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Research Progress and Prospects of Detection Technology for Tri-Rare Elements in Coal from the Lianghuai Coalfield

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Abstract

"Triple-rare" minerals (referring to rare elements, scattered elements, and rare earth elements) are key strategic resources supporting the new generation of information technology, new energy, and high-end equipment manufacturing, and their safe supply has risen to the national strategic height. Coal-bearing associated tripleple-rare elements, as important alternative resources to traditional minerals, show great development potential worldwide. As a core energy base in East China, the Lianghuai Coalfield contains abundant lithium, gallium, germanium, and rare earth element resources in its deep coal-bearing strata. However, the superposition of multi-stage tectonic movements and magmatic hydrothermal fluids has resulted in high ash and high sulfur content of coal and extremely complex occurrence states of tripleple-rare elements, posing severe challenges to analytical and detection technologies. This paper systematically combs the research progress of tripleple-rare elements in coal at home and abroad, and focuses on analyzing the core bottlenecks faced by detection technologies under the special geological background of the Lianghuai Coalfield. The research shows that the international community has established a genetic classification system for rare earth elements in coal and a general detection method based on low-ash and low-sulfur coal, but there is a significant mismatch in geological background. Domestically, preliminary achievements have been made in the geochemical characteristics and enrichment rules of tripleple-rare elements in the Lianghuai Coalfield, but the detection system still has shortcomings such as insufficient pertinence, lack of special reference materials, and weak regional research foundation. Finally, this paper discusses the development trend of detection technology for tripleple-rare elements in coal, and proposes that establishing a targeted digestion system based on element occurrence states, constructing a quality control network adapted to the regional geological background, and improving the resource availability evaluation standards are the key research directions in the future, which can provide technical support for the precise exploration and high-value utilization of tripleple-rare resources in the Lianghuai Coalfield.

Keywords

Geochemistry; Triple-rare Elements (Rare Elements, Scattered Elements, Rare Earth Elements); Lianghuai Coalfield.

1. RESEARCH STATUS AND DEVELOPMENT TREND AT HOME AND ABROAD

As key strategic resources supporting the new generation of information technology, new energy, and high-end equipment manufacturing, the safe supply of "tripleple-rare" minerals (rare elements, scattered elements, and rare earth elements) has risen to the national strategic height. China's "tripleple-rare" resources have the characteristics of "rare earth not being earthy,

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rare elements being common, and scattered elements not being scattered". As an important energy base in East China, the Lianghuai Coalfield has great economic potential of key elements such as lithium, gallium, germanium, and rare earths in its deep strata. However, the Lianghuai area has experienced the superposition of multi-stage tectonic movements and magmatic hydrothermal fluids, resulting in large variation coefficient of coal quality, high sulfur content, and extremely complex occurrence states of "tripleple-rare" elements: rare earth elements occur in silicate lattices in the form of isomorphism, lithium and beryllium are mainly organically compatible, and gallium and germanium exist in the form of sulfide-bound state[1]. This complex matrix with high ash and high sulfur poses a severe challenge to analysis and detection: conventional acid digestion methods are difficult to completely destroy silicate lattices[2], leading to incomplete release of refractory elements (such as Zr, Hf, REY) [3]; while high contents of organic matter and sulfur will cause serious mass spectral interference (such as ArO^+ interference on Fe, CeO^+ interference on Eu) and non-spectral interference (matrix inhibition effect) in ICP-MS testing [4]. Therefore, developing a standardized detection method for the special geological background of the Lianghuai Coalfield is not only a technical need to fill the domestic gap, but also a prerequisite for realizing the precise evaluation and high-value utilization of "tripleple-rare" resources in this region.

1.1. International Research Progress

The distribution of high-rare earth coal abroad shows strong regional specificity and amazing enrichment potential. The Cenozoic coalfields in Siberia and the Far East of Russia show high enrichment capacity, and the total rare earth content in raw coal can soar to 1000 μg/g in local coal seams, while it is surprisingly enriched to 0.2%~1.0% in the corresponding coal ash, and even up to 1.5% in some areas [5], which completely meets or even exceeds the industrial grade of traditional rare earth deposits, becoming a very potential alternative resource. The content of rare earth elements in bituminous coal ash in eastern Kentucky, USA can reach up to 4198 μg/g [6].

Seredin and Dai [7] systematically summarized the distribution rules of rare earth elements in coal worldwide, pointing out that rare earth elements in coal mainly occur in apatite and clay minerals. The "Seredin-Dai classification standard" proposed by Seredin and Dai has become an internationally recognized evaluation criterion, dividing coal-based rare earth resources into four genetic types: terrigenous, volcanic ash, infiltration, and hydrothermal [7]. In particular, the super-large lithium deposits found in coalfields such as Ningwu and Junggar have confirmed the abnormal enrichment mechanism under specific paleogeographic environments (such as Ordovician limestone weathering crust). Studies have confirmed that rare earth elements mainly occur in coal in the form of fine-grained authigenic minerals (such as aluminum phosphates, sulfates) and organic compounds, and during the combustion process, due to the high positive correlation between rare earth elements and matrix elements such as aluminum, silicon, and iron, they are prone to secondary enrichment in fly ash[8.9]. Studies in Poland and other European countries have also shown that although the grade of rare earths in fly ash is relatively lower than that of primary ores, it is regarded as a very potential rare earth resource because it requires no mining cost and is already in fine particles [10].

SRM 1632 (Trace Elements in Coal) and RM 8499 (Bituminous Coal) released by the National Institute of Standards and Technology (NIST) are globally recognized reference materials, and their certified values cover most "triple-rare" elements, providing a standard for method verification [11]. In terms of detection technology, developed countries such as Europe, America, and Australia generally adopt ICP-MS combined with collision/reaction cell (CRC) technology. By optimizing radio frequency power, nebulizer gas flow rate, and introducing He/H_2 mixed gas, matrix effects and mass spectral interference are effectively eliminated, and the method

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detection limit can reach ng/g or even pg/g level [12]. Finkelman et al. [13] used LA-ICP-MS technology to realize in-situ analysis of trace elements in individual mineral particles in coal.

However, the main research objects abroad are mostly low-ash, low-sulfur thermal coal or coking coal (such as the Illinois Basin in the United States and the Ruhr Coalfield in Germany) [14, 15], and their pretreatment mostly adopts a mild HNO_3-H_2O_2 microwave digestion system [16]. When this "clean coal" analysis process is applied to the complex coal-bearing strata with high sulfur, high ash, and strong reducibility in the Lianghuai area, the results are often low due to the inability to completely decompose pyrite and silicate lattices, resulting in a significant mismatch in geological background. For high-ash and high-sulfur coal, conventional acid digestion methods are difficult to completely destroy silicate lattices, leading to incomplete release of refractory elements (such as Zr, Hf, REY) [17]; while high contents of organic matter and sulfur will cause serious mass spectral interference (such as ArO^+ interference on Fe, CeO^+ interference on Eu) [4] and non-spectral interference (matrix inhibition effect) [18, 19] in ICP-MS testing. Therefore, developing a standardized detection method for the special geological background of the Lianghuai Coalfield is not only a technical need to fill the domestic gap, but also a prerequisite for realizing the precise evaluation and high-value utilization of "triple-rare" resources in this region.

1.2. Domestic Research Status

Domestically, research on coal-bearing "triple-rare" resources has developed rapidly in recent years. The research on triple-rare elements in the Lianghuai Coalfield mainly focuses on the geochemical characteristics, enrichment rules, and occurrence states of trace elements in coal. Studies have shown that the trace elements in coal from the Lianghuai Coalfield have significant regional differences. For example, the coal in the Huainan Coalfield is slightly enriched in elements such as As, B, Be, Cd, Sb, Se, and Sn, while the coal in the Huaibei Coalfield is slightly enriched in elements such as Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, U, and V. The Huainan Coalfield is mainly enriched in light and medium rare earth elements, while the Huaibei Coalfield is mainly enriched in heavy rare earth elements.

In terms of research methods, standardized treatment and enrichment factor calculation are adopted [5] to analyze the enrichment rules of triple-rare elements in coal. The enrichment types of rare earth elements in the Late Permian coal of the Huainan Coalfield are diverse, mainly enriched in heavy rare earth elements, and the enrichment characteristics of trace elements in coal are affected by many factors. For example, the enrichment of Li element is mainly related to the clastic materials from the provenance area input into the peat swamp during the syngenetic stage, while magmatic hydrothermal activity has little impact on the enrichment of Li element. The enrichment of Ga element is closely related to the migration and enrichment of the major element Al. The positively charged $Al(OH)_3$ colloids produced by the weathering of Al-rich intermediate-acid igneous rocks migrate to the peat swamp with water flow and co-precipitate with negatively charged colloidal SiO_2 and humic acid, leading to the enrichment of Ga in coal. In addition, during the Late Permian sedimentary process of the Huainan Coalfield, the fluvial action was strengthened, and the sedimentary environment was closer to the land side, which was not conducive to the accumulation of organic matter, resulting in the relatively low organic matter content and relatively high ash yield of 11-2 coal, thus leading to the relative enrichment of trace elements compared with 13-1 coal.

In the research of rare earth elements, Academician Dai Shifeng proposed the REY tripartite method, which standardizes light rare earth elements (LREY: La, Ce, Pr, Nd), medium rare earth elements (MREY: Sm, Eu, Gd, Tb, Dy, Y), and heavy rare earth elements (HREY: Ho, Er, Tm, Yb, Lu), and uses the ratios of standardized La, Sm, Gd, and Lu to judge the enrichment types of light, medium, and heavy rare earth elements [5]. Studies have shown that the enrichment types of rare earth elements in 13-1 coal and 11-2 coal of the Late Permian in the Huainan Coalfield are

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mainly heavy rare earth enrichment, which provides a theoretical basis for the evaluation of rare earth enrichment in coal.

At present, there are still the following shortcomings in the standardized detection methods of coal-bearing triple-rare elements:

(1) The analytical testing technology system has been initially established, but the pertinence is insufficient. The National Center for Geological Experimental Testing has established an inorganic multi-element analysis system covering rocks and soils, and the industry has generally begun to adopt internal standard correction method combined with CRC technology to improve the accuracy of ICP-MS. However, the special pretreatment process for coal-bearing high-organic matter matrix is not yet mature. Most laboratories use the general standards of the geology and mineral industry (such as GB/T 14506.30-2010) without optimizing the digestion acid system for the high-sulfur characteristics of the Lianghuai Coalfield.

(2) Lack of reference materials and difficulty in value traceability. Although a series of reference materials for soil and rocks have been developed in China, there are no nationally approved "triple-rare" certified reference materials (CRM) with the characteristics of high ash and high sulfur in coal-bearing strata. Most existing studies use NIST SRM 1632e for external standard calibration. At present, the reference materials for triple-rare elements in coal on sale are NIST SRM 1633c and NIST SRM 8499, which can be used as reference materials in research for quality control purposes.

(3) The research on ion-adsorbed rare earth leaching and resource utilization is lagging behind. Although the extraction process of ion-adsorbed rare earth ores has formed a green and efficient system of "magnesium sulfate replacing ammonium sulfate" in the southern granite weathering crust, and the Richards equation has been used to establish a solute transport model, the research on the leaching of rare earth elements in coal-bearing strata is still in the exploration stage [20]. The high content of pyrite and organic matter in coal-bearing strata will consume a lot of leaching agents, and the strong adsorbability of coal matrix is likely to lead to "re-fixation" of rare earths. The traditional ion-adsorbed rare earth leaching process (such as ammonium salt system) is prone to side reactions in high-sulfur coal, resulting in waste and environmental risks. At present, there is no special standard for the availability evaluation of "triple-rare" elements in the Lianghuai coal-bearing strata in China [21].

(4) The regional research foundation of the Lianghuai area is weak. Special studies on the Lianghuai Coalfield are mostly focused on coal resources themselves, and the attention to "triple-rare" elements is mainly concentrated on the census of single elements (such as lithium or germanium) in local mining sections, lacking systematic data of the whole element spectrum. Although Anhui Provincial Public Welfare Geological Work has launched relevant investigation projects, it has not yet established a full-process quality control system and standardized detection procedures adapted to the regional geological background of this area.

2. EXISTING RESEARCH GAPS: BOTTLENECKS IN REFERENCE MATERIALS AND ELEMENT CLASSIFICATION PROCESSING

2.1. Matrix Mismatch of Reference Materials:

There is a lack of special "triple-rare" reference materials for high-ash and high-sulfur coal-bearing strata in China. Although NIST standards are authoritative, they are different from the sulfide-bound environment of the Lianghuai Coalfield, leading to doubts about the detection accuracy of sulfide-bound elements (such as Ga, As, Se).

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2.2. Lack of Element Classification Processing Strategy

The geochemical properties of "triple-rare" elements are very different (such as volatile Li, Be and refractory REY, Zr), but the existing detection mostly adopts a "one-size-fits-all" digestion mode, lacking a classified pretreatment process based on element occurrence states, which is the fundamental reason for large data dispersion and poor comparability.

2.3. Establishment of Enrichment Rules and Availability Evaluation System for "Tri-Rare" Elements

There is a lack of standardized detection procedures for ion-adsorbed rare earths adapted to the Lianghuai area. There is a large gap in the supporting synchronous detection data of raw coal and coal ash. The inconsistency of test methods leads to poor data comparability; only scattered enrichment phenomena have been found, and the core source of high-enrichment fly ash has not been delineated; the existing evaluation directly applies the traditional ore deposit standards, without combining the characteristics of easy leaching and low-cost extraction of ion-adsorbed rare earths, which cannot accurately judge the actual development value of resources.

3. TECHNOLOGY DEVELOPMENT TREND AND CUTTING-EDGE DIRECTIONS

In view of the above bottlenecks, combined with the current interdisciplinary frontier of coal quality and analytical chemistry, the technology development shows the following trends:

(1) "Classification" and "Precision" of Detection Methods

The future pretreatment technology will evolve towards "targeted digestion". Based on the geochemical affinity of elements (organic affinity, sulfur affinity, rock affinity), a differentiated digestion system will be established: HNO_3-H_2O_2 microwave digestion is adopted for easily soluble elements such as Li and Be; high-pressure closed digestion with HF-HNO_3-$HClO_4$ or alkali fusion method is adopted for refractory elements such as Ga, Ge, and REY to ensure complete destruction of lattices. At the instrumental analysis end, high-resolution ICP-MS (HR-ICP-MS) combined with reaction cell technology is used to accurately eliminate isobaric interference (such as Ba interference on Eu), and an internal standard correction system is introduced to completely solve the signal drift under high-salt matrix.

(2) "Geochemicalization" of Quality Control System

Constructing a laboratory quality control network is an inevitable trend. The chondrite standardization model is introduced as a geochemical quality control method: by calculating the smoothness of the rare earth element distribution pattern and the Ce and Eu anomaly values, the reliability of test data is reversely verified, and single-point anomalies caused by pretreatment loss or instrument drift are identified [22, 23].

(3) High-Value Closed-Loop of Waste:

For solid wastes such as coal gangue and fly ash, the technical trend is to establish a cross-industry circular chain of "building materials-chemical industry-metallurgy". For example, the residue after extracting rare earths from fly ash can be used to prepare metallurgical-grade alumina or high-performance building materials, realizing the full-component utilization.

4. SUMMARY

1. International research: The four major genetic classification standards for rare earth elements in coal and the general ICP-MS detection system based on low-ash and low-sulfur coal have been established, but the method is seriously mismatched with the geological background of high-ash and high-sulfur coal in the Lianghuai area, and the detection results are prone to be low.

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2. Domestic research: The regional distribution differences of triple-rare elements in the Lianghuai Coalfield (light-medium rare earth enrichment in Huainan, heavy rare earth enrichment in Huaibei) and the main controlling factors of enrichment of elements such as Li and Ga have been clarified, but the detection technology still uses the general standards for rocks and soils, with insufficient pertinence.

3. Core bottlenecks: There is a lack of special reference materials for triple-rare elements in high-ash and high-sulfur coal-bearing strata in China; the "one-size-fits-all" digestion mode is generally adopted, without distinguishing the geochemical properties of elements; the resource evaluation directly applies the traditional ore deposit standards, which cannot reflect the actual development value of coal-bearing triple-rare elements.

4. Future directions: Develop targeted digestion and precise detection technologies based on element affinity; develop regionally characteristic reference materials and construct a geochemical quality control system; establish resource evaluation methods combined with leaching performance; carry out systematic investigation of the whole regional and whole element spectrum in the Lianghuai area.

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