/g)	Migration rate of Mg (mg/g)	
J2-1	Dolomite soaking experiment solution	1.00	0.61	3.79	10.83	182	56.52	2.9	17.73	298	92.51	0.77	1.78	20.75	8.59	4.87	
J2-2		2.99	-	1.24	0.02	5.71	9.06	-	-	-	-	-	0.58	0.04	0.27	0.78	
J2-3		5.00	0.16	0.97	0.01	2.39	3.24	3.08	2.9	0.04	15.26	20.71	0.2	0.46	0.01	0.11	0.28
J2-4		7.00	-	1.39	-	2.72	3.08	-	-	-	-	-	0.65	-	-	0.13	0.26
J2-5		9.00	-	1.39	-	2.53	2.94	-	-	-	-	-	0.65	-	-	0.12	0.25
J2-6		10.99	0.02	2.29	0.01	2.82	1.90	1.90	54.07	0.34	1.42	96.21	0.02	1.07	0.01	0.13	0.16
J2-7	Massive laterite Soaking experiment solution	1.00	73.65	86.73	20.75	119	40.39	0.55	0.28	1.62	0.55	6.44	2.15	1.89	244	16.03	
J2-8		3.00	0.05	3.64	0.04	6.59	6.08	6.08	34.28	0.87	1.33	12.2	0.01	0.09	0.01	13.49	2.41
J2-9		5.01	0.22	2.1	0.14	2.75	3.49	3.49	4.48	0.64	12.58	15.93	0.02	0.05	0.01	5.63	1.38
J2-10		7.01	2.72	7.2	1.46	7.28	3.15	3.15	1.23	0.54	2.67	1.16	0.24	0.18	0.13	14.9	1.25
J2-11		9.00	0.79	3.61	0.46	4.17	4.21	4.21	2.14	0.59	5.30	5.35	0.07	0.09	0.04	8.54	1.67
J2-12		11.00	2.51	6.21	1.34	6.43	2.33	2.33	1.16	0.54	2.57	0.93	0.22	0.15	0.12	13.16	0.93
J2-13	Massive laterite Soaking experiment solution	1.49	355	195	89.34	169	49.57	0.26	0.25	0.48	0.14	31.04	4.83	8.13	345	19.67	
J2-14		3.00	105	95.76	217	85.39	26.7	26.7	0.42	2.06	0.81	0.25	9.23	2.38	174	10.59	
J2-15		4.99	8.16	9.53	5.39	8.49	32.69	32.69	0.55	0.66	1.04	4.01	0.71	0.24	0.49	17.38	12.97
J2-16		7.00	2.98	3.47	0.70	2.86	30.04	30.04	0.54	0.24	0.96	10.08	0.26	0.09	0.06	5.85	11.92
J2-17		9.00	1.97	6.78	1.01	6.29	28.5	28.5	1.61	0.51	3.19	14.46	0.17	0.17	0.09	12.87	11.31
J2-18		2.18	60.9	61.51	21.21	71.82	27.49	27.49	0.47	0.35	1.18	0.45	5.33	1.53	1.93	147	10.91
J2-19	3.00	51.84	40.62	24.24	45.13	23.66	23.66	0.37	0.47	0.87	0.46	4.54	1.01	2.21	92.36	9.39	
J2-20	5.01	25.83	28.64	15.49	44.16	30.4	30.4	0.52	0.6	1.71	1.18	2.26	0.71	1.41	90.4	12.06	
J2-21	7.01	16.09	24.12	10.12	40.09	28.49	28.49	0.7	0.63	2.49	1.77	1.41	0.6	0.92	82.05	11.31	
J2-22	9.01	15.57	21.68	9.88	41.73	28.92	28.92	0.65	0.63	2.68	1.86	1.36	0.54	0.90	85.4	11.48	

3.2.3 Method of data processing

Because we used continuous sampling method and sampled a large amount volume of solution from flask, we converted the data to make the experiments more accurate. All data this article mentioned are the result of conversion. The convert method explain as follows: assuming first, second, third sampling..., and concentrations of element a are a_1, a_2, a_3, \dots mg/L respectively, so the net contents of element a in select samples are $v \cdot a_1, v \cdot a_2, v \cdot a_3, \dots$ mg respectively, now the conversion concentrations of soaking and leaching solutions are $a_1, (V \cdot a_2 + v \cdot a_1) / V, (V \cdot a_3 + v \cdot a_2 + v \cdot a_1) / V, \dots$ mg/L respectively. The V (L) is the total volume of the soaking or leaching solutions and v (L) is the volume of the select samples.

The method of element migration rate (K_x) calculation is referred and improved to the formula from Chen and Zhu (1984):

$$K_x = (a_x \cdot V) / A_x \cdot M \text{ or } K_x = (a_x \cdot V) \cdot 1000 / A_x \cdot M$$

A_x is the concentration of the soaking of leaching solutions (ppm); V is the total volume of the soaking or leaching solutions (L); A_x is the abundance (wt%) of the elements in rock sample; M is the weight (g) of the rock sample. The physical meaning of element migration rate (K_x) is the mg or μ g number of the elements migration by the soaking or leaching solutions during the experiment in 1000 g sample, if every element is just 1 g.

4 Results and Discussions

4.1 Major elements geochemistry

The Al₂O₃ contents in three different types of bauxite vary from 44.89 wt% to 76.84 wt%; the Fe₂O₃ content in high iron bauxite reached as much as 6.29 wt%, and another two are 2.18 wt% and 2.20 wt% respectively (Table 1). The ferriferous minerals in high iron bauxite are mainly star dot pyrite, siderite clumps (Figs. 3c, 3d) and a little bit of epigenetic oxidation of hematite and goethite, which indicate that the Lindai bauxite deposit was formed with the reducing environment (Butler and Rickard, 2000; Zarsavandi et al., 2008). The concentrations of SiO₂ in LD-7 and LD-10 are as low as only 1.20 wt% and 1.53 wt% respectively, but it is as much as 34.49 wt% in LD-8. This may be the result of the more contents of clay minerals such as kaolinite (Mameli et al., 2007). The contents of Ti are higher than the usual ones, which might be formed the alteration of micas mineral, such as biotite, or from clay minerals with high Ti contents (Öztürk, 2002).

The chemical indexes of alteration (CIA) (Nesbitt and Young, 1982) of all the three bauxites are over 97, which means that the source rock had undergone a complete process of weathering, whereas the two laterite sample's CIA are just around 73, which means it have not been

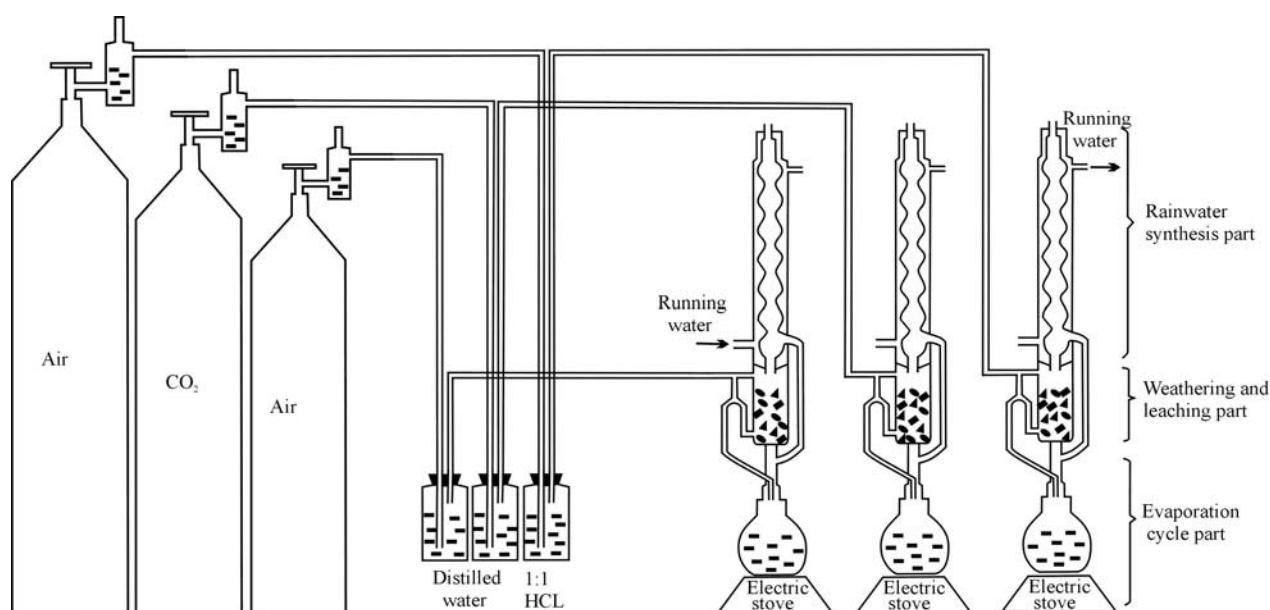


Fig. 4. Schematic diagram of leaching device.

Table 3 Concentration of leaching solution for laterite in the Lindai bauxite

Characteristic of solution	Sample number	Experiment Times (d)	Al (ppm)	Fe (ppm)	SiO ₂ (ppm)	Si/Al	Fe/Al	pH values	Migration rate of Al (μg/g)	Migration rate of Fe (μg/g)	Migration rate of Si (μg/g)
Air leaching solution with pH=7.00	Air-1-2	1	0.53	0.34	68.1	60.2	0.64	6.47	14.2	7.24	400
	Air-2-2	3	0.67	0.41	130	89.9	0.6	6.46	18.2	8.79	763
	Air-3-2	6	0.06	0.05	124	897	0.83	7.63	1.73	1.15	727
	Air-4-2	9	0.07	0.04	177	1180	0.64	7.72	1.88	0.96	1039
	Air-5-2	12	0.06	0.06	130	1098	1.01	9.03	1.48	1.19	763
	Air-6-2	15	0.08	0.06	190	1103	0.72	9.27	2.16	1.24	1115
CO ₂ leaching solution with pH=5.11	CO2-1-2	1	0.01	0.01	51.7	1772	0.54	8.07	0.37	0.16	304
	CO2-2-2	3	0.01	0.01	88.2	3923	0.73	7.98	0.28	0.17	518
	CO2-3-2	6	0.01	0.01	124	5406	1.09	7.82	0.29	0.25	732
	CO2-4-2	9	0.01	0.01	118	2124	2.99	7.95	0.07	0.17	697
	CO2-5-2	12	0.01	0.01	116	6830	0.69	7.68	0.21	0.12	684
	CO2-6-2	15	0.02	0.01	124	3593	0.55	8.21	0.43	0.19	730
HCl leaching solution with pH=3.48	HCl-1-2	1	0.01	0.01	37.6	6518	3.41	7.62	0.07	0.20	221
	HCl-2-2	3	0.01	0.01	80.9	9356	0.68	7.35	0.11	0.06	476
	HCl-3-2	6	0.02	0.01	112	2282	0.44	7.5	0.62	0.22	661
	HCl-4-2	9	0.05	0.01	129	1296	0.21	7.38	1.25	0.21	756
	HCl-5-2	12	0.68	0.27	192	133	0.39	5.36	18.2	5.74	1129
	HCl-6-2	15	0.19	1.13	262	646	5.95	4.84	5.10	24.29	1540

fully weathered and is still undergoing the weathering process at the time. At last, classifying the bauxites by Ki index [$Ki = (SiO_2/Al_2O_3) \times 1.78$] (Al-Bassam, 2005), the Ki values of LD-7, LD-10 and LD-8 are 0.03, 0.01 and 1.37 respectively, which indicate that LD-7 and LD-10 are the high quality bauxite while LD-8 is the bauxite clay.

4.2 Rare earth (REE) and trace elements geochemistry

4.2.1 Rare earth element (REE) geochemistry

Rare earth element (REE) geochemistry data (Table 1) indicate that the Σ REE (23.58–459.12 ppm, average 280.65 ppm) varied widely, with LREE significant enrichment and Eu medium depletion, except dolomite. LREE/HREE values 2.04–8.77 while $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Lu)_N$ values 3.74–9.57, 2.61–4.30 and 1.22–2.40

respectively. REE patterns are the right curve (Fig. 5a) with the patterns of the three bauxites and two laterites are similar to the underlying dolomite. Moreover, in contrast to the dolomite, HREE and LREE are strongly enriched, with their curve patterns similar to the dolomite ones as well. The analyses above indicate that the same source of rock that bauxites and laterites share might be the underlying Shilengshui Formation dolomite. And the weathering laterite is the in-process products from mother rock to the bauxite.

The Σ REE, LREE and LREE/HREE values of massive bauxite LD-8 (bauxite clay) are the highest of the three bauxites. It might be caused by the different effect on the rare earth elements absorption for clay minerals. Also, contents of clay minerals are positive correlations to the

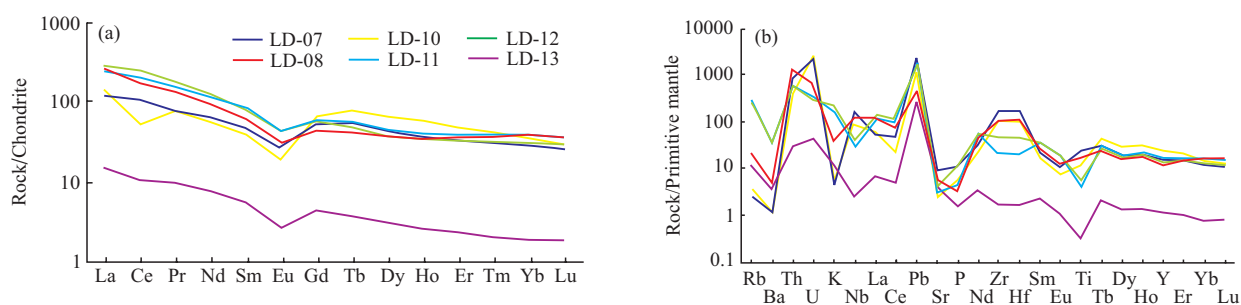


Fig. 5. Chondrite-normalized REE patterns (a) and primitive mantle-normalized trace element patterns (b) of samples in Lindai bauxite (after Masuda et al., 1973; McDonough et al., 1992).

values of Σ REE. The absorption energy of REE^{3+} is related to the size of the ionic radius and would increase in ascending order from La-Ce to Yb-Lu with the decrease in ionic size (Ye et al., 2007). So massive bauxite rich in clay minerals LD-8 (bauxite clay) is enriched Σ REE, LREE with higher LREE/HREE values. The Ce is medium depletion in the high iron bauxite (LD-10) with the equation $\text{Ce}/\text{Ce}^* = 2\text{Ce}_N / (\text{La}_N + \text{Pr}_N)$ (Taylor and McLennan, 1985; Abedini and Calagi, 2013) and Ce/Ce^* values 0.53 because Ce is a price change element and it has two prices, Ce^{3+} and Ce^{4+} . Ce^{3+} is more easily migrated by groundwater than Ce^{4+} because it is more active. Therefore, Ce mainly exists in the form of Ce^{3+} in a reducing environment and significant migration of Ce^{3+} resulted in Ce depletion.

4.2.2 Trace element geochemistry

Trace element patterns of the two laterite samples are similar to the ones of dolomite (Fig. 5b). But only Sr depletion takes place because Sr, as a large ion lithophile element, could easily dissolve in water and has active geochemical properties. So in the process of weathering, it could be easily migrated by groundwater to the open sea at last, which is the reason why Sr contents are higher in marine sediments than those in continent sediments as well. Spider diagrams of three bauxite samples are also similar to the dolomite (Fig. 5b) with Rb, Ba, Sr and a few other elements anomaly. This is because bauxites have processed the more complex stage of diagenetic and epigenetic changes while laterites have not. All above indicate that the bauxites and laterites have the inheritance relationship with the dolomite.

In the plot of Ni vs. Cr concentration (Schroll and Sauer, 1968), the bauxite sample plots are close to the karst type bauxite area (Fig. 6). It indicates that the bauxite deposit should belong to the karst type bauxite (sedimentary type or paleo-laterite type) though there are some deviations of the sample plots caused by the epigenetic weathering and leaching effects (Ling et al., 2013). The La/Y values are 0.55 for LD-7, 0.38 for LD-10 and 1.46 for LD-8 respectively, which shows that the first two high quality

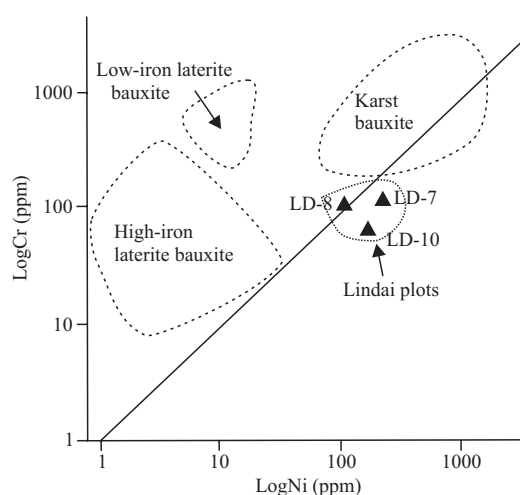


Fig. 6. Plot of Ni vs. Cr concentration for various types of bauxite (after Schroll and Sauer, 1968).

bauxites were formed in an acid environment and the formation of high iron bauxite (LD-10) had lower pH values. However, the Al_2O_3 content for bauxite clay is just 44.89 wt%, which means that it was formed in an alkaline environment (Crnicki and Jurkovic, 1990; Maksimovic and Panto, 1991). It just indicates that bauxite mineralization progress of Si, Fe removal and Al enrichment required acid conditions (low pH values).

4.3 Condition experimental discuss

4.3.1 Leaching experiments

The concentration of Si can be achieved to 200 ppm but the concentrations of Al and Fe are less than 1 ppm on massive laterite leaching experiment (Fig. 7). It means Si could be easily transported but Fe and Al are difficult to migrate. Therefore, Fe migration becomes the key of bauxite formation. However, Fe migration is as difficult as Al under natural conditions, so only in some special environment could the high quality bauxite be formed with Fe removed and Al remained. Although the concentrations of those three elements might not be the highest in an acid leaching solution at the beginning, the experiment with pH=3.48 leaching solution had the highest element concentration as the experiment

progresses (Figs. 7a, 7b, 7c), and the abnormal of the element concentrations might be the results of the flushing effects on samples by leaching solution at the beginning of the experiments. The leaching experiments shows that migration rates of Al, Si and Fe in acid condition are higher than that in neutral conditions. But the migration rate of Al in strong acid condition of pH=3.48 is 10 to 20 times higher than that in neutral condition (Table 3), so significant migration of Al makes against the formation of the bauxite obviously. As a result, it is not conducive to form high quality bauxite with the strong acidic conditions in bauxite mineralization process.

The graph of Values of Si/Al and Fe/Al for massive laterite leaching solutions (Fig. 8) could explain the question of Al migration conditions. In the later stage of the experiments, values of Si/Al in leaching solution with condition of pH=5.11 and 7.00 are larger than those with pH=3.48 (Fig. 8a), which means neutral and weak acidic conditions are conducive to Si removal and Al enrichment. The leaching solution with condition of pH=3.48 has the highest Fe/Al value (Fig. 8b), showing that strong acid condition is good for Fe removal and Al enrichment. However, the migration rate of Al is also high in strong acid condition, which obviously shows that significant migration of Al will not be good for high quality bauxite formation. All above suggest that the mineralization of bauxite is a complex process, and require a relatively strict pH conditions. Neutral and weak acidic conditions are conducive to Si removal and Al enrichment, but not good for Fe removal, so the high iron low quality bauxite formed at last; strong acid conditions may be easy for Fe removal but difficult for Si removal, so the high silicon low quality bauxite formed. In conclusion, in the forming process of bauxite, it must experience one or more times changes in pH cycles, from neutral and weak acidic to strong acid or reverse, thus it can make Si, Fe removed and Al enriched to form the high quality bauxites.

4.3.2 Soaking experiments

In dolomite soaking experiments, the elements migration rates (activity) in natural condition (pH=3.00–9.00) ordered from high to low: Si>Mg>Ca>Al>Fe. In strong acid (pH=3.00–1.00) conditions (Fig. 9), the migration rate of five elements obviously increased, and some even increased several orders of magnitude, among which Fe changed most.

In massive laterite soaking experiments with different pH and Eh values, the order of elements migration rates (activity) changed in natural conditions (pH=3.00–9.00) in contrast to the dolomite: Ca>Mg>Si>Al>Fe. The orders of Ca, Mg and Si changed except Al and Fe (Fig. 10a). The migration rate of Si is higher than that of Mg and Ca; this

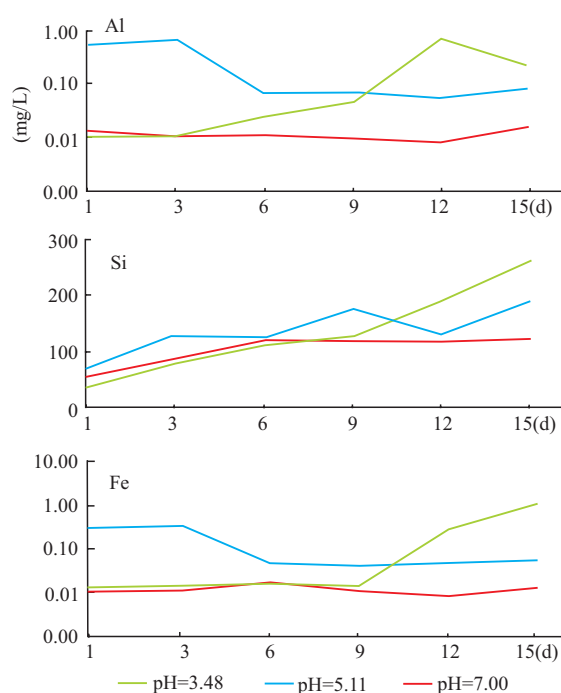


Fig. 7. Concentration of Al, Si, Fe for massive laterite leaching experiments.

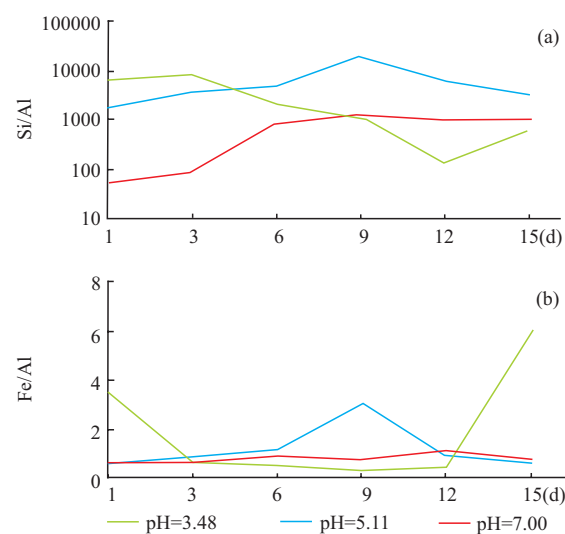


Fig. 8. Values of Si/Al (a) and Fe/Al (b) for massive laterite leaching experiments.

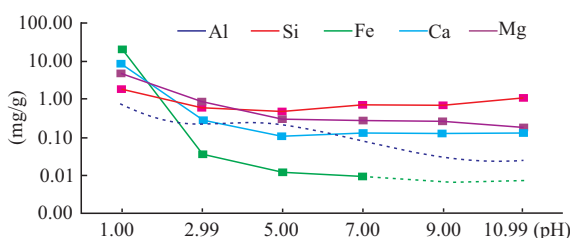


Fig. 9. Migration rate of each element for Dolomite soaking experiments (The dotted lines are speculated).

may be caused by the higher concentration of MgO and CaO in dolomite than massive laterite, which led to Mg

and Ca oversaturated precipitation affecting the migration rates. At the filtration process for dolomite soaking solution, we filtered out a lot of white sediments. In order to identify the main components of the sediment substances, the authors did chemical experiments as followed: first, dried the white sediments by the oven thermostat; second, instilled dilute hydrochloric acid to the sediments, and most dissolved and produced large amounts of colorless, odorless gas. Third, divided the solution into two parts, one was to instill the NaOH solution and it appeared white sediment $Mg(OH)_2$, while the other was to instill the $BaCl_2$ solution and it appeared white sediment $BaSO_4$. So, the authors speculate that the white sediments in dolomite soaking solutions are carbonate and sulfate of Ca and Mg.

In laterite soaking experiments with reducing acid (oxalic acid) in $pH \leq 5.00$, migration rate of Al and Fe in solutions are much higher than those without reducing acid (oxalic acid) (Fig. 10b). It suggests that acid and reducing condition can strongly promote Fe and Al migration. And the migration of five elements in solutions with organic acid (citric acid) obviously increased and with the gentle curve (Fig. 10c), which suggest that the organic acid can strongly promote the migration of the five elements. It probably resulted from the organic acid complexes with five elements that promote the elements to be dissolved and migrated. For a single element, the gentle concentration curve may be the small effect of elements migration rate from changes of pH values and the strong effect of the organic acid, which indicate that the effect of organic acid conditions on promoting elements migration rate is much better than that of pH value conditions.

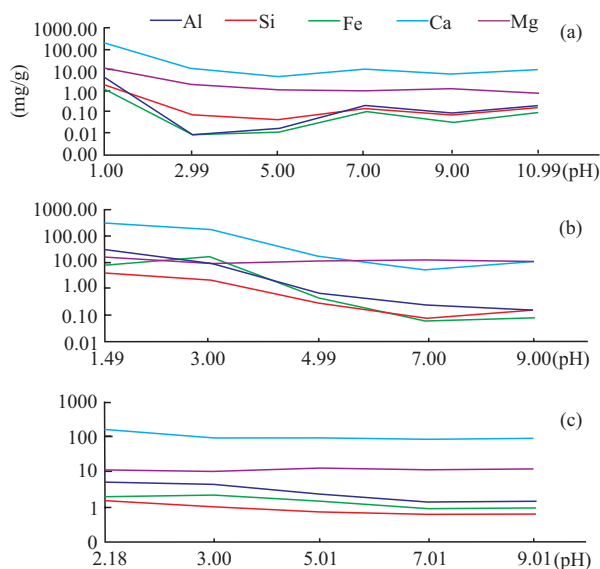


Fig. 10. Migration rate of each element for massive laterite soaking experiments with HCl (a), oxalic acid (b), citric acid (c).

The values of migration rate of Si division by migration rate of Al (K_{Si}/K_{Al}) are higher in soaking experiment solutions with inorganic acid than those with reducing acid and organic acid. Furthermore, the Si/Al values are all more than 1 in $pH=3.00-9.00$, and reached as high as 20.86 in $pH=3.00$ (Fig. 11a). It means that it is conducive to Si removal and Al enrichment under natural condition with no reducing substance, and the neutral and weak acid with non-reducing condition is the best. However, Fe/Al values are different. Only in the condition of $pH=3.00$ the K_{Fe}/K_{Al} value is over 1 and reached 2.14. Besides, it is only 0.2–0.4 in strong acid ($pH=1.00$) condition (Fig. 11b). It shows that the migration rate of Al is higher than that of Fe in strong acid condition, and is obviously not good for bauxite formation, of which the conclusion is the same with massive laterite leaching experiment. All above, the conditions of Fe removal from high aluminum laterite to form bauxite are strict. Only in acid and reducing environment can make Fe removal and Al enrichment. Because of this, many bauxite mines have the high iron bauxite (red ore) around the world, such as Zagros bauxite in Iran, west Jiyuan bauxite in Henan Province, Xiaoshanba bauxite in Guizhou province (Zarasvandi et al., 2008; Chen, 2007; Ye et al., 2007). And the research area also has the high iron bauxite as well, such as the sample LD-10 (Figs. 3c, 3d). Overall, its average grade and quality are not as good as low iron bauxite.

5 Metallogenic Model

According to the conclusion through weathering simulation experiments, we propose the metallogenic

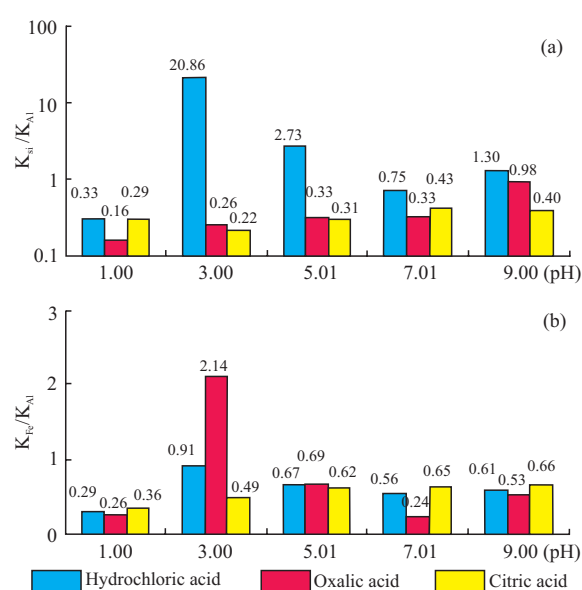


Fig. 11. Values of K_{Si}/K_{Al} (a) and K_{Fe}/K_{Al} (b) for massive laterite soaking experiments.

model of bauxite in central Guizhou province (Fig. 12):

(1) The central and north Guizhou was uplift to land by the late Paleozoic Caledonian movement, and then processed razed denudation and peneplane for almost 100Ma which led this area to missing Devonian, Silurian and Ordovician stratum. Until Al-bearing rock series deposit at early carboniferous, central Guizhou old land had formed a quasi-lysogenic landform which widely distributed of karst depressions and catchment basin, having formed the favorable place for bauxite deposit (Gao et al., 1992).

(2) According to the paleomagnetic remanence analysis, Guizhou area, located at south latitude 8–14 degrees in carboniferous (Liu et al., 1990), belonged to the hot and humid tropical climate and conducive to forming the laterite weathering crust, which provided the necessary climate conditions for the Guizhou bauxite formation. After intense weathering in tropical humid climate of Middle Cambrian Shilengshui Formation impure carbonate rock, K, Na, Ca, Mg and other active elements were moved out while Fe, Al, Ti, Si and other inactive elements were remained in paleo-weathering crust to form the aluminum-rich laterite. Then with the invasion of South China Sea water from south to north at early carboniferous, aluminum-rich laterite or situ or transported to karst depression, catchment basin or doline funner by surface runoff and marine transgression, deposition to form the “original bauxite material”, the precursor of bauxite. Lindai bauxite was the product of paleo-laterite deposited in “Xiuwe, Qingzhen karst depression” (Gao et al., 1992).

(3) Tropical humid and hot climate led to lush

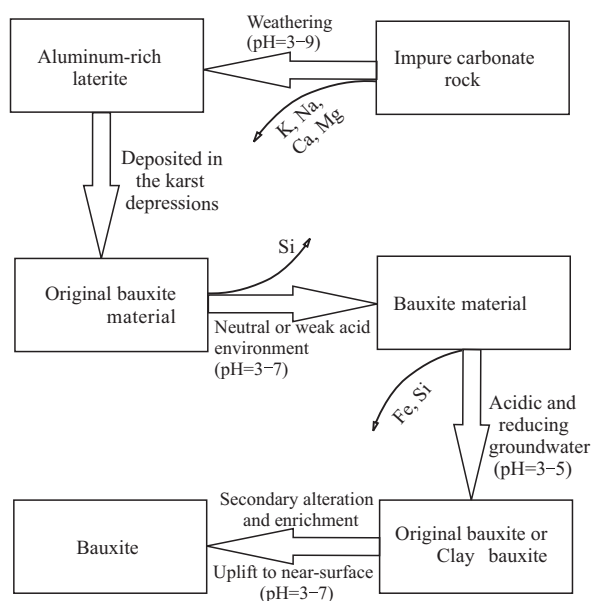


Fig. 12. The metallogenic model diagram of bauxite in central Guizhou province, China.

vegetation on lands, and a large amount of plants decomposition to produce humid acid flowed towards high aluminum laterite deposit area such as closed and semi-closed karst depressions. As a result, the neutral or weak acid environment formed and it provided the favorable environment conditions for Si removal and Al enrichment. Moreover, the more closed the basin was, the more conducive it was to maintain water acidic property, and to have the “original bauxite material” alteration with Si removal and Al enrichment in acidic or weak acidic conditions (nature with unreduced conditions) (Wang et al., 2011).

(4) After the investigation and researched for carboniferous Jiujiayu Formation Al-bearing rock series in central Guizhou Province, Permian Liangshan Formation Al-bearing rock series in north Guizhou Province, Permian Heshan Formation Al-bearing rock series in Guangxi Province, Carboniferous Benxi Formation and Permian Wujiaping Formation Al-bearing rock series in Yunnan Province Al-bearing rock series, we found that bauxite beds are often accompanied with the rich iron beds and coal beds, constituting a “coal-bauxite-iron” special structure, which is also widespread in foreign deposits such as Ghiona bauxite deposit in Greece, Nurra bauxite deposit in Italy, Kanisheeteh bauxite deposit in Iran (Kalsitzidis et al., 2010; Mameli et al., 2007; Calagari and Abedini, 2007; Zhang et al., 2012). After the long term of Al enrichment and Si removal, the “original bauxite material” developed into “bauxite material” with a lower Si contents (<20 wt%). Afterwards it deposited the organic-rich sediments at the top of the bauxite beds which were precursor of the “coal” of “coal-bauxite-iron” structure. Because the pyrite and other sulfide in “coal” could be easily oxidized, the acidic and reducing groundwater (H_2S , H_2SO_4 , etc.) it produced percolated downwards, resulting in bleaching and Al enrichment of the upper part of the underlying bauxite (Kalsitzidis et al., 2010). It also could reduce Fe^{3+} to the easily migrated Fe^{2+} and transport it down near the basal carbonate to make precipitations of the “iron” (FeS_2 , $FeCO_3$, etc.) of the “coal-bauxite-iron” structure. Thus, after the Fe removed and further removed of the Si for the bauxite material, the “original bauxite” or clay bauxite formed in a certain geological period. Research and studies have shown that it is the positive correlation between the thickness of Lower Carboniferous Jiujiayu formation Al-bearing rock series in central Guizhou Province and lower segment “Qingzhen-type iron deposit”. The thicker bauxite beds were, the thicker ferruginous rocks were; the thinner bauxite beds were, the thinner ferruginous rocks were or absent (Yang et al., 2011). This can be better shown that bauxite beds are close link with the lower segment ferruginous rocks

that the thicker bauxite beds are, the more Fe^{2+} were transported down to the lower segment by acidic and reducing groundwater and then the thicker ferruginous rocks formed.

(5) Guizhou area experienced the crust uplift at late Triassic and had its conversion from sea to land after all the sea water regressed till Rhaetia (Guizhou Provincial Bureau of Geology and Mineral Resources, 1987). Then the later Tectonic movements uplift the “original bauxite” or clay bauxite to near-surface, so the coal beds or carbonaceous shale continued to produce the acidic and reducing groundwater to have secondary alteration and enrichment for the “original bauxite” or clay bauxite, which ultimately formed the high quality bauxite available to industrial exploitation.

6 Conclusions

(1) The source rock of Lindai bauxite may be the underlying Shilengshui Formation dolomite and the weathering laterite is the in-process products from mother rock to the bauxite.

(2) Weathering simulation experiments (leaching experiment and soaking experiment) show that the neutral and acid non-reducing condition is the most conducive to the Al rich and Si removal, and the acid reducing conditions is the most conducive to the Al rich and Fe removal.

(3) During the process of bauxite formation, Coal beds or other rock formation rich in organic material overlying the Al-bearing rock series produce acid reducing groundwater which may be important for bauxite mineralization.

(4) Propose the metallogenic model of bauxite in central Guizhou Province (Fig. 12) and put forward three new words which are “original bauxite material”, “bauxite material” and “original bauxite”. “Original bauxite material” is the precursor substances of bauxite which transition from the aluminum-rich laterites after it were deposited in karst depressions or catchment basins. “Bauxite material” which with a lower Si contents (<20 wt%) is the product of desilication of “Original bauxite material”. And “original bauxite” is the bauxite or clay bauxite which haven't uplifted to near-surface.

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