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Study on REEs as tracers for late permian coal measures in Bijie City, Guizhou Province, China

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Abstract: Analyses of Rare Earth Elements (REEs) in 13 coal samples collected from Late Permian coal measures of Bijie City in western Guizhou Province were conducted using Inductively Coupled Plasma-Mass-Spectrometry (ICP-MS). The results indicated that REEs patterns were not controlled by materials from the sea, whereas the contribution of land plants was about 1%. The major sources of REEs were from terrigenous material as indicated by negative Eu anomaly. There were similar distribution curves of REEs between Bijie's coal and Emeishan basalt. M12 coal seam, which had the highest ∑REE, appeared near the boundary between Longtan Formation and Changxing Formation, which was closely correlated to the eruption of Emeishan basalt. The Emeishan basalt contributed to REEs enrichment of M12. So the sources of REEs were controlled by terrigenous material, and the Emeishan basalt was the predominant source of terrigenous material, which dominated the enrichment and pattern of REEs in Late Permian coal measure from Bijie.

Keywords: coal measure; material source; Emeishan basalt; Late Permian; Bijie; rare earths

REEs are good geochemical indicators to study coal-forming origin [1,2], and have practical significance for rational utilization of coal resources, environmental protection, and exploitation of associated elements in coal. The source of REEs in coal is diverse, with one or several dominant sources in a specific coal basin. According to the research methods and previous studies [3-16], a total of 13 coal samples of Bijie were studied to shed a light on the material source of REEs in Bijie coal measures.

Meanwhile, the relationship between Emeishan basalt and mineralization attracts more and more Chinese and foreign scholars' interests, but little attention has been paid to the relationship between Emeishan basalt and coal's REEs. However, Wang et al.[17] showed that multi-tuffs interbedded with coal measures; interbedded kaolinite-mudstones appear in many seams, which are transformed by acidic volcanic ashes. To understand the relationship between REEs enrichment in coal measure and Emeishan basalt, the authors have conducted systematic REEs geochemical studies for the Late Permian coal measure from Bijie City in western Guizhou Province, China.

1 Sample collection and analytical methods

Bijie City, located in western Guizhou Province, China, contains major coal resources of Guizhou Province. According to Guizhou Provincial Land and Resources Department, total proved coal reserves in Bijie City is about 25.69 billion tons, accounting for more than 45% of the provincial proved coal reserves by the end of 2004. The coal-bearing stratum is Permian. The main coal-bearing strata, Longtan Formation and Changxing Formation of Late Permian are widely distributed in Bijie City. Longtan Formation is the most important coal-bearing stratum and mainly consists of sandstone, siltstone, mudstone, coal, marl and so on (Fig.1).

A total of 13 representative coal-seam channel samples from Bjie (11 workable coal seams) were taken (Fig.1) from fresh faces in underground mines. All samples were collected and stored in plastic bags to ensure as little contamination and oxidation as possible. The method of sample collection followed the Chinese National Standard for Collecting Channel Samples GB482-1985. REEs geochemical analysis were conducted in State Key Laboratory for Mineral Deposits Research, Nanjing.

REEs geochemical analysis were conducted in State Key Laboratory for Mineral Deposits Research, Nanjing University, after these samples had been crushed and ground to less than 0.1 mm. Finnigan Element II high-resolution plasma mass spectrometry is used in the analysis. Chondritic values by Herrmann[18] are used for normalization with the modifi-

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cation of REEs. The concentration of REEs in the coal seam from Bijie City, as well as in ba salt and in chondrite are presented in Table 1.

2 Research on material sources of REEs

2.1 Marine sources

Seawater enriched with both LREE and HREE (Table 2), however, the REEs concentration is low [24]. Cerium is negative anomaly in seawater, because Ce^{3+} is oxidized into Ce^{4+}, and is preserved in solution in the form of CeO_2, but other REEs retain +3 in the ocean conditions. In all the 13 samples, δ_{Ce} are 0.792–0.960, their arithmetic mean is 0.914. Ce shows free or slightly negative anomaly, indicating that REEs in coal measure from Bijie are not derived from marine material.

The concentration of REEs in seawater and coral in modern ocean and in coal measure from Bijie City are listed in Table 2. Fig.2 is drawn from Table 2. From Fig.2 it can be seen that the concentrations of REEs in coal measure are significantly higher than those in seawater and corals, including ΣREE or HREE or LREE. So REEs in coal measure from Bijie is unlikely come from ocean where the concentration of REEs is lower.

A study of REEs in representative continental shelf seabed sediment in Chinese Bohai Sea, Yellow Sea, East Sea and South Sea by Zhao et al.[24] shows that REEs in modern continental shelf seabed sediments are mainly from mainland weathered rock, instead of sea water or biological debris, because the concentrations of REEs in the latter is too low. Also, different studies by Dai et al.[14] and Ure et al.[27] show that the concentrations and distribution patterns of REEs in coal measure are less affected by seawater. To conclude, REEs in coal measure of Bijie are not mainly derived from sea material.

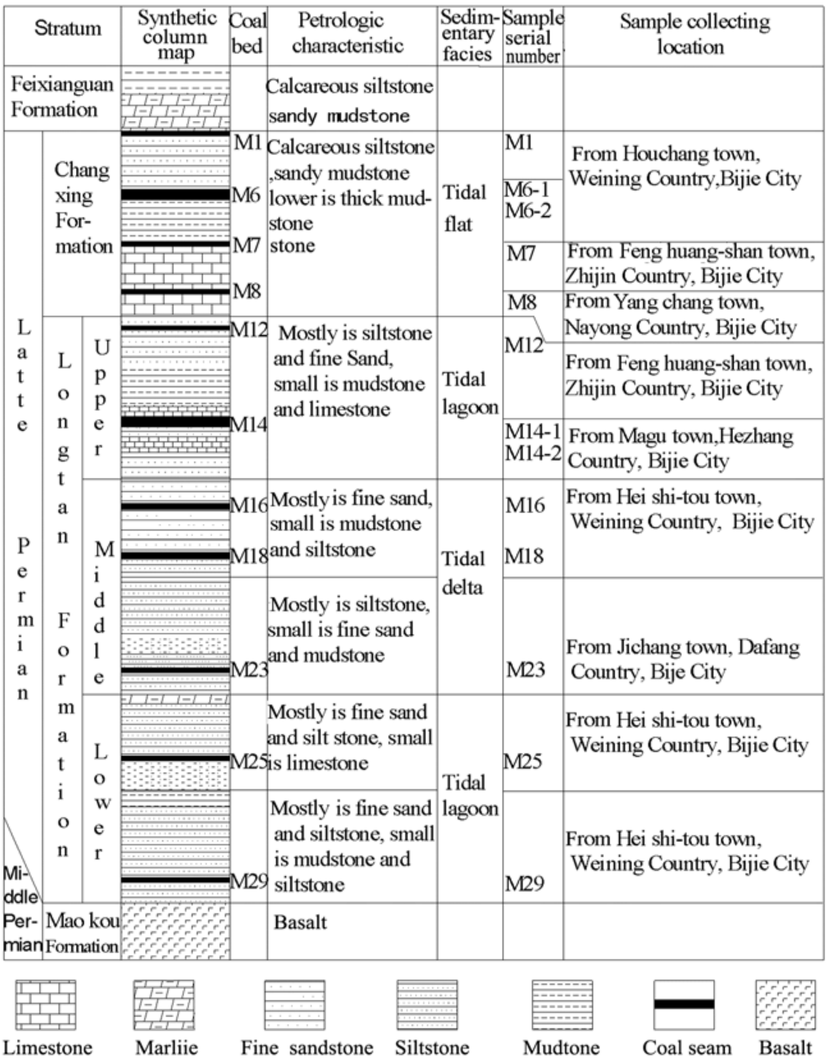

Fig.1 Collection information of coal-sample in Bijie city, Guizhou province (Modified from《Coal geological report in Late Permian in Guizhou Province, China》[19], 1987)

Table 1 Analytical results for REEs of coal samples in Bijie coal measure(1×10^{-6})

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	LREE	HREE	∑REE	LREE/HREE	δ_{Ce}	δ_{Eu}
M1	5.676	12.383	1.291	5.126	1.184	0.109	0.771	0.138	0.987	0.238	0.712	0.103	0.704	0.101	25.769	3.754	29.523	6.86	0.953	0.388
M6	7.828	13.221	1.227	4.239	0.625	0.113	0.509	0.078	0.479	0.100	0.274	0.042	0.273	0.043	27.253	1.798	29.051	15.16	0.889	0.684
M6-2	4.623	8.937	0.852	3.313	0.532	0.109	0.557	0.090	0.528	0.091	0.250	0.035	0.220	0.032	18.366	1.803	20.169	10.19	0.939	0.683
M7	10.992	24.541	2.586	9.096	1.882	0.382	1.793	0.259	1.745	0.356	0.929	0.137	0.907	0.134	49.484	6.26	55.744	7.90	0.960	0.709
M8	16.221	37.277	4.046	13.571	2.754	0.230	2.002	0.378	2.490	0.553	1.397	0.198	1.185	0.163	74.099	8.366	82.465	8.85	0.959	0.334
M12	24.829	52.674	5.850	22.834	3.522	0.319	1.984	0.286	1.663	0.361	0.897	0.141	0.889	0.139	110.03	6.36	116.39	17.30	0.911	0.412
M14	16.631	35.693	3.850	13.915	2.513	0.232	1.944	0.374	2.528	0.526	1.399	0.203	1.218	0.167	72.834	8.349	81.183	8.72	0.930	0.358
M14-2	5.935	11.674	1.170	4.582	0.880	0.153	0.686	0.129	0.721	0.147	0.401	0.056	0.337	0.053	24.241	2.53	26.771	9.58	0.923	0.673
M16	12.716	25.362	2.557	9.747	1.616	0.166	1.590	0.248	1.270	0.250	0.590	0.086	0.562	0.090	75.2	4.686	79.886	16.05	0.927	0.353
M18	16.998	38.801	4.233	15.453	3.170	0.300	2.068	0.273	1.627	0.356	1.006	0.159	1.107	0.177	78.955	6.713	85.688	11.76	0.954	0.399
M23	6.441	13.173	1.518	4.597	0.868	0.118	0.467	0.079	0.538	0.129	0.390	0.068	0.483	0.083	26.715	2.237	28.952	11.94	0.878	0.633
M25	3.437	7.223	0.873	3.085	0.621	0.108	0.665	0.089	0.569	0.111	0.294	0.047	0.279	0.043	16.012	2.097	18.109	7.16	0.869	0.572
M29	2.615	5.976	0.917	5.022	1.964	0.369	1.852	0.315	1.607	0.338	0.750	0.086	0.514	0.088	16.863	5.55	22.413	3.04	0.792	0.660
chondrite*	0.32	0.94	0.12	0.60	0.20	0.073	0.31	0.050	0.31	0.073	0.21	0.033	0.19	0.31	&46.216	&4.654	&50.872	&10.182	&0.914	&0.528
basalt**	37.17	86.29	9.76	46.46	10.08	3.02	9.10	1.27	6.53	1.13	2.53	0.21	1.41	0.21	192.78	22.39	215.17	8.61	1.09	0.96

Note: REEs data of coal samples were analysed in State Key Laboratory for Mineral Deposits Research, Nanjing University; LREE=La+Ce+Pr+Nd+Sm+Eu; HREE=Gd+Tb+Dy+Ho+Er+Tm+Yb+Lu; ΣREE=LREE+HREE; $\delta_{Eu}=Eu_n/(Sm_n\times Gd_n)^{1/2}$; $\delta_{Ce}=Ce_n/(La_n\times Pr_n)^{1/2}$; & the average value of LREE, HREE, ΣREE, LREE/HREE, δ_{Ce} and δ_{Eu}; * from Herrmann[20], 1971; ** from Mao et al.[21], 1992

Table 2 Comparison of REEs in seawater, coral and in coal measure from Bijie (1×10^{-6})

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Seawater*	3.4	1.2	0.64	2.8	0.45	0.13	0.7	0.14	0.191	0.22	0.87	0.17	0.82	0.15
Coral*	0.34	0.29	0.129	0.65	0,21	0.037	0.171	0.02	0.141	0.037	0.121	0.022	0.14	0.024
Bijie**	10.38	22.07	2.382	8.814	1.702	0.208	1.299	0.211	1.289	0.273	0.715	0.105	0.668	0.101

Note: *from Zhao et al.[24] 1996, ** The average value of Bijie's coal samples

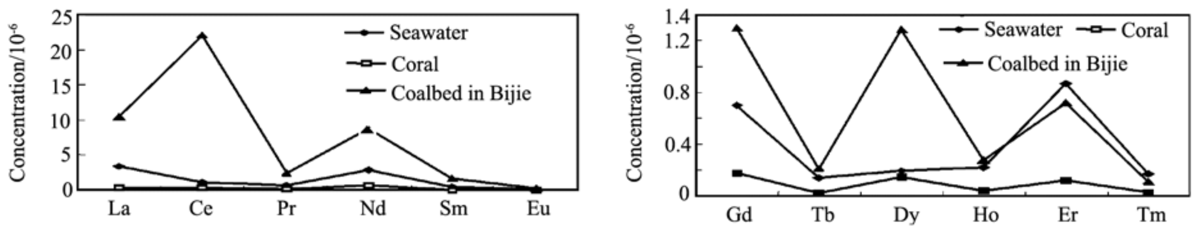

Fig.2 Comparison of REEs in seawater, coral and in coal measure from Bijie(1×10^{-6})

2.2 Terrestrial plant sources

The concentration of REEs in terrestrial plants is very low. The concentration of La or Ce is no more than 1 μg/g in dry plants [26,27]. The average concentration of La is 130 μg/g, and that of Yb is 13 μg/g in ash plant[26,27]. An approximate calculation by Eskenazy[28] shows that only 2%–3% of the total La concentration (an average of 4.8 μg/g) in coal is possibly derived from plants in Pirin Desposit in Bulgaria. The arithmetic mean of La in this article is 10.38 μg/g, and only less than 1% of REEs may be derived from coal-formation plants according to the calculation model by Eskenazy[26].

2.3 Terrigenous material sources

The major inorganic minerals in coal are clay mineral, quartz, pyrite, but the predominant one is clay mineral. In the clay mineral, kaolinite is the most important one, accounting for about 70%–80%[29]. Correlation analysis and cluster analysis show that REEs concentration are highly correlated to Si, Al. Clay mineral in coal is mechanically transferred from land, and shows its terrigenous characteristic, and its content roughly reflects the availability of terrigenous material. It is generally believed that clay minerals play a great role in the source of REEs if the content of Si and Al is high. The REEs content is high in the clay mineral. The δ_{Eu} value of the samples in this article varies from 0.338 to 0.709, the arithmetic mean is 0.528. It is believed that the negative anomaly of Eu is derived from the original rock, because one distinct feature of terrigenous rock is the negative anomaly of Eu[26,28,30]. Our results on δ_{Eu} strongly suggest that REEs in the Bijie's coal measure is controlled by terrigenous materials.

Therefore it is suggested that the source of REEs in coal measure is mainly influenced and controlled by terrigenous material sources in Late Permian from Bijie City.

3 Discussion on relationship between REEs in coal measure and emeishan basalt

As noted above, REEs source is terrigenous material, then it is asked what kind of terrigenous material is it? Study on this topic is not only for further trace study of REEs, but also for the verification of the above-mentioned conclusions on source material.

3.1 Comparison of LREE, HREE and ΣREE in coal measure and Emeishan basalt

The comparison of LREE, HREE and ΣREE in coal measure and Emeishan basalt are shown in Fig.3. It can be seen that the distribution curves are similar.

However, such similarity just provides possible relationship between them. To demonstrate clear relationship between them, further studies are needed.

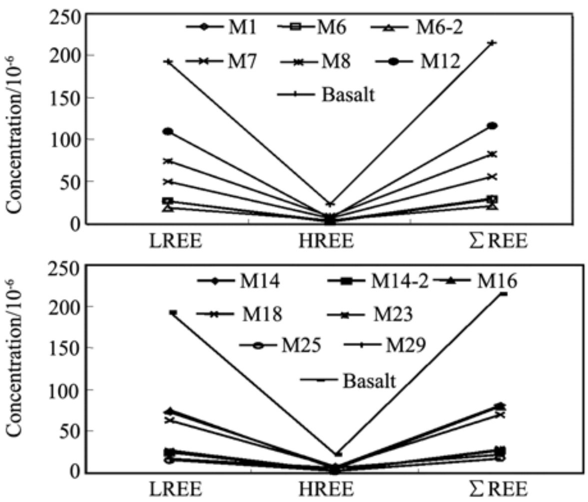

Fig.3 LREE, HREE and ΣREE distribution curves of coal measure and basalt (1×10^{-6})

3.2 Comparison of REEs distribution curves in coal measure and Emeishan basalt

The REEs distribution curves of coal measures and Emeishan basalt is drawn according to Table 1 (Fig.4). From Fig.4, it can be seen that REEs distribution curves are similar not only among coal seams (it indicates that coalfields in Bijie City are similar in deposition process and evolution), but also between coal seams and Emeishan Basalt, in which REEs normalized value decreased gradually with elements from La to Lu. As a whole, REEs distribution curve is high on the left side and low on the right side.

Wang et al.[17] reported that coal-rich zones in western Guizhou (mainly in Bijie City and Shuicheng City) in Late Permian lie in the triangular region, surrounded by north-west Ziyun-Yakou rupture, north-east of Luoping-Guiyang rupture, and north-south Xiao-jiang rupture(west of the studied area, in Yunnan Province). It is worth noticed that this triangular area is the region of extensively developed Emeishan basalt. A study by Du et al.[29] shows that the major source in Late Permian coal measure in southwestern China is basalt, and REEs content mainly relates to the fine heavy minerals which are derived from weathered basalts, such as apatite mineral, tourmaline, barite, rutile, zircon, or celestite-yttrium phosphate rock-monazite portfolio.

Therefore, the authors suggest that basalt not only controls REEs distribution pattern, but also the major source of REEs in Late Permian coal measure from Bijie City.

3.3 Relationship between REEs enrichment in M12 and Emeishan basalt

Comparison of LREE, HREE and ΣREE amongst the 11 workable seams from Table 1 shows that REEs are abnor-

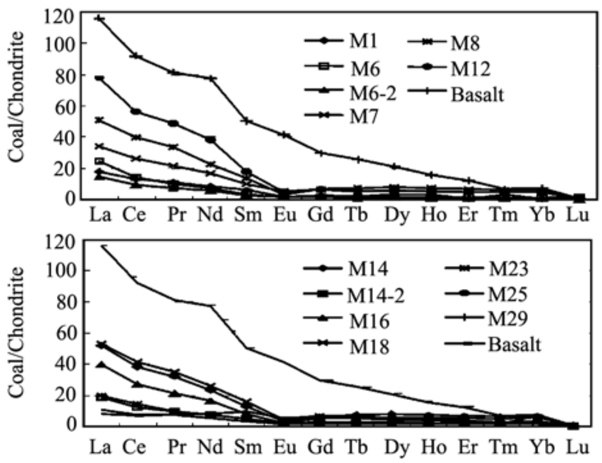

Fig.4 REEs distribution curves of coal in Bijie and basalt

mally enriched in M12 seam: the arithmetic mean of LREE in 13 coal samples is 46.22×10^{-6}, but that in M12 is 110.03×10^{-6}; the arithmetic mean of HREE in 13 coal samples is 4.82×10^{-6}, but that in M12 is 6.36×10^{-6}; the arithmetic mean of ∑REE in 13 coal samples is 51.04×10^{-6}, but that in M12 is 116.39×10^{-6}. Based on the previous research results[17,21,31], the article suggests that there is positive correlation between abnormal enrichment of REEs in M12 coal seam and Emeishan basaltic eruption.

Chen et al.[31] reported that eruption of basalt in Longtan Formation is classified into three cycles. Compared with the former two, the third eruption is weakened, but it centers on western Guizhou Province, including Bijie City. Lithofacies include a complete system of land system, hybrid system, carbonate platform system, and slope basin system[21]. According to the distribution of rough gravel basalt, it can be inferred that there are many volcanic eruption mouths in Weining County (under Bijie City), southern Shuicheng City, Panxian County, and Puan County; local eastern of basaltic distribution edges into the sea. Bijie City and other places have started to take the shape of a barrier, which controls the formed coal basin.

In geological time, M12 seam is located at the end of eruption strata (upper side of the Longtan Formation, and near the boundary). So the abnormal enrichment of REEs in M12 seam is closely related to the eruption of Emeishan basalt, and is controlled by the eruption of Emeishan basalt.

4 Conclusion

The Emeishan basalt was emitted frequently during the Late Permian age, which formed basaltic mountains in the Kangdian area. A considerable number of scattered tuffaceous materials were deposited in the extended low plain, which formed kaolinite and iron weathered crust. During the formation of the sedimentary basin, these kaolinite weathered shells were the main carriers for REEs, and clay minerals were major amongst them. Clay minerals enriched with REEs by the surface adsorption and ion exchange, and transported REEs to the basin by mechanical suspension. Most REEs were leached through the humus, formed sediments containing REEs under appropriate conditions. During plants transformation, part of REEs turned into organic structure, but most of the REEs remained in the clay minerals. These clay minerals are the sources of REEs in coal measures. Therefore, the material source of REEs are mainly affected and controlled by terrigenous material sources, and Emeishan basalt is a predominant one, which dominates the enrichment and pattern of REEs in Late Permian coal measured from Bijie City.

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References:

[1] Zhao Zhigen, Tang Xiuyi, Yang Qi, Huang Wenhui. Research on relationship between ranks of coal and geochemical features of REE in Hami and Huaibei coal. *Journal of China University of Mining & Technology* (in Chin.), 2001, **30**(2): 165.

[2] Li Dahua, Tang Yuegang, Chen Kun, Deng Tao. Concentration, Distribution, and Occurrence of REEs in coal from Chongqing, Southwest China. *China Univ. of Mining&Tech.* (in Chin.), 2005, **15**(3): 227.

[3] Lan Xianhong, Wang Hongxia, Zhang Zhixun, Lin Zhenhong, Li Rihui, Wang Zhongbo. Distributions of rare earth elements and provenance relations in the surface sediments of the south Yellow Sea. *Journal of Rare Earths* (in Chin.), 2006, **24**(6): 745.

[4] Niu Manlan. Comparative studies of rare earth elements for early cretaceous volcanic rocks along the southern segment of Zhangbaling uplift belt. *Journal of Rare Earths* (in Chin.), 2006, **24**(6): 739.

[5] Brik D, White J C. Rare elements in bituminous coals and underclays of the Sydney Basin, Nova Sctia: Element sites, distribution, mineralogy. *International Journal of Coal Geology*, 1991, **19:** 219.

[6] Kortenski J, Bakardjiev S. Rare earth and radioactive elements in some coals from the Sofia, Svoge and Pernik Basins, Bulgaria. *International Journal of Coal Geology,* 1993, **22:** 237.

[7] Wang Yunquan, Ren Deyi, Lei Jiajin. A preliminary study on the distribution characteristics of trace elements in coal. *Scientia Geologica Sinica* (in Chin.), 1997, **32**(1): 65.

[8] Eskenazy GM. Aspects of the geochemistry of rare earth elements in coal: an experimental approach. *International Journal of Coal Geology*, 1999, **38:** 285.

[9] Ren Deyi, Zhao Fenghua, Wang Yunquan. Distribution of minor and trace elements in Chinese coals. *International Journal of Coal Geology*, 1999, **40:** 109.

[10] Pollock S M, Goodarzi F, Riediger C L. Mineralogical and elemental variation of coal from Alberta, Canada: an example from the No.2 seam, Genesee Mine. *International Journal of Coal Geology*, 2000, **43**: 259.

[11] Zhao Zhigen, Tang Xiuyi, Li Bahua. Geochemistry of rare earth elements in coal from Huainan Coalfield. *Acta Sedimento Logica Sinica* (in Chin.), 2000, **18**(3): 454.

[12] Bouska V, Pesek J, Sykorova I. Probable modes of occurrence of chemical elements in coa1. *Acta Montana. Ser, B. Fuel, Carbon, Mineral Process. Praha*, 2000, **10**(117): 53.

[13] Dai Shifeng, Ren Deyi, Li Shan. Geochemical and mineralogical anomalies of the Late Permian coal in the Zhijin Coalfield of Southwest China and their volcanic. *International*

Journal of Coal Geology, 2003, **55**: 117.

[14] Dai Shifeng, Ren Deyi, Li Shengsheng. Modes of occurrence of rare earth elements in some Late Paleozoic coals of north China. *Acta Geosicientia Sinica* (in Chin.), 2003, **24**(3): 273.

[15] Dai Shifeng, Ren Deyi, Shao Longyi, Zhao Mingjun. Variation of coal geochemistry and special textures of Late Permian coals in the western Guizhou Province and their volcanic origin. *Geochimica* (in Chin.), 2003, **32**(3): 239.

[16] Zheng Liugen, Liu Guijian, Zhang Haoyuan, Gao Lianfen, Xue Jian. Study on geochemistry of rare earth elements(REEs) in Permian coal from Huaibei coalfield. *Geological Journal of China Universities* (in Chin.), 2006, **12**(1): 41.

[17] Wang Liting, Lo Jinhui, Wang Changwei, Wang Min. Geology and coal-accumulating regularity of the paralic coal fields of Late Permian in western Guizhou. *Guizhou Geology* (in Chin.), 1993, **37**(4): 291.

[18] Zhao Zhigen. Effect of different chondrite on the parameter of rare-earth elements. *Reporting of Standardization* (in Chin.), 2000, **21**(3): 15.

[19] Guizhou Provincial Institute of Geological Survey. Coal geological report in Late Permian in Guizhou Province, China. Guiyang: Guizhou Provincial Institute of Geological Survey (in Chin.), 1987.

[20] Herrmann A G, Yurium and Lantbanides, Wedepohl K H. Handbook of Geochemistry. Berlin: Springer-Verlag, 1971. 1.

[21] Mao Deming, Zhang Qihou, An Shuren. Emeishan basalt and its mineral in western Guizhou Province, China. Guiyang: Guizhou Technology Publishing House (in Chin.), 1992. 24.

[22] Valkovic V. Trace Elements in Coal. Boca Raton, Fla: CRC Press, l983. 558.

[23] Finkelman R B. Trace elements in coal. Engel M H, Macko S A. Organic Geochemistry. New York: Plenum, l993. 593.

[24] Zhao Yiyang, Wang Jinshi, Qin Chaoyang. Rare-earth elements in continental shelf sediments of the China seas. *Acta Sedimentologica Sinica* (in Chin.), 1990, **8**(1): 37.

[25] Zhu Fohong (Translation). Marine REEs geochemistry. *Marine Geology Letters* (in Chin.), 2006, **22**(4): 15.

[26] Brik D, White J C. Rare elements in bituminous coals and underclays of the Sydney Basin, Nova Sctia:Element sites, distribution, mineralogy. *International of Coal Geology*, 1991, **19**: 219.

[27] Ure A M, Bacon J R. Scandium, yttrium and rare earth contents of waterlily (Nuphar lutea). *Geochim Cosmochim Acta,* 1978, **42:** 651.

[28] Eskenazy G M. Rare earth elements in a sampled coal from the Pirin deposit, Bulgaraia. *International Journal of Coal Geology*, 1987, **7**: 301.

[29] Du Meixia, Zhuang Xinguo. A Characteristic study of rare-earth elements in southern China Late Permian and Late Triassic Coals. *Coal Geology of China* (in Chin.), 2006, **18**(2): 22.

[30] Bouska V. Geochemistry of Coal. Amsterdam: Elsevier, 1981. 284.

[31] Chen Wenyi, Liu Jiaren, Wand Zhonggang, Zheng Qijin. Study on lithofacies palaeogeography during the Permian Emeishan basalt explosion in Guizhou Province. *Journal of Palaeogeography* (in Chin.), 2003, **5**(1): 17.