Features and geological significance of trace elements of Laowashan bauxite in Zunyi area, northern Guizhou, China

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Abstract. By analysing features of trace elements in ZK-CS1 Laowashan Bauxite of Zunyi by geochemical methods, it was found that these elements could be divided into four types according to features of their vertical distribution. For instance, the content of elements such as Ga, Li and Sc was relatively low in the middle part of the ore-bearing rock series, but increasingly higher towards the top and bottom, and the highest at the bottom or near the bottom. Nb and Ta, Zr and Hf migrated in pairs during metallogenesis. The dolomite in the underlying Loushanguan Formation of the ore-bearing rock series was one of provenances of the Laowashan bauxite.

Keywords. Bauxite, Trace Elements, Correlations, Zunyi area.

1. Introduction
Zunyi, situated in northern Guizhou Province of China, is a critical metallogenic belt, where lots of bauxites formed in the Carboniferous-Permian period. There have been many studies on bauxites of this area (Liu et al., 1990; Gao et al., 1992; Yin et al., 2011; Weng et al., 2011; Liu, 2012; Liu et al., 2015, 2016). Notwithstanding much relevant research, attention has been mainly focused on bauxite of other mines rather than Laowashan, and Laowashan bauxite have been seldom examined, so relevant research remains to be performed.

Trace elements migrate and are enriched during metallogenesis of bauxites. It is not only helpful for understanding the metallogenic mechanism of bauxite, but also favorable for exploring enrichment and metallogenesis laws of trace elements by studying features of these elements. In this paper, migration laws of trace elements in Laowashan bauxite were explored by geochemical methods to analyze laws of vertical changes to these elements of Laowashan bauxite. Besides, this paper discussed relationships among trace elements and their associations with Al2O3, thereby providing more data for exploring bauxites of Zunyi area.

2. Geological setting
In Zunyi area, bauxites are located the Yangtze platform. In the north, they are connected to the metallogenic belt of bauxite in the Wuchuan-Zhengan-Daozhen area. In Zunyi area, the strata exposed are mainly cambrian-triassic, among which Carboniferous Jiujialu formation is an ore-bearing rock series (Liu et al., 1990; Gao et al., 1992), which is approximately 0 to dozens of meters thick. This
series, covered by black muddy share of the Liangshan Formation or limestone of the Qixia Formation, has underlying dolomites of Cambrian Loushanguan formation or Ordovician Tongzi formation. Regional strata exposed include Cambrian Loushanguan formation, Permian Liangshan-Qixia formation, and carboniferous Jiujialu formation, which primarily strike at 75° and incline at 15°. The natural types of bauxite are identical to those of sedimentary bauxite. According to their natural types, bauxite may be divided into compact, semi-muddy, clastic and politic, but semi-muddy bauxites are rarely seen in this area.

![Fig.1 Geology map of the Laowashan bauxite in Zunyi area](image)

3. Analysis and tests
7 drilled ZK-CS1 core samples (Fig. 2) in the southeast of Laowashan Mine (Fig. 1) were sent to China Railway Langfang Geophysical Prospecting Co., Ltd for analysis and tests to obtain data about the trace elements. The tests were performed based on GB/T 14506.28-2010 Methods for Chemical Analysis of Silicate Rocks. The samples were numbered from LWS-1 to LWS-7. Their sampling position and features of bauxites/dolomites are shown in Fig. 2. Table 1 shows the analysis and test results of Al2O3 and trace elements.
| System               | Formation         | Code | Lithology | Sampling Location | Petrographic Description                                      | Pictures |
|----------------------|-------------------|------|-----------|-------------------|----------------------------------------------------------------|----------|
| The middle premier   | Liangshan formation | P₁₁ |           |                   | black shale                                                    |          |
|                      |                   |      |           |                   | light massive bauxite, contains clastic particles              |          |
| The lower carboniferous | Jiujiala formation | C₁₂ |           | LWS-1             | clastic bauxite with massive structure                        |          |
|                      |                   |      |           | LWS-2             | light grey clastic bauxite with abundant oolites               |          |
|                      |                   |      |           | LWS-3             | massive bauxite with clastic particles                         |          |
|                      |                   |      |           | LWS-4             | high grey massive bauxite with lower grade                     |          |
|                      |                   |      |           | LWS-5             | light green massive bauxite with lower grade                   |          |
| The lower cambrian   | Loushanguan formation | C₁₅ |           | LWS-6             | light green bauxite                                            |          |
|                      |                   |      |           | LWS-7             | light green dolomite                                           |          |

Fig.2 Column of drill hole


Table 1 Data of trace elements and Al2O3

| Trace Elements | LWS-1 | LWS-2 | LWS-3 | LWS-4 | LWS-5 | LWS-6 | LWS-7 |
|----------------|-------|-------|-------|-------|-------|-------|-------|
| Al2O3          | 45.74 | 74.38 | 79.14 | 40.28 | 38.83 | 34.43 | 1.538 |
| Li             | 181.90| 9.48  | 1.13  | 476.00| 436.70| 29.03 | 21.02 |
| Be             | 1.29  | 1.93  | 2.26  | 1.29  | 3.72  | 4.24  | 0.66  |
| Sc             | 4.19  | 1.97  | 0.90  | 1.57  | 1.36  | 10.85 | 25.75 |
| V              | 354.40| 610.80| 597.10| 284.20| 152.00| 224.70| 12.35 |
| Cr             | 200.90| 215.40| 268.40| 253.40| 118.60| 119.20| 6.20  |
| Co             | 0.58  | 0.44  | 0.79  | 3.32  | 96.65 | 7.37  | 3.36  |
| Ni             | 19.28 | 6.23  | 5.43  | 34.66 | 173.80| 29.41 | 5.55  |
| Cu             | 18.22 | 19.39 | 17.68 | 21.06 | 24.07 | 23.33 | 11.90 |
| Zn             | 14.98 | 16.74 | 15.72 | 13.71 | 18.31 | 16.45 | 15.88 |
| Ga             | 33.13 | 24.41 | 19.40 | 12.99 | 18.22 | 37.00 | 1.80  |
| Rb             | 43.18 | 10.97 | 1.85  | 5.27  | 13.18 | 72.92 | 17.05 |
| Sr             | 5.87  | 6.43  | 5.09  | 18.28 | 1.52  | 334.60| 156.00|
| Zr             | 426.90| 600.10| 889.10| 390.70| 593.50| 516.10| 20.10 |
| Nb             | 36.25 | 42.69 | 21.02 | 26.37 | 28.40 | 25.25 | 0.98  |
| Mo             | 2.52  | 0.99  | 1.37  | 0.48  | 0.48  | 1.04  | 0.21  |
| In             | 0.14  | 0.08  | 0.05  | 0.08  | 0.03  | 0.10  | 0.10  |
| Cs             | 3.61  | 0.91  | 0.10  | 0.89  | 1.48  | 10.23 | 5.00  |
| Ba             | 56.33 | 20.50 | 0.63  | 17.57 | 16.03 | 188.20| 826.60|
| Hf             | 10.11 | 14.03 | 20.75 | 9.07  | 13.73 | 11.90 | 0.57  |
| Ta             | 2.80  | 0.80  | 1.60  | 0.93  | 1.10  | 2.02  | 0.49  |
| W              | 26.18 | 23.80 | 12.79 | 12.37 | 8.81  | 9.57  | 6.59  |
| Tl             | 0.42  | 0.14  | 0.07  | 0.08  | 0.25  | 0.33  | 0.80  |
| Pb             | 2.49  | 2.44  | 3.19  | 5.91  | 3.91  | 14.32 | 15.68 |
| Bi             | 1.17  | 0.77  | 0.85  | 0.83  | 0.61  | 1.04  | 0.80  |
| Th             | 4.14  | 7.07  | 15.99 | 2.98  | 4.40  | 21.16 | 1.13  |
| U              | 0.39  | 1.02  | 8.55  | 4.01  | 0.76  | 3.19  | 0.61  |

4. Migration Laws of Elements

Li often appears as an associated element of bauxite which can be comprehensively utilized. Li is heavily enriched in LWS-4 and LWS-5, which meets the standard for comprehensive utilization. Li is distributed at the top, in the middle and lower parts, with the highest content in the lower part. Its enrichment is approximately negatively correlated to Al.

Sc and Li were similar in content changes, showing approximate negative correlations with Al. Being relatively low, the content of Sc was only as high as 10.85ppm at maximum at the bottom and far below the requirement for industrial utilization, which suggested that this element was heavily lost during metallogenesis of bauxites. This formed a significant contrast with the loss of Li in the middle part and more enrichment in the lower part.
The content of Ga was the lowest in the middle part, but tended to increase significantly at the top and the bottom, between which the differences were insignificant.

Sr and Ba often appeared in groups, evidently enriched at the bottom. The content of Sr and Ba in LWS-6 was far higher than that in 5 samples in the lower part.

Like Li, the content of Ni was the lowest in the middle part, but increased significantly at the top and the bottom, with the highest value in LWS-5. The content of Cr was the highest in the middle part and at the top, but the lowest in the lower part. Cr showed no significant differences from other elements in terms of vertical changes, which suggested that Cr was quite stable in the course of metallogenesis.

The changes to Th were not very regular, but undulating and repeated in the middle part. In samples with the highest and lowest content of Al, Th was fairly high. Like Th, the content of U was pretty high in LWS-2 and LWS-6. Nevertheless, it reached the peak in LWS-3, which was in the lower part of LWS-2, and even exceeded LWS-6.

As a whole, the vertical distribution of trace elements was more or less regular in ZK-CS1: 1) The content of Li, Sc, Ni, Ga, Rb, Cs, Ba, Ta and Bi was relatively low in the ore-bearing rock series, but increasingly higher towards the top and bottom and the highest at or near the bottom. 2) The content of V, Cr, Zr, Nb and Th was high in the middle part of the section, which was generally the same as the content of Al. 3) The content of Be, Co, Cu, Sr and Pb generally increased towards the bottom of the drilled hole, while the content of Sr reached the anomaly peak. 4) The positions where the content of U and Hf was high were consistent with those with high content of Al. 5) the content of Mo, In, W, Tl and Bi generally tended to decline towards the bottom of the drilled hole.

5. Analysis on correlations of elements

Correlations of elements in Laowashan bauxite were analyzed through the binary scatter plots. Zr, Cr, Ni and Li presented stronger correlations with Al₂O₃ (Fig. 3). The content of Zr was high on strata with high content of Al₂O₃ (Fig 3, a). Although the content of Al was lower at the bottom, the content of Zr was still relatively high. Zr mainly existed as heavy mineral and kept relatively stable during metallogenesis. Cr was linearly correlated to Al₂O₃, and both these two elements exhibited relatively significant positive correlations (Fig 3, b). Ni and Al₂O₃ were mostly negatively correlated, whereas some values were anomaly (Fig 3, c). Relatively significant negative correlations existed between Li and Al₂O₃ (Fig 3, d). The content of Li was extremely low in LWS-6, possibly because the Li in the upper part didn’t totally migrate to the bottom. Generally, Nb and Ta were linearly correlated to Al₂O₃ (Fig 3, e-f), whereas their correlations with Al₂O₃ were not as significant as those with Zr, Cr, Ni and Li. The tenor of samples with high content of Al was above the trend line, while the tenor of all other samples was below the trend line.

Nb had significant and linear correlations with Ta (Fig 4, a), and the underlying dolomite were relatively far away from samples of bauxite. Nevertheless, Nb was also significantly and positively correlated to Nb/Ta (Fig 4, b), and Nb/(Nb/Ta) of underlying dolomite was above the trend line of bauxite, which suggested that bauxite had certain genetic relationships with dolomite.

Zr and Hf exhibited significant linear correlations (Fig 4, c). The trend of Zr-Hf in underlying dolomite was consistent with that in bauxite. In bauxite, the correlations between Zr and Zr/Hf were a little weaker, but still significant and linear (Fig 4, b). Nonetheless, Zr/(Zr/Hf) in dolomite deviated a little from that in bauxite, which indicated that dolomite of the Loushanguan formation was not the sole source of bauxite. According to diagrams about correlations between Zr/Hf and Zr/(Zr/Hf), Zr and Hf migrated in pairs during metallogenesis of bauxite, while the dolomite of Loushanguan formation under the Jiujialu formation was one of potential sources of the bauxite in Zunyi area.
Fig. 3 Binary plots of trace elements (ppm) against Al2O3 (Wt.%)  

Fig. 4 Plots diagrams of trace elements Nb, Ta, Zr and Hf
Sr/Ba was often used for analyzing sea and land environment. The Sr/Ba above 1, between 0.6 and 1, and below 0.6 represented marine face, transitional face and land face respectively (Shi, 2003; Yu, 2009). In Laowashan bauxite, Sr-Ba of most samples indicated land face, but only a minority of samples were associated with marine face (Fig. 5), which was in accordance with the fact that Laowashan bauxite were karst bauxite but impacted by sea water. To analyze sedimentary environment of bauxite based on Sr/Ba, the impacts of leaching should be taken into account (Cui et al, 2013; Du et al., 2013). Although the Sr/Ba for Laowashan bauxite was affected by leaching, the migration laws of Sr and Ba in the process of leaching were more or less identical. On the premise of comprehensively considering different factors, Sr/Ba was helpful for analyzing sedimentary environment for the formation of bauxite.

Fig.5 Plots of Sr(ppm) against Ba(ppm)

6. Conclusion
After analyzing trace elements of Laowashan bauxite in Zunyi area, conclusions were reached as follows: 1) The vertical distribution of trace elements was a little regular. The content of elements such as Ga, Li and Sc was lower in the middle part of the ore-bearing rock series, but gradually increased towards the top and the bottom, and the highest at or near the bottom. 2) Nb and Ta were significantly and linearly correlated to each other, so were Zr and Hf, which suggested that both pairs of elements were relatively stable during metallogenesis of bauxite. 3) The ratio of trace elements revealed that the underlying Loushanguan Formation of the ore-bearing rock series was one of provenances for bauxite. 4) On the premise of comprehensively taking multiple factors into account, it was of certain significance for analyzing sedimentary environment of bauxite.

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