

Anomalously high REE diaspore formed in bauxite overlying paleokarstic surface

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ABSTRACT

Bauxite overlying the paleokarstic surface is rich in rare earth elements (REE), but its occurrence is debatable, which has severely hampered its extraction and utilization. More than 5 billion tons of karstic bauxite were deposited in the North China Craton (NCC) in the Late Carboniferous. This study thoroughly analyzed REE concentrations and occurrences in the major minerals of karstic bauxite in the northern NCC, with the aim of elucidating their migration and enrichment. Bauxite occurs in the Carboniferous Benxi Formation and consists of three layers from bottom to top: Fe-bearing claystone, bauxite, and claystone. The lower Fe-bearing claystone contains primarily illite, kaolinite, diaspore, hematite, goethite, and anatase; the middle bauxite is dominated by diaspore, kaolinite, hematite, goethite, illite, and anatase; and the upper claystone consists primarily of kaolinite, illite, goethite, hematite, diaspore, and anatase. Total REE (Σ REE) increases from top to bottom along the profile, mainly due to the decrease in pH and leaching. REE are released in the acidic conditions of surface weathering, migrate downward, and accumulate in the alkaline environment of the bottom Fe-bearing claystone (up to 961 ppm). In situ elemental analysis revealed anomalously high REE diaspores (up to 11 666 ppm), suggesting that the diaspore is the main host mineral for REE. The similar geochemical behavior of Al, Ti, and REE in single and different diaspores, as well as the significant negative correlation between Σ REE and Al ($r = -0.36$), coupled with the slightly larger diaspore cells of this study compared to the standard diaspore cells, confirms that numerous larger REE³⁺ enter the diaspore lattice and replace Al³⁺ during supergene precipitation. The differences in the concentration and occurrence of REE in minerals formed at different stages (e.g., diaspore, anatase, kaolinite, hematite, and goethite) indicate that the occurrence of REE is closely related to the crystal structure and formation process of these minerals. The diaspore and anatase formed during the metallogenic stage are controlled by the rapid nucleation and crystallization process of minerals, resulting in the incorporation of REE into the mineral lattice mainly by isomorphic substitution. Oolitic hematite is also formed by rapid crystallization, but, due to its dense crystal structure and large surface area, REE are adsorbed on the mineral surface primarily via inner-sphere complexation. In minerals formed during the early metallogenic stage (e.g., kaolinite, hematite, and goethite), prolonged weathering processes lead to the predominant incorporation of REE into the mineral lattice via isomorphic substitution. Clarification of the distribution and occurrence of REE in the NCC karstic bauxite provides insight into the enrichment and occurrence of REE in global karstic bauxite deposits.

Keywords: Karstic bauxite deposits, northern North China Craton, rare earth elements, migration process, enrichment mechanism