

Research Progress on Sources of Rare Earth Minerals from Permian in Western Guizhou

Ruxian Zhou

School of Mining Engineering, Guizhou University of Engineering Science, Bijie, Guizhou, China

Abstract: As an important strategic mineral resource of the country, rare earth plays a key role in various fields such as national defense industry, electronics industry, medical treatment, metallurgy, machinery, petroleum, chemical industry, agriculture and animal husbandry. As a country with rare earth resources, the main types of ore deposits in China are magmatic type, pegmatite type, gas-derived hydrothermal type, sedimentary rock type, placer type and weathered crust type. As a newly discovered type of deposit, Permian rare earth deposits in northwest Guizhou have attracted more and more attention in recent years. The source of rare earth materials is the basis of the study on the genetic mechanism and distribution of ore deposits, and has important research value. The source of rare earth materials in this area can be identified by petrological, geochemical and geochronological methods. Through comprehensive analysis, it is concluded that the source of rare earth materials in this area is closely related to the large igneous province of Emei Mountain, mainly including basic basalt, medium acid igneous material and pyroclastic material.

Key words: Rare Earth; Ore-bearing Rock Series; Provenance; Guizhou; Emei Mountain Large Igneous Rock

1. Introduction

Rare earth not only has excellent photoelectromagnetic and other physical properties, but also can form a variety of new materials with other materials, so it has important application value in the field of national defense and civil industry, and is an important strategic mineral resource of the country. Rare earth is not evenly distributed around the world, mainly in China, Brazil, Vietnam and Russia and other countries. As a

major country in rare earth resources, China's rare earth reserves account for about 37% of the global total [1], and it has a long history of exploration and development of rare earth.

Predecessors believed that rare earth deposit types mainly include magmatic type, pegmatitic type, gas-derived hydrothermal type, sedimentary rock type, placer type and weathering crust type [2]. However, in recent years, a new type of rare earth deposit has been discovered in Weining area, northwest Guizhou Province, and its origin is still controversial. Wang believe that it belongs to weathering crust type [3], and Zhou believe that it belongs to sedimentary type [4]. Zhang believe that it belongs to the sedimentation-transformation type [5], while Gong et al. believe that it has both weathering and sedimentary metallogenic characteristics [6].

The discussion of the type of rare earth deposit involves the study of the mineralization process of the deposit, in which the determination of the material source is the most fundamental link. At present, there are different opinions on the source of layer of rare earth ore-bearing rock series in Weining area of northwest Guizhou Province, and no unified understanding has been formed, which restricts the further improvement of the deposit theory in this area. This study will systematically sort out the views on the sources of rare earth minerals in this area, and summarize the similarities and differences between them, so as to provide certain directions and ideas for subsequent research.

2. Geological Background

The study area is located in the southwest margin of the Yangtze Plate [7]. In the Middle and late Permian, the Emei Mountain igneous province formed in this area contains a large number of volcanic rocks, ferrimafic intrusive rocks and a small amount of felsic rock output. The formation mechanism of the Emeishan large igneous province is as follows: the ascent

of mantle plume first caused rapid dome-like uplift of the crust, resulting in differential denudation of the Maokou formation on the surface to form the corresponding karst landform. The crust was further uplifted by magmatic effusion and volcanism in the later period, resulting in the strongest erosion in the higher inner zone and the accumulation of weathering products in the middle zone and the transition zone between the middle zone and the outer zone. From west to east, denudation area, continental clastic rocks, coastal shallow-sea clastic rocks and carbonate platform are formed successively^[8].

The ore-bearing rock series in this area is formed in the terrigenous clastic rock area, and the strata are mainly Carboniferous, Permian, Triassic, Jurassic and Quaternary. The strata associated with the REE deposits in this study are mainly Emishan Basalt Formation and Xuanwei Formation of the Upper Permian Series. The faulted structures in the direction of NE and NW are developed in the area. With the development of fold structure, the northeast-trending Hala River syncline and Zhe Jue compound syncline are developed from north to south, and the strata of the Xuanwei Formation occurring in the ore-bearing rock series are distributed in the flank of the syncline^[8]. From north to south, typical rare earth ore-bearing rock series profiles include Lufang, Zhangsigou, Maojiaping, Xiaoqinggou, Haiwai and Zhe Jue mines.

3. Geological Characteristics of Deposit

Taking Maojiaping and Xiaoqinggou sections located in different sedimentary areas as examples, the sedimentary characteristics and ore body characteristics of ore-bearing rock series in the area are discussed.

3.1 The Lithologic Profile of Maojiaping

Located in Maojiaping, Heishi Town, south east wing of the northern margin of the Hala River syncline, the rare earth ore-bearing rock series is located in the lower part of Xuanwei Formation (Figure 1), which is in unconformable contact with the underlying Emei Mountain basalt. From bottom to top, The lithology of the rare earth ore-bearing rock series is successively grayish yellow ferruginous tuffaceous claystone, purplish red massive ferruginous mudstone, purplish red thick layered ferruginous silty mudstone,

grayish green medium thick layered ferruginous silty mudstone, light grayish green dense aluminaceous mudstone, black thin layered silty aluminaceous mudstone, grey thick layered dense aluminaceous mudstone and grayish white thick layered dense aluminaceous mud rock, gray medium and thick layered carbonaceous ferruginous mudstone, gray-black thick layered carbonaceous siltstone, black massive carbonaceous ferruginous siltstone, gray-green thick layered ferruginous argillaceous siltstone, black medium layered ferruginous mudstone, gray-green medium layered siltstone. The lithology of the mineral layer is gray and gray white aluminite mudstone, black carbonaceous mudstone, carbonaceous siltstone, gray green silty mudstone and gray ferric mudstone.

3.2 The Lithologic Profile of Xiaoqinggou

The lithology of the ore-bearing rock series is successively gray-black ferruginous tuffaceous mudstone, yellow-green thin-layered ferruginous argillaceous siltstone, gray massive aluminaceous mudstone, light gray massive aluminaceous mudstone, grayish-white medium-thick dense aluminaceous mudstone, gray medium-thick aluminaceous ferruginous gravel coarse sandstone and gray thin-layered aluminaceous fine sandstone (Figure 1). The lithology of the deposit is mainly gray and light gray aluminaceous mudstone and yellow-green ferruginous argillaceous siltstone.

To sum up, the lithology of ore-bearing rock series in this area is mainly mudstone, argillaceous siltstone, silty mudstone and siltstone, and some areas are relatively carbonaceous. The ore types are mainly aluminaceous mudstone, followed by carbonaceous mudstone, ferric mudstone, ferric siltstone and carbonaceous siltstone.

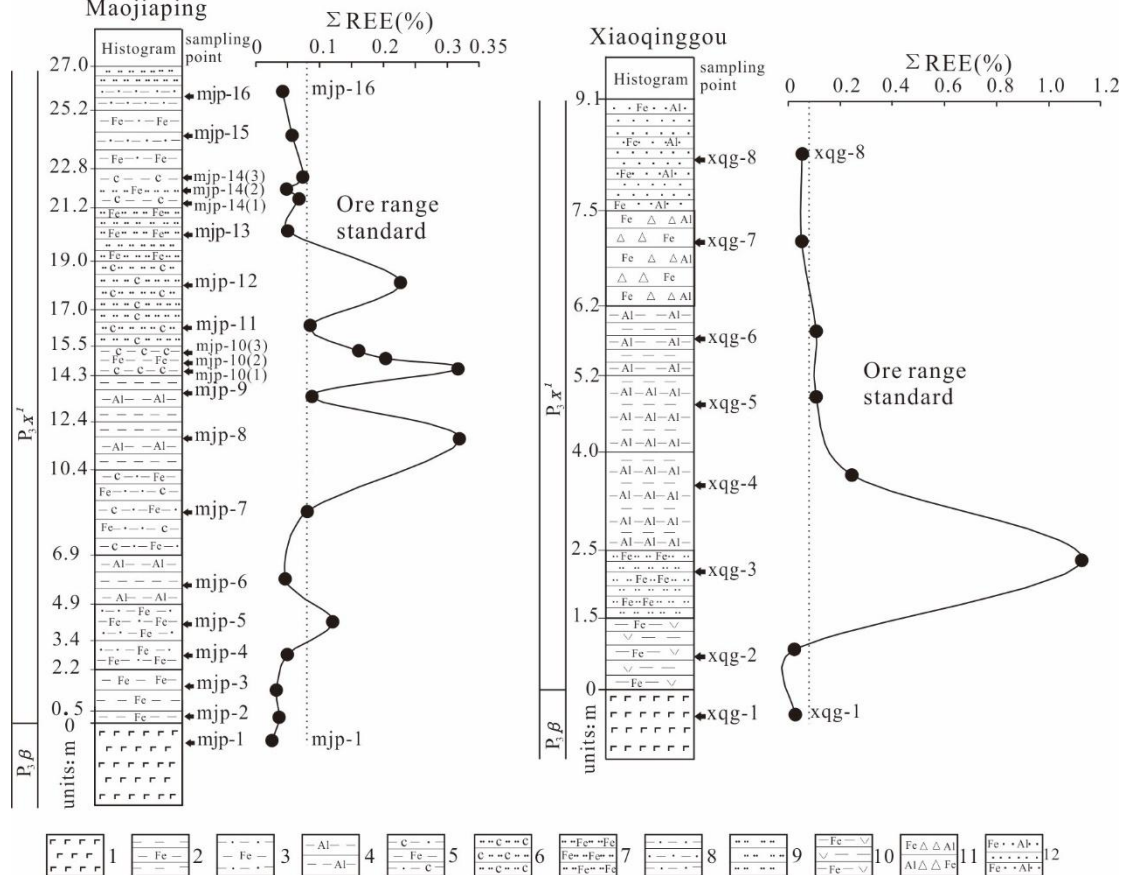
4. Discussion on Material Source

4.1 The Reflection of Ore Structural Characteristics on Provenance

From the above description of the characteristics of ore-bearing rock series, it can be seen that the ore is mainly composed of fine clastic structure, argillaceous structure and tuff structure. Tian et al. identified the clastic components of tuff samples with tuff structure under microscope^[9] and found that about 92%

of the clasts were pyroclastic. Its identification characteristics are semi-plastic-plastic, with flattening, elongating deformation, semi-orientation, slightly developed internal chlorite almond body, condensation edge development, etc. In addition, there are intergranular hidden structures and intergranular hidden structures

among the fragments. The above structural characteristics indicate that the sediment source is closely related to the activity of the basalt in Emei Mountain, and the material source of the ore-bearing rock series is related to the volcanic eruption material.



1-basalt; 2-ferric tuffaceous claystone; 3-ferric silty mudstone; 4-aluminaceous mudstone; 5-ferric carbonaceous silty mudstone; 6-ferric carbonaceous siltstone; 7-ferric argillaceous siltstone; 8 silty mudstone; 9- siltstone; 10-ferric tuffaceous mudstone; 11-al-ferric gravelly coarse sandstone; 12- aluferric fine sandstone.

Figure 1. Column Diagram and Rare Earth Content of Maojiaping and Xiaoqinggou Profiles

4.2 The Reflection of Ore Composition Characteristics to Provenance

Zhang [5] identified the rare earth ore in the area, and the lithology showed that it was mainly fine-grained lithic sandstone and argillaceous siltstone. The debris includes basalt debris and volcanic debris. Specific pyroclasts include volcanic breccia, lithic tuff and clayified lithic tuff. The above characteristics show that the rare earth minerals in this area come from the basalt and pyroclastic rocks of Emei Mountain.

Tian analyzed the ore minerals by sampling X-ray powder diffraction analysis method, and found that in addition to kaolinite, hematite,

chlorite, anatase, magnetite, albitite, chlorite, sodalite and other minerals [9], β-quartz with certain environmental indicator characteristics also appeared. Since β-quartz is mainly produced in medium acid igneous rocks, it indicates that the source of rare earth ore-bearing rock series in this area includes medium acid igneous rocks formed in the late eruptive period besides Emei Mountain basalt.

4.3 The Reflection of Geochemical Characteristics on Provenance

4.3.1 Major Element

Based on the analysis results of 248 chemical samples, Rollinson proposed a discriminant function for distinguishing sediments whose

provenance was mainly ferric magnesium, neutral to felsic and quartz^[10]. The discriminant function is calculated as discriminant function 1 = $-1.773\text{TiO}_2 + 0.607\text{Al}_2\text{O}_3 + 0.76\text{Fe}_2\text{O}_3(\text{total}) - 1.5\text{MgO} + 0.616\text{CaO} + 0.509\text{Na}_2\text{O} - 1.224\text{K}_2\text{O} - 9.09$; discriminant function 2 = $0.445\text{TiO}_2 + 0.07\text{Al}_2\text{O}_3 - 0.25\text{Fe}_2\text{O}_3(\text{total}) - 1.142\text{MgO} + 0.438\text{CaO} + 1.475\text{Na}_2\text{O} + 1.426\text{K}_2\text{O} - 6.861$. Using this criterion, Zhang Hai^[5] conducted the placement of 64 rare earth ore samples, showing that except for a few sample sites, most of the sample sites were located in the ferromagnesia region. It shows that the rare earth minerals in the study are derived from the basalt and pyroclastic rocks of Emei Mountain.

4.3.2 Trace Elements

Since Th element is enriched in acidic rocks and Sc element is enriched in basic rocks, Th/Sc ratio is a good indicator of magmatic chemical differentiation process, and does not change with sedimentary recycling, and can be used to determine whether the sediment belongs to felsic or ferrimafic origin^[9]. Tian et al. analyzed the samples in the area^[9] and found that the iron clay rocks, clay siltstone and a small amount of aluminaceous clay rocks mainly distributed in the range and vicinity of the high-titanium basalt of Emei Mountain in a linear trend, indicating that the material source is closely related to the high-titanium basalt of Emei Mountain.

4.3.3 Rare Earth Element

The rare earth content in sedimentary rocks is mainly controlled by the composition of source rocks, and weathering and diagenesis have a minor effect on the change of rare earth content, which is reflected in that they have little effect on the redistribution of REE, so REE can be used as source tracing^[11]. The specific operation is to identify the provenance through REE distribution pattern curve. The REE distribution model diagram takes atomic number as the horizontal coordinate and ordinate as the pair value of sample normalized abundance base 10. The source of the original material can be determined by comparing the distribution pattern of each sample. Ge sampled the rare earth ore-bearing rock series of Zhejue Section and Haiwai section and the basalt of Emei Mountain at the bottom, tested the rare earth elements, and made the relevant rare earth element

partitioning curve^[8], and found that the rare earth element partitioning curve characteristics of the samples of rare earth ore-bearing rock series were similar to the underlying Emei Mountain basalt, indicating that the rare earth ore in the section is related to the basalt of Emei Mountain. The material of rare earth may come from the basalt of Emei Mountain.

In addition to the rare earth partition curve, the δEu value indicating the Eu anomaly can be used as an important parameter to identify the source of the material. Generally, sedimentary rocks formed by weathering of medium-acid igneous rocks have obvious negative Eu anomalies, while sedimentary rocks formed by weathering of basic igneous rocks such as basalt have no negative Eu anomalies or show relatively weak negative Eu anomalies^[12]. Ge analyzed the rare earth ore-bearing rock series in Zhejue and found that δEu ranged from 0.30 to 0.87^[8], with an average value of 0.63, while δEu of rare earth ore-bearing rock series in Haiwai profiles ranged from 0.75 to 0.103, with an average value of 0.86. It can be found that the degree of Eu anomaly varied greatly, from obvious negative anomaly to weak negative anomaly to no anomaly. The results show that the source of rare earth ore-bearing rock series is not only Emei Mountain basalt, but also some medium acidic magmatic material.

4.4 The Reflection of Chronological Evidence on Provenance

Du et al. conducted a chronological analysis of hard claystone samples from rare earth ore-bearing rock series in Huize area of Yunnan Province, and the results of zircon U-Pb isotope analysis show that the formation age of the ore is between 254-260Ma^[13], which is consistent with the age of the Emeishan basalt measured by He Bin et al. from 255 Ma to 260Ma. It is concluded that the source of ore-forming materials of these supergenetic niobium-rare earth polymetallic deposits may mainly come from basalt. For this study area, Wang Changwei et al. determined the formation age of Yuba rare earth ore-bearing rock series in Weining^[14], and obtained a zircon U-Pb age of 251.9-252 Ma, which is also consistent with the age of Emei Mountain basalt, indicating that the material source of rare earth ore-bearing rock series in northwest Guizhou is also closely related to the

underlying rock formation Emei Mountain basalt.

4.5 Type of Material Source

In summary, the source of rare earth minerals in Guizhou is closely related to the formation of Mount Emei igneous province, and runs through the formation process of the whole igneous province. At the late stage of the evolution of the large igneous province of Emei Mountain, the magma formed moderately acidic igneous materials under the process of differentiation, and the middle and lower part of the large igneous province were mainly basalt and the top was a combination of moderately acidic materials ^[15]. In the process of providing material source for rare-earth ore-bearing rock series under weathering in the large igneous province of Emei Mountain, the medium acid igneous material at the top is first subjected to weathering denudation and is mainly deposited at the bottom of rare-earth ore-bearing rock series. The basalt in the middle and lower part was subsequently denuded and mainly deposited in the middle and upper part of the rare earth ore-bearing rock series. Therefore, the material sources of rare earth ore-bearing rock series include Emei Mountain basalt and medium acid material.

In addition, during the formation of the large igneous province of Mount Emei, there were not only magma overflow, but also corresponding pyroclastic material ejection. The most common is that volcanic ash material migrated with the atmosphere and eventually settled into the corresponding water body, and the corresponding rare earth material was extracted from the sea, providing the corresponding material basis for the formation of rare earth ore ^[16].

5. Conclusion

(1) The mantle plume activity from the middle of Permian period raised the crust, and eventually led to large-scale magma intrusion and eruption, forming a pattern with the eruption center as the inner zone, and the outer zone as the outer zone. The inner zone is the highest in the terrain and suffers from strong weathering, which provides abundant material sources for the formation of rare earth ore.

(2) At present, the source of rare earth minerals can be discussed from the aspects of petrology, geochemistry and geochronology.

The specific mechanism is the mineral composition, structural and structural characteristics of rare earth minerals, major elements, trace elements, rare earth elements in geochemical characteristics, U-Pb isotope analysis in geochronology, which can provide the corresponding indication of the source of rare earth materials.

(3) In summary, the sources of rare earth materials mainly include basic basalt, medium acid igneous material and pyroclastic material.

Acknowledgements

This paper is supported by Guizhou Provincial Department of Education youth science and technology talent development project (Project number: Qian Jiao He KY character [2022] No. 126).

References

- [1] Klaus J. Schulz, John H. DeYoung, Robert R. Seal II, Dwight Bradley. Critical mineral resources of the United States: economic and environmental geology and prospects for future supply. Geological Survey, 2018. 1-863.
- [2] Wang Denghong, Wang Ruijiang, Li Jiankang, et al. Review on the progress of strategic investigation and research of three rare mineral resources in China. *Geology of China*, 2013, 40 (2): 361-370.
- [3] Wang Wei. Study on the weathering crust of Permian basalt and its rare earth enrichment in western Guizhou. Guizhou University, 2008.
- [4] Zhou Lingjie. Geological and geochemical characteristics of depositional kaolinite claystone rare earth deposits in western Guizhou. Guiyang: Institute of Geochemistry, Chinese Academy of Sciences, 2012.
- [5] Zhang Hai. Study on geological and geochemical characteristics and metallogenic mechanism of rare earth deposits in northwest Guizhou. Chengdu: Chengdu University of Technology, 2014.
- [6] Gong Daxing, Hui Bo, Dai Zongming, et al. A New Type of REE Deposit Found in Clay Rock at the Top of the Permian Emeishan Basalt in the Yunnan-Guizhou Area. *Acta Geologica Sinica-English Edition*, 2020, 91 (1): 204-205.
- [7] Liu Youping, Cheng Guofan, Liu Kun, et al. Mineralization and metallogenic model

- of "basalt-ancient weathering crust deposit" iron ore in western Guizhou Province. *Geological science and technology information*, 2017, 36 (4): 107-112.
- [8] Ge Zhihua. Study on migration and enrichment mechanism of rare earth in weathering crust of basalt in Weining area. Guizhou University, 2018.
- [9] Tian Enyuan, Gong Daxing, Laiyang, et al. Genesis and enrichment of sedimentary rare-earth rich rock series in Weining area, Guizhou Province. *Geoscience*, 2021, 46 (8): 2711-2731.
- [10] Rollinson, H.R. Using geochemical data: evaluation, presentation, interpretation, Longman Singapur Press, 1993, 208.
- [11] Tian Jingchun, Zhang Xiang. Sedimentary geochemistry. Beijing: Geological Publishing House, 2016: 84-105.
- [12] Gun Mingshan, Cai Guosheng, Zeng Daoguo, et al. Discovery and significance of scandium-niobium-rare earth mineralized enrichment layer of ancient weathering crust on top of Permian Emei Mountain basalt in western Guizhou. *Journal of Mineralogy*, 2021, 41 (Z1): 531-547.
- [13] Du Shenjiang, Wen Hanjie, Luo Chongguang. Provenance tracing of paleo-weathered sedimentary niobium polymetallic deposits in Yunnan-Guizhou area: Inspiration from basalt sphene. *Journal of palaeogeography*, 2021, 23 (04): 871-872.
- [14] Wang Changwei, Zhang Kexin, He Weihong, et al. Zircon U-Pb age of rare earth ore-bearing rocks in Yuba, Weining, Guizhou Province. *Geology of guizhou*, 2020, 37 (01): 14-23.
- [15] He Bin, Xu Yigang, Huang Xiaolong, et al. Age and duration Of the Emeishan Flood volcanism, SW China: Geochemistry and SHRIMP Zircon U-Pb dating of silicie ignimbrites, post-volcanic Xuanwei Formation and clay tuff at the Chaotian section. *Earth and Planetary Science Letters*, 2007, 255 (3-4), 306-323.
- [16] Dai S, Zhou Y, Zhang M, et al. A new type of Nb (Ta)-Zr(Hf)-REE-Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: Possible economic significance and genetic implications. *International Journal of Coal Geology*, 2010, 83 (1): 55-63.