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Invited Review

A critical review of critical metals in coal and coal-bearing strata: Characteristics, enrichment mechanisms, extraction techniques, and strategic significance

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ABSTRACT

Critical metals are pivotal to the global energy transition and modern high-tech industries. As conventional ore reserves face growing supply chain vulnerabilities, coal measures are increasingly recognized as promising unconventional reservoirs for essential elements, particularly lithium (Li), gallium (Ga), germanium (Ge), and rare earth elements (REEs). This paper systematically summarizes the occurrence patterns, mineralization drivers, recovery methodologies, and geopolitical value of these strategic resources within coal-bearing formations. The enrichment of these metals is shown to be controlled by complex geological processes, including sedimentation, magmatism, and hydrothermal activities, with material sources varying from terrigenous clastics to deep-seated fluids. Furthermore, this paper critically evaluates current extraction methodologies, including physical beneficiation, chemical leaching, and bioleaching. While physical methods offer low costs, their efficiency is limited by the complex occurrence modes of metals. Chemical leaching ensures high recovery but faces environmental challenges, whereas bioleaching is eco-friendly yet slower. Ultimately, advancing eco-friendly, highly efficient, and synergistic extraction systems is crucial for maximizing the value of coal-based resources and safeguarding domestic mineral supply chains.

1 Introduction

Against the backdrop of global energy transition and industrial transformation, critical metals, as the essential material foundation supporting the development of modern high-tech industries [1–3], have witnessed an increasingly prominent strategic status. The Critical Materials Report released by the U.S. Department of

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Energy and the White Paper on the Development of Strategic Metals and Critical Mines in China provide authoritative perspectives for an in-depth analysis of the global pattern and strategic significance of critical metals [4–6] and hold great value for guiding relevant research and industrial development.

The Critical Materials Report of the U.S. Department of Energy focuses on the applications, supply risks, and impacts on energy technology development of critical metals in the energy sector, thereby providing a scientific basis for the United States to formulate energy-related critical metal strategies. The report comprehensively evaluates the indispensability of various critical metals in energy storage, conversion, and transmission processes. For example, it emphasizes the vital functions of lithium (Li), cobalt (Co), nickel, and other related metals in battery systems [7, 8], together with the core position of rare earth elements (REEs) in permanent magnets and energy-efficient utilization devices.

In contrast, China's White Paper on the Development of Strategic Metals and Critical Mines in China adopts a domestic-oriented and global perspective. The white paper not only sorts out the endowment characteristics and exploration and development status of China's critical metal resources but also conducts an in-depth analysis of the challenges and opportunities faced in the global supply chain. It particularly emphasizes China's global influence in the fields of advantageous critical metals such as rare earths, tungsten, and molybdenum [9, 10], as well as the strategic measures to ensure domestic demand in response to external supply chain restrictions.

Coal, as a traditional fossil energy source, still occupies an important position in the global energy structure. Critical metals contained in coal and coal-bearing strata are gradually emerging as a new focus of resource research and development [11–13]. On the one hand, the mineralization mechanisms of key metal elements within coal deposits are complex and varied, involving the coupling of multiple factors such as geological structure, sedimentary environment, and hydrothermal activity [14, 15]. In-depth exploration of these mechanisms is conducive to revealing geochemical cycling processes and improving the metallogenic theoretical system. On the other hand, with the continuous growing demand for key metals, the recovery of strategic metals from coal-bearing sequences provides a new approach to alleviating resource shortages. The investigation of critical metals in coal and coal-bearing strata holds profound strategic significance for safeguarding national critical metal resource security and boosting the green and sustainable development of the energy and resource industries.

2 Overview of critical metals in coal and coal-bearing strata

2.1 Definition and scope of critical metals

Critical metals refer to a category of metals that are vital to the development of modern industry and high and new technologies while facing supply risks. Based on the assessment of applications and supply challenges of critical metals within energy technologies, the report of the U.S. Department of Energy lists Li, Co, nickel, REEs, and others as critical metals [4]. As the core material for manufacturing Li-ion batteries, Li plays an irreplaceable role in electric vehicles and energy storage; Co is a key component of battery cathode materials and also has important applications in superalloys, magnetic materials, and other fields; nickel serves as a vital element in high-capacity Li-ion battery cathodes, where it plays a decisive role in increasing energy density and extending the cruising range of electric vehicles; REEs are extensively applied in permanent magnets, catalysts, electronic components, and related fields, which are crucial to the efficient utilization of energy as well as the advancement of information and communication systems [16].

China's White Paper on the Development of Strategic Metals and Critical Mines in China points out, the strategic metals not only include some critical metals listed in the U.S. report but also incorporate tungsten, molybdenum, indium, germanium (Ge), and others in light of China's resource endowments and industrial needs. Tungsten, characterized by high melting point and high strength, is indispensable in the manufacture of cemented carbides and special steels; molybdenum is used in the steel industry to improve the strength, toughness, and corrosion resistance of steel, and is also an important raw material in electronics, chemical industry, and other fields; indium and Ge play pivotal roles in emerging industries such as semiconductors and optoelectronics.

Common critical metals in coal and coal-bearing strata include Ge, gallium (Ga), Li, scandium, and REEs. The mineralization of Ge within coal deposits is closely associated with sedimentary environments, material sources, and later-stage geological processes, and it is widely used in infrared optics, semiconductors, and other fields; Ga is often associated with elements such as aluminum, existing in coal in the form of isomorphism or adsorption, and is a key material for the semiconductor and communication industries [17, 18]; Li in coal measures is mainly connected with clay minerals and other substances, and with the development of the new energy industry, the development potential of coal-measure Li resources has gradually attracted attention [19]; despite the low concentration of scandium in coal, it possesses significant application value in high-end fields such as aerospace and nuclear energy; REEs occur in coal in various forms, which play a vital role in advancing modern industry as well as national defense science and technology.

2.2 Characteristics of the presence of key metals in coal and coal-bearing strata

As carriers of critical metals, coal and coal-bearing strata possess numerous unique advantages. In terms of distribution scope, coal resources are widely distributed across the globe, with substantial occurrences in both terrestrial and marine sedimentary basins. According to statistics, the world's proven coal reserves are extremely considerable [20], which renders the potential distribution range of coal-measure critical metal resources equally extensive. In contrast, the distribution of many traditional critical metal deposits is relatively limited. For instance, Co deposits are predominantly concentrated in a small number of countries like the Democratic Republic of Congo, while Li deposits are mainly distributed in specific regions of countries like Chile and Australia [21].

The reserves of critical metals in coal measures are also quite substantial. In the Jungar Mining Area of China's Ordos Basin, coal resources not only boast enormous reserves but also are associated with abundant critical metals. The reserve of alumina reaches as high as 3.5 billion tons, nearly 12 times the recoverable reserve of bauxite in China [22]; the associated Ga reserve amounts to 860,000 tons, equivalent to 80% of the world's total reserve [22, 23]; and the corresponding Li reserve totals 2.6 million tons, making up 51% of China's total reserves [24].

Critical metals in coal measures exhibit diverse occurrence forms. In addition to existing in organic matter and minerals of coal in the forms of isomorphism and adsorption, they can also be enriched in roof and floor strata, partings, and other positions of coal seams. For example, in certain coal-bearing sequences, key metals including Li and rubidium (Rb) are usually associated with clay minerals and adsorbed onto their surfaces via ion exchange [25]; REEs may form complexes with organic matter in coal or exist in the roof and floor strata of coal seams as independent minerals. This diversity of occurrence forms introduces a certain

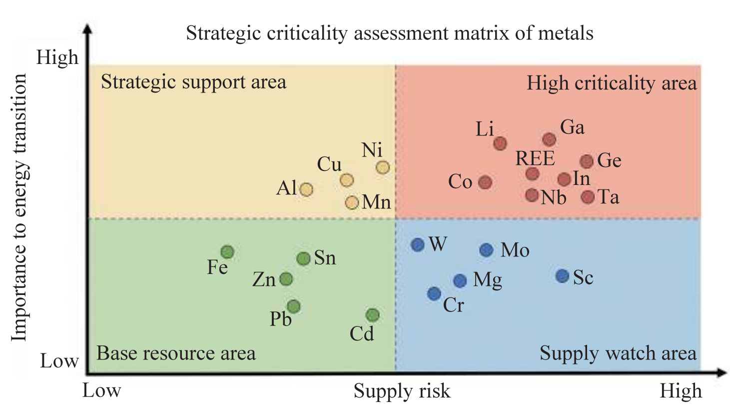

Figure 1 Strategic criticality assessment matrix of metals

degree of complexity to the extraction of coal-measure critical metals but also offers more possibilities for developing various extraction technologies. In traditional critical metal deposits, however, the occurrence forms of metals are relatively single, usually existing as independent minerals.

3 Enrichment mechanisms

3.1 Impacts of geological processes on the enrichment of critical metals

In the metallogenic process, the enrichment of critical metals in coal measures is closely linked to the coal-forming process. Coal formation undergoes stages such as peatification and coalification. During this long geological history, various geological processes including sedimentation, diagenesis, and metamorphism exert significant impacts on the migration and enrichment of critical metals [26]. Factors such as material supply, water chemistry, and biological activities in the sedimentary environment determine the initial content of critical metals; processes such as compaction, cementation, and metasomatism during diagenesis further alter the occurrence modes and distribution characteristics of key metals; subsequent tectonic movements and hydrothermal activities may result in the redistribution and re-concentration of critical metals. In contrast, the metallogenic processes of traditional critical metal deposits are mainly controlled by factors such as magmatic activity and hydrothermalism, which are significantly different from the metallogenic mechanisms of coal-measure critical metals.

Sedimentation is a crucial geological process for the initial enrichment of critical metals in coal and coal-bearing strata. Different sedimentary systems, such as fluvial, lacustrine, and marine systems, exhibit distinct sorting and enrichment effects on critical metals. In fluvial facies deposits, the transportation and sorting of water flow lead to the separation of heavy and light minerals, potentially causing the enrichment of some high-density critical metal minerals in specific locations. In lacustrine facies deposits, the relatively stable water body allows fine-grained sediments (e.g., clay minerals) to adsorb a large number of critical metal ions, providing a material foundation for the subsequent concentration of key metals within coal. In marine coal-bearing deposits, the interaction between metal ions in seawater and terrigenous clastic materials also influences the initial content and distribution of critical metals [27, 28].

Magmatic activity exerts a significant impact on the accumulation of key metals in coal and coal-bearing sequences. When magma intrudes into coal-bearing strata, it brings abundant thermal energy and volatile components, triggering hydrothermal activity. Elements such as potassium (K), sodium, and calcium in magma chemically react with organic components and mineral phases within coal, altering the structure and composition of coal and creating conditions for the enrichment of critical metals. For example, when acidic magma intrudes into coal-bearing strata, volatile components (e.g., fluorine and chlorine) in the magma combine with metal elements in coal to form water-soluble complexes.

Hydrothermal activity acts as a crucial controlling factor for the further concentration of key metals in coal and coal-bearing strata. Hydrothermal fluids possess multiple origins, including magmatic hydrothermal fluids, metamorphic hydrothermal fluids, and groundwater hydrothermal fluids. Metal ions in hydrothermal fluids engage in ion exchange and adsorption with organic matter and minerals in coal, resulting in the progressive enrichment of critical metals. Components including sulfur and oxygen in hydrothermal fluids combine with metal ions to form various minerals (e.g., metal sulfides and oxides), which precipitate in coal and coal-bearing strata, raising the abundance of critical metals. In some coalfields, minerals formed by hydrothermal activity (e.g., pyrite and sphalerite) are often associated with critical metals such as Ga and Ge [31].

3.2 Material sources and migration pathways

The material sources of critical metals mainly include terrigenous clastics, volcanic substances, and deep-seated strata. Terrigenous clastics represent one of the important material sources of critical metals in coal and coal-bearing strata. Weathering breaks down terrestrial rocks, releasing critical metal elements that are transported into coal-bearing basins by rivers, wind, and other agents to participate in the coal-forming process. In the coal-bearing strata of North China, terrigenous clastics are primarily derived from the weathering products of surrounding ancient strata [29]; minerals such as feldspar and mica in these clastics contain critical metal elements (e.g., Li, rubidium, and cesium (Cs)), providing a material foundation for the enrichment of these metals in coal.

Volcanic substances are also important sources of critical metals. Volcanic eruptions transport deep-seated terrestrial materials to the surface, and these materials are rich in various metal elements. Volcanic ash and volcanic clastics are deposited in coal-bearing basins, with their critical metal elements entering coal and coal-bearing strata. The formation of Late Permian coal-bearing strata in Southwest China is closely related to volcanic events within the Emeishan Large Igneous Province [34]. High-titanium basalts and alkaline volcanic clastics brought by volcanic eruptions provide abundant material sources for the concentration of key metals (e.g., Li, niobium (Nb), and tantalum (Ta)) within coal [32].

Metal elements in deep-seated strata can also migrate to coal and coal-bearing strata through processes such as hydrothermal activity. As deep-seated hydrothermal fluids rise, they dissolve critical metals from deep-seated strata; when these fluids reach coal-bearing strata, changes in physicochemical conditions cause critical metals to precipitate and enrich. Magmatic activity in deep-seated strata may also induce the migration of critical metals: Hydrothermal fluids rich in critical metals, generated by magmatic differentiation, interact with coal-bearing strata, leading to the concentration of key metals in coal.

During geological history, the migration pathways of critical metals are complex and diverse. In the sedimentary stage, critical metals are mainly transported within coal-bearing basins by water flow, wind, and other carriers. In the diagenetic stage, as sediments are compacted and dehydrated, pore water carries critical metal ions to migrate and precipitate in favorable locations. During metamorphism, the extreme thermobaric environment forces the mineral components within the carbonaceous strata to recrystallize and chemically transform, which consequently drives the mobilization and spatial reorganization of these strategic elements. Hydrothermal activity is a crucial driving force for the migration of critical metals during geological history: Hydrothermal fluids flow through rock pores and fractures, transporting metal ions from one location to another and achieving the enrichment of critical metals.

3.3 Typical case studies

A prominent case is the Xintian Coal Mine, situated in the western segment of the Pingle Depression (Jiangxi Province, China), which exhibits a remarkable concentration of the critical metal Cs. Mineralogical assessments reveal that organic components and kaolinite dominate the composition of the coal, with lesser

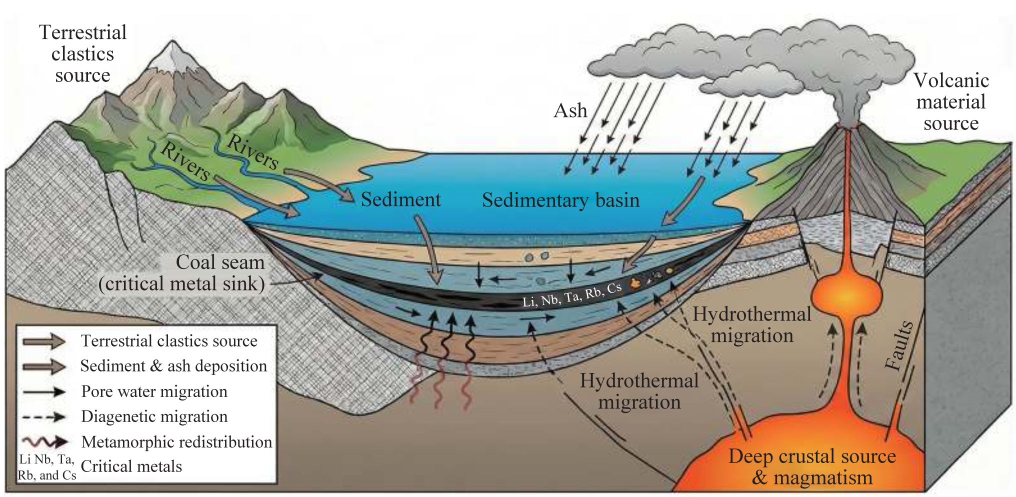

Figure 2 Material sources and migration pathways of critical metals in coal measures

amounts of quartz, illite, and feldspar. The occurrence states of Cs here manifest in three primary ways: displacing Rb and K within the feldspar lattice, substituting for K inside illite, or co-adsorbing with Li onto the surfaces of clay minerals. By evaluating geochemical indicators—such as Al_2O_3/TiO_2 ratios and REE characteristics—alongside the regional tectono-magmatic activity history of the Xintian Mining Area, researchers conclude that the initial Cs supply originated from terrigenous clastics. This material was produced by the weathering of Paleozoic granite situated along the southern margin of the Pingxiang Coal-Bearing Basin. Subsequently, aqueous fluids loaded with Cs, driven by magmatic hydrothermal fluids during the Yanshanian Period, permeated the formations and significantly amplified the ultimate enrichment of Cs in coal [33]. Another compelling example is found within the Tailai Coal Mine in the northwestern Guizhou Coalfield, specifically the No. 9 Coal Seam of the Upper Permian Longtan Formation, which demonstrates a profound accumulation of critical metals including Li, Nb, and Ta. Detailed evaluations of both major and trace elements, combined with mineralogical assessments across the coal seam and its adjacent roof and floor strata, indicate a mineral composition dominated by kaolinite, alongside quartz and illite. Investigations into sediment provenance and mineral occurrence characteristics suggest that materials derived from the Emeishan intermediate volcanic rocks and high-titanium basalts significantly fed the material supply of this coal-bearing basin. Furthermore, post-depositional hydrothermal activity was instrumental in driving the pronounced concentration of these strategic resources. Consequently, the contents of Li, Nb, and Ta in this specific deposit exceed the global averages for world coal by factors of 7.9, 7.8, and 8.7, respectively [27, 35].

A further instance can be observed in the Bao'an Coal Mine, located within the Ningwen Coalfield, Shandong Province. The coal measures in this region present elevated concentrations of major elements like SiO_2 and Al_2O_3, accompanied by a moderate accumulation of trace elements such as Li and Co. Specifically, the No. 3 (Upper) Coal Seam yields a mean Li concentration of 41.8 μg/g (peaking at 72.3 μg/g), substantially surpassing global baseline values. Additionally, the No. 3 (Lower) Coal Seam demonstrates an average Co level of 11.8 μg/g, which similarly eclipses world coal averages. Evaluations of geochemical indicators like Al_2O_3/TiO_2 ratios and REE distribution patterns deduce that the terrigenous materials primarily originated from felsic and intermediate igneous rocks. Furthermore, the depositional setting was largely controlled by a fluvial-deltaic system, experiencing minimal transgressive influence. Together, these distinct geological factors steered the enrichment process of critical metals within these specific coal measures [37].

In summary, the enrichment of critical metals across these diverse geological settings reveals a universally applicable mineralization pattern: the coupling of specific terrigenous material supply and subsequent hydrothermal modification. In all the aforementioned cases, the initial critical metal budget is fundamentally provided by the weathering and degradation of surrounding magmatic or volcanic parent rocks (e.g., granites and high-titanium basalts). Following their transportation and deposition within the coal-bearing basin—often scavenged by or incorporated into clay minerals like kaolinite—these pre-enriched horizons are frequently subjected to post-depositional hydrothermal fluid circulation. This fluid activity acts as a crucial secondary mechanism to remobilize and further concentrate the strategic elements. Therefore, a comprehensive "source-deposition-hydrothermal upgrading" enrichment sequence can be identified as a generalized framework. This sequence not only elucidates the complex genesis of coal-measure critical metals but also provides a theoretical basis for the subsequent selection of targeted extraction technologies. The specific occurrence modes and key applications of typical critical metals are summarized in Table 1.

4 Extraction methods

4.1 Classification and principles of existing extraction technologies

Physical beneficiation achieves separation primarily based on differences in physical properties between critical metals, coal, and other impurities. Gravity

Table 1 Occurrence and applications of typical critical metals in Chinese coal and coal-bearing strata

Element	Dominant occurrence modes	Specific carrier/ mineral phases	Representative basin/mine	Enrichment characteristics	Key applications
Li	Mineral-associated (isomorphic substitution) & ion-exchangeable	Clay minerals (kaolinite, illite, chlorite), mica phases	NW Guizhou (Longtan Formation), Ordos	Longtan 9# coal: ~ 7.9× world average	Li-ion batteries, energy storage
Ga	Mixed: mineral-associated & organic-bound	Aluminosilicates (boehmite, kaolinite), organic macromolecules	Ordos (Jungar, etc.)	Significant associated reserves with bauxite	Compound semiconductors (5G)
Ge	Dominantly organic-bound; minor sulfide-associated	Organic functional groups (O/N/S-containing), pyrite, sphalerite	North China Coalfields	Significant local enrichment in specific seams	Infrared optics, semiconductors
REY	Highly diverse: mineral-associated, ion-adsorbed, & organic-bound	Phosphates (monazite), carbonates, clay surfaces, organic chelates	Multiple coal basins	Variable; heavy REEs enriched in specific ashes	Permanent magnets, catalysis
Nb/Ta	Mineral-associated (often discrete nano-minerals)	Volcanic-derived heavy minerals (rutile, anatase, zircon)	NW Guizhou (Longtan Formation)	~ 7.8 × /~ 8.7 × world average	Superconductors, special alloys
Cs	Mineral-associated (lattice substitution) & adsorbed	Feldspar (replacing K/Rb), illite, kaolinite surfaces	Xintian (Jiangxi)	Magmatic-hydrothermal enrichment	Catalysis, optoelectronics

separation utilizes density disparities among minerals to separate heavy and light minerals in gravitational or centrifugal fields. For high-density critical metal minerals in coal, methods such as dense-medium separation and jigging can be employed to separate them from coal. Magnetic separation is based on the differences in mineral magnetic characteristics: Within a magnetic field, magnetic minerals are subjected to attraction whereas non-magnetic minerals stay unchanged, thus realizing the enrichment of critical metals. In partial coal-bearing strata, magnetic separation can be adopted to extract critical metals provided that these metal minerals possess magnetic features [38].

Chemical leaching involves using chemical reagents to react with critical metals in coal, converting them into soluble compounds, which are then recovered from the leachate. Acid leaching typically employs strong acids including sulfuric acid and hydrochloric acid as leaching lixiviants; by dissolving minerals in coal, critical metals are transferred into the solution [39]. For Ge-bearing coal, sulfuric acid leaching can convert Ge into ionic form in the solution [41]. Alkali leaching is suitable for critical metals with high solubility under alkaline conditions—for example, aluminum oxide can dissolve in alkaline solutions to form aluminate [42]. Chlorination leaching utilizes chlorine or other chlorinating agents to react with critical metals, forming water-soluble chlorides for subsequent extraction [43, 44].

Fundamentally, the efficiency and industrial scalability of these chemical extractions are intrinsically governed by their underlying thermodynamic and kinetic mechanisms. For critical elements like Li and REEs that are tightly encased within the aluminosilicate matrices of coal measures, the leaching kinetics are classically interpreted through the shrinking core model (SCM). Kinetically, the overall dissolution rate is predominantly controlled by either surface chemical reactions or intra-particle diffusion through the porous ash layer.

Temperature acts as the most critical thermodynamic and kinetic catalyst. Thermodynamically, the disruption of robust Al–O and Si–O bonds to liberate encapsulated metals is typically an endothermic process; thus, elevated temperatures shift the equilibrium to favor maximum metal dissolution. Kinetically, higher temperatures exponentially enhance the reaction rate constant in accordance with the Arrhenius equation, effectively overcoming the high activation energy barrier (often > 40 kJ/mol for chemical reaction-controlled regimes). Concurrently, increasing the acid concentration elevates the proton (H^+) activity, establishing a steeper concentration gradient that accelerates the inward diffusion of the lixiviant toward the unreacted core. Furthermore, optimizing the solid-to-liquid (S/L) ratio is highly essential for mass transfer. A lower S/L ratio minimizes slurry viscosity and reduces the thickness of the hydrodynamic boundary layer surrounding the particles, thereby preventing localized saturation and facilitating the rapid outward diffusion of dissolved metal complexes (e.g., Li^+ or REE^{3+}) into the bulk solution.

Bioleaching achieves extraction by leveraging the effects of microorganisms or their metabolic products on critical metals in coal. Microorganisms transform critical metals in coal into soluble forms through oxidation, reduction, adsorption, and other processes. Certain bacteria can oxidize sulfides in coal to produce sulfuric acid, lowering the solution pH and thereby promoting the dissolution of critical metals [48]. Additionally, microorganisms can secrete specific organic substances that form complexes with critical metals, increasing their solubility in the solution [49].

4.2 Comparison of technical advantages and disadvantages

Physical beneficiation features relatively simple operation, low cost, minimal environmental impact, and relatively low equipment investment, making it suitable for large-scale production. However, this method can only separate critical metal minerals with significant differences in physical properties. For critical metals existing in coal in forms such as isomorphism and adsorption, it has low extraction efficiency, struggles to achieve deep enrichment, and has a limited scope of application.

Chemical leaching generally offers high extraction efficiency and can realize the extraction of multiple critical metals. Furthermore, the leaching efficiency and selectivity of critical metals can be elevated by optimizing leaching parameters, thereby endowing it with a broad application range. Nevertheless, the chemical leaching process requires the use of large quantities of chemical reagents, leading to high costs. It may also generate substantial wastewater, waste gas, and solid waste, causing significant environmental pollution. Additionally, the technology is complex, with high requirements for equipment and operation [50, 51].

Bioleaching boasts the advantages of environmental friendliness and low energy consumption. The metabolic processes of microorganisms are relatively mild, eliminating the need for harsh conditions such as high temperature and high pressure, thus reducing energy consumption and being eco-friendly. It is also capable of processing certain low-grade ores that are challenging to handle via conventional approaches. Nevertheless, it suffers from slow extraction rates and lengthy production cycles. The growth and metabolism of microorganisms are significantly influenced by environmental conditions including temperature, pH, and nutrient supply, leading to inferior stability and comparatively high extraction expenses. A comprehensive comparison of the technical advantages, limitations, and industrialization stages of these extraction methods is presented in Table 2.

4.3 Technical development trends and challenges

Future extraction technologies will move towards high efficiency and environmental friendliness, which drives the parallel optimization of existing methodologies. This will be achieved by developing new types of physical beneficiation equipment and processes to improve the separation efficiency and initial enrichment degree of critical metals; modifying microorganisms through technologies such as genetic engineering to improve the efficiency and speed of bioleaching; and optimizing chemical leaching processes to enhance selectivity while reducing environmental impact.

Driven by increasingly stringent environmental protection requirements, the optimization of chemical leaching is undergoing a paradigm shift towards non-traditional "green" solvents, most notably ionic liquids (ILs) and deep eutectic solvents (DESs) [44–47]. Over the past 1–2 years, these novel solvent systems have demonstrated disruptive potential in replacing conventional volatile and highly corrosive aqueous acids. ILs offer highly tunable physicochemical properties; by designing task-specific ILs with customized

Table 2 Comparison of extraction and separation technologies for coal-measure critical metals

Technical unit	Applicable occurrence	Advantage	Limitation	Cost evaluation	Industrialization stage	Typical destination
Pre-concentration (gravity/mag/float)	Discrete mineral particles	Low energy footprint, rapid volume reduction	Ineffective for adsorbed or isomorphic states	Low (driven by physical comminution)	Commercial (mature)	Reduced volume, upgraded grade
Acid leaching	Multiple modes (Ge, Ga, rare earth elements and yttrium (REY), etc.)	Fast kinetics, high extraction yield	Massive acid consumption & wastewater treatment	Moderate–high (high OPEX for reagents & waste disposal)	Pilot to commercial	PLS
Alkaline leaching	Al/Si-bearing mineral phases	Highly effective for aluminosilicate systems	Narrow applicability, high energy consumption	Moderate (energy and alkali intensive)	Pilot scale	Aluminate solution system
Chlorination leaching	Refractory phases (Li, REY, etc.)	Strong selective potential	Severe equipment corrosion & toxic gas control	High (high CAPEX for anti-corrosion equipment)	Lab to pilot scale	Chloride solution system
Bioleaching (new addition)	Sulfide-associated or organically bound	Eco-friendly, low reagent & energy consumption	Sluggish kinetics, vulnerable to heavy metal toxicity	Low–moderate (low OPEX, but long capital turnaround)	Lab to pilot scale (for coal measures)	Dilute solution system
Solvent extraction/ ion exchange	PLS	Precise element-level purification & separation	Complex solvent management, phase separation issues	Moderate–high (solvent loss & continuous replenishment)	Commercial (mature)	High-purity compounds/metals

functional groups, researchers can achieve precise coordination with target elements directly from complex coal-based leachates, significantly enhancing selectivity while suppressing the co-dissolution of undesired matrix elements [45–47]. Concurrently, DESs have gained tremendous momentum as a more cost-effective and biodegradable alternative [44]. Typically synthesized by mixing naturally derived hydrogen bond acceptors and donors, DESs exhibit remarkable capability to dismantle the robust aluminosilicate networks inherent in coal fly ash (CFA) and coal gangue under relatively mild thermal conditions. By facilitating proton transfer and forming stable metal-ligand complexes, DESs can efficiently liberate critical metals without generating massive volumes of hazardous acidic wastewater [44]. Furthermore, the inherent recyclability of both ILs and DESs establishes a closed-loop extraction framework, representing a critical trajectory for sustainable resource recovery.

Although individual techniques are continuously advancing, single-method approaches often face inherent limitations. Consequently, the combined application of multiple technologies has become an inevitable trend. By combining the advantages of physical beneficiation, chemical leaching (including novel green solvents), and bioleaching, combined extraction processes will be developed to improve the comprehensive recovery rate based on the characteristics of different coal types and the occurrence of critical metals [40]. A typical synergistic flowchart involves: First, critical metals will be preliminarily enriched via physical beneficiation to reduce the processed volume; then, they will be further extracted using chemical leaching for deep recovery; and finally, the remaining tailings will be subjected to secondary recovery through bioleaching.

Despite these promising trends, improving overall extraction efficiency and reducing costs remain the primary challenges faced. The occurrence states of critical metals in different coal types and coal-bearing strata are complex and diverse, making it difficult to develop highly efficient extraction technologies with broad applicability. Furthermore, the research and development of new equipment and customized processes require substantial capital and technical investment; how to reduce scale-up and operational costs while

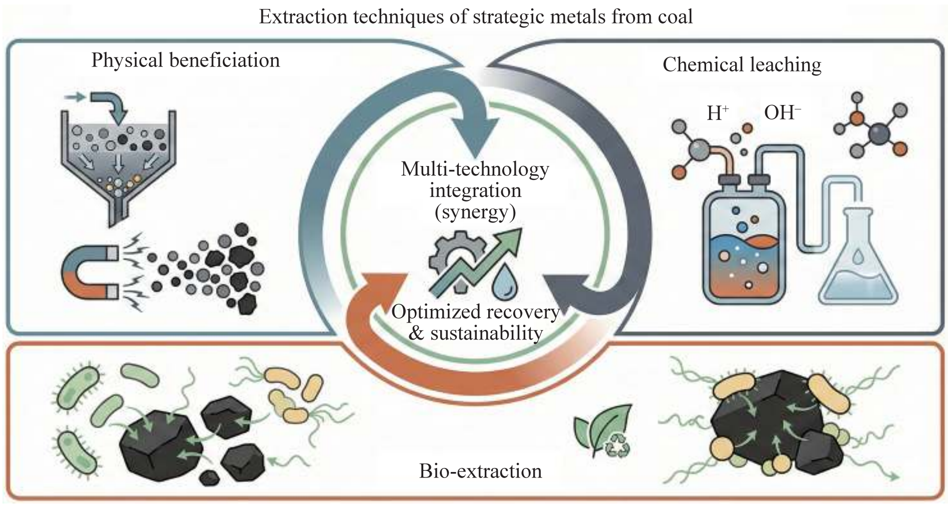

Figure 3 Multi-technology combined extraction process

ensuring extraction effectiveness is an urgent problem to be solved, which necessitates a comprehensive economic evaluation (as detailed in Section 4.4). In terms of reducing environmental impact, although green extraction technologies have made certain progress in laboratories, they still need further industrial-scale improvement. The treatment of wastewater, waste gas, and solid waste generated during large-scale traditional chemical leaching processes remains highly challenging. Additionally, the issues regarding the adaptability and long-term stability of engineered microorganisms to complex industrial environments during the bioleaching process also remain to be addressed.

To systematically overcome these environmental and economic hurdles, the conceptualization of "green integrated processes" must be substantiated by specific chemical engineering strategies, particularly concerning acid consumption and wastewater management. To minimize reagent consumption, industrial operations should transition from batch processes to multi-stage counter-current leaching (CCL) systems. CCL maximizes the thermodynamic concentration gradient between the lixiviant and the solid matrix, drastically reducing the demand for fresh acid while yielding a more concentrated pregnant leach solution (PLS). Furthermore, incorporating targeted pre-treatment steps—such as mild physical beneficiation or selective alkaline pre-desilication—can proactively remove acid-consuming gangue minerals (e.g., reactive carbonates) prior to the main extraction stage, thereby preventing wasteful acid neutralization.

Regarding wastewater management, adopting a minimum liquid discharge (MLD) or zero liquid discharge (ZLD) framework is critical for sustainable extraction. This can be engineeringly achieved by deploying cascading membrane separation technologies, such as acid-resistant nanofiltration (NF) and reverse osmosis (RO). These membrane networks not only concentrate dilute critical metal streams but also recover high-purity water and unreacted free acid for internal recycling. Additionally, the acidic aqueous raffinate generated after the solvent extraction (SX) stage must be systematically circulated back to the primary leaching circuits. By strictly enforcing these closed-loop chemical engineering practices, the overall environmental footprint and operational expenditure of coal-measure metal extraction can be substantially mitigated.

4.4 Economic feasibility and cost-benefit analysis

While the aforementioned extraction technologies are technically viable, their industrial implementation is fundamentally governed by economic feasibility. Compared to conventional hard-rock mining, extracting critical metals from coal-bearing strata and coal utilization by-products presents a highly disruptive cost-benefit paradigm.

For associated resources within coal measures (e.g., roof/floor strata and coal gangue), the immense capital expenditures (CAPEX) for geological exploration and deep excavation are inherently absorbed by the primary coal mining operations. Furthermore, when targeting coal combustion by-products (such as CFA)—an extraction pathway of significant current industrial focus—the feedstock entirely bypasses the energy-intensive comminution (crushing and grinding) stages. In conventional mining, comminution alone typically accounts for up to 50% of the total energy consumption. Conversely, coal by-products have already been pulverized and thermally activated during power generation, representing a massive reduction in initial operational expenses (OPEX).

From an environmental economics perspective, processing these coal-based materials transforms industrial liabilities into revenue streams. Mining enterprises and power plants generally incur significant tipping fees for the landfill disposal of coal gangue and CFA. Utilizing these materials for metal extraction directly eliminates these disposal expenses, effectively providing a "negative-cost" feedstock to the extraction facility.

However, the primary economic challenge lies in the hydrometallurgical processing costs. Because the absolute concentrations of target elements in coal measures (e.g., 300–600 ppm for total REEs) are typically lower than those in high-grade primary ores, extraction of a single metal is rarely profitable. Recent techno-economic assessments indicate that true commercial viability heavily relies on an integrated, "zero-waste" utilization model. The break-even point can only be achieved through the co-extraction of a full spectrum of high-value elements (e.g., synthesizing Li, Ga, and REEs simultaneously). More importantly, after leaching, the remaining bulk residues (accounting for over 90% of the mass) must be commercialized, typically serving as supplementary cementitious materials or precursors for geopolymers. By synergizing the revenues from multi-metal sales, the financial savings from avoided tipping fees, and the profits from bulk residual materials, the comprehensive extraction from coal and coal-bearing strata emerges as a highly competitive economic alternative to traditional mining.

5 Resource significance

5.1 Supporting role in energy transition

Against the backdrop of global energy transition, the new energy industry is booming, and critical metals play an indispensable role therein [52, 53, 59]. Within the solar energy sector, compounds like cadmium telluride (CdTe) and copper indium Ga selenide (CIGS) serve as key materials for high-efficiency solar cells [54]. Among these, critical metals including tellurium, indium, and Ga play a decisive role in improving the photoelectric conversion efficiency of solar cells. CdTe solar cells, which are characterized by low costs and high conversion efficiency, have been extensively applied in large-scale photovoltaic power generation; copper indium Ga selenide solar cells, boasting superior stability and a high theoretical conversion efficiency, have emerged as a research focus in the solar photovoltaic industry.

In wind power generation, rare earth permanent magnet materials are the core materials for manufacturing permanent magnet direct-drive systems of wind turbines. High-performance neodymium-iron-boron permanent magnets, by virtue of their characteristics such as high residual magnetism, high coercivity, and high magnetic energy product, enable wind turbines to convert wind energy into electrical energy more efficiently, thereby improving power generation efficiency and reducing energy consumption.

Energy storage technology serves as a key link in ensuring the stable supply of renewable energy, and Li-ion batteries are presently among the most extensively utilized energy storage battery types. Critical metals including Li, Co, and nickel constitute essential components of Li-ion batteries. As the core element of the battery, Li determines the energy density and charge-discharge performance of the battery; Co plays a role in stabilizing the structure and improving the cycle life of the battery in cathode materials; the addition of nickel helps to enhance the energy density and charge-discharge rate of the battery [55].

5.2 Economic value and strategic significance

Critical metals in coal and coal-bearing strata possess enormous economic value. Take Ga as an example: it is an important scattered metal with wide applications in semiconductors, communications, optics, and other fields. With the popularization of 5G communication technology and the rapid development of the semiconductor industry, the demand for Ga has increased sharply. According to statistics, the global annual consumption of Ga is constantly rising, and its market value has accordingly surged. In China, some coal-bearing strata have considerable Ga reserves; for instance, the associated Ga reserves in the Jungar Mining Area reach 860,000 tons.

From a strategic perspective, critical metals are an important component of national resource security strategies. Against the backdrop of the current complex and volatile international situation, the supply security of critical metals is directly related to national economic security and national defense security [56]. As a leading manufacturing nation, China's demand for critical metals keeps rising alongside the advancement of strategic emerging industries including new energy, electronic information, and aerospace. The exploitation and utilization of coal-measure critical metal resources can boost China's independent supply capacity for critical metals, cut down on reliance on overseas imports, ease supply risks arising from international market volatility, and protect national resource security [57].

Within the domain of national defense, critical metals hold even greater indispensability. REEs exert a pivotal function in military installations encompassing missile guidance systems, radar systems, as well as satellite communication facilities. REEs including samarium, europium, and terbium are used to manufacture high-performance permanent magnet materials, which can improve the performance and precision of weapons and equipment; The utilization of REEs like lanthanum and cerium in optical glass and laser materials contributes to boosting military reconnaissance and communication capabilities. The development of rare earth resources in coal measures holds important strategic significance for strengthening China's national defense capabilities.

5.3 Correlation with the global resource pattern

The exploitation and utilization of critical metals within coal and coal-bearing formations have a profound influence on the global resource landscape. In terms of resource distribution, critical metal resources are unevenly distributed worldwide: some countries and regions are endowed with abundant critical metal reserves, while others are heavily dependent on imports. The discovery and development of

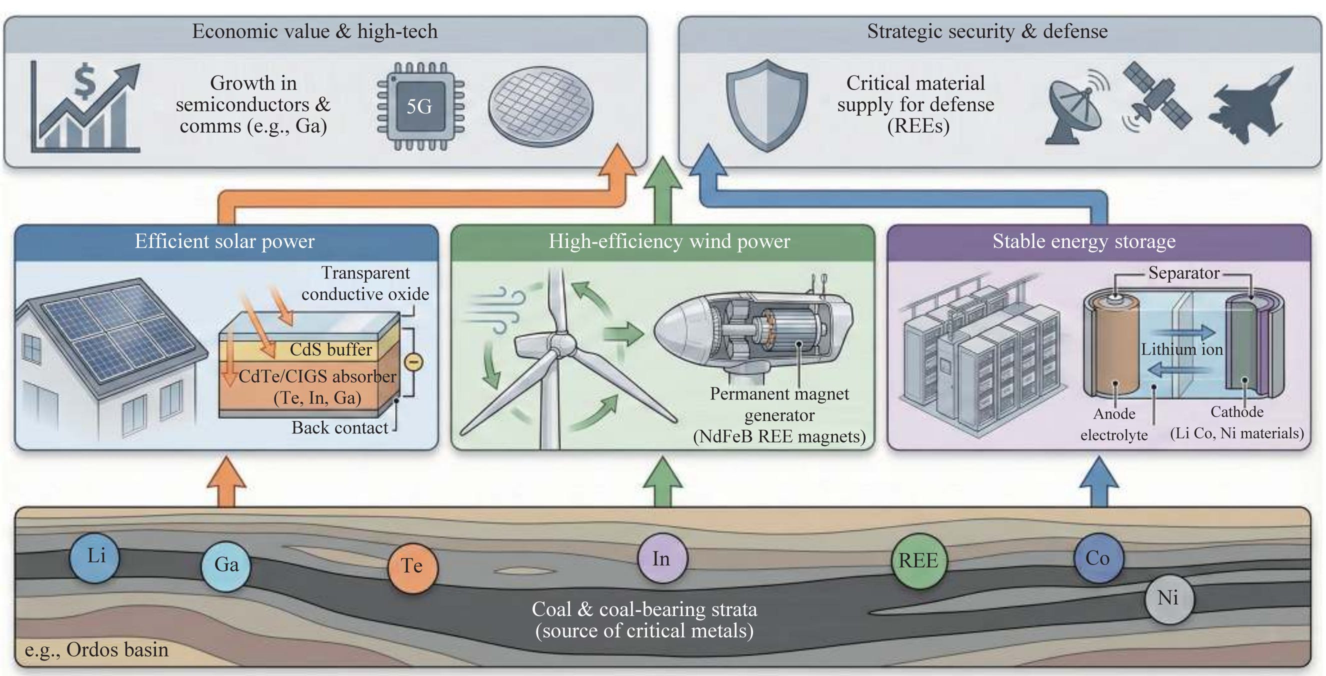

Figure 4 Economic value and strategic significance of critical metals in coal and coal-bearing strata

coal-measure critical metal resources have changed the distribution pattern of traditional critical metal resources, providing a new approach to resource acquisition for countries relatively lacking in resources.

In terms of international trade, the development of coal-measure critical metals will affect the trade flow and price system of global critical metals. With the increase in the output of coal-measure critical metals, the supply pattern of critical metals in the international market will change, which may lead to adjustments in the pattern of trade negotiations and changes in trade policies [58]. If China expands the exploitation and utilization of coal-measure Li resources, this will to some degree impact the trading price and market share of global Li resources.

For China, the development of coal-measure critical metal resources brings both opportunities and challenges. The opportunities lie in the fact that China is rich in coal-measure critical metal reserves; developing and utilizing these resources can enhance China's voice in the global critical metal market, promote the development of related industries, and drive economic transformation and upgrading. China can leverage its advantages in coal-measure critical metal resources to attract international investment and technological cooperation, and strengthen international cooperation and exchanges in the field of critical metals.

However, the challenges cannot be ignored. The development of coal-measure critical metals involves high technical difficulty and requires substantial capital and technological investment [60]; the development process may also face issues such as environmental protection and comprehensive resource utilization. The international market is highly competitive, and other countries are also actively developing critical metal resources. China needs to continuously improve its technical level and industrial competitiveness to meet the challenges of the international market.

6 Summary and outlook

6.1 Summary of research findings

The enrichment mechanisms of critical metals within coal and coal-bearing formations stem from the synergistic effects of various geological processes. Sedimentation lays the foundation for the initial distribution of critical metals, while magmatic activity and hydrothermal activity further promote the migration and enrichment of critical metals. Under different geological backgrounds, the material sources and migration pathways of critical metals vary. For instance, the Cs enrichment in Xintian Coal Mine of Jiangxi Province is associated with terrigenous clastic materials and superimposed alteration caused by magmatic hydrothermal fluids. Critical metal enrichment in Tailai Coal Mine of the northwestern Guizhou Coalfield is affected by the input of volcanic materials originating from the Emeishan Large Igneous Province, along with subsequent hydrothermal activity.

Existing extraction technologies include physical beneficiation, chemical leaching, and bioleaching, each with its own advantages and disadvantages. Physical beneficiation features simple operation and low cost but has limited extraction efficiency; chemical leaching offers high extraction efficiency but is associated with environmental pollution and high costs; bioleaching is environmentally friendly and low in energy consumption but suffers from slow extraction speed and poor stability.

Critical metals contained in coal and coal-bearing formations serve as a vital support for the energy transition and are extensively applied in renewable energy sectors including solar power, wind power, and energy storage systems [61]. They possess enormous economic value, far-reaching significance for national resource security strategies and national defense construction, and also exert an impact on the global resource pattern.

6.2 Prospects for future research directions

In the future, it is essential to further explore the enrichment mechanisms of critical metals within coal and coal-bearing formations. By comprehensively applying various advanced technical means, such as high-resolution microscopy and synchrotron radiation technology, in-depth studies should be conducted on the micro-occurrence states and migration and transformation laws of critical metals in coal [25]. Strengthen research on the metallogenic models of coal-measure critical metals under different geological conditions, establish a more complete metallogenic theoretical system, and provide more accurate guidance for resource exploration.

Developing efficient and green extraction technologies for critical metals is an important direction for the future. Explore new physical beneficiation methods and equipment to improve the separation efficiency of critical metals; develop green chemical leaching reagents and processes to reduce environmental pollution; utilize cutting-edge technologies such as synthetic biology to construct high-efficiency microbial strains and enhance the efficiency and stability of bioleaching [49].

Further intensify the evaluation of critical metal resources within coal and coal-bearing formations. Combine multidisciplinary methods such as geological exploration, geophysics, and geochemistry to accurately assess resource reserves and quality, providing a scientific basis for resource development [23]. Boost international collaboration to jointly conduct the R&D of critical metal resources.

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Author contributions

Peidong Su: Funding acquisition, Methodology, Supervision, Writing—review & editing. **Haocheng Ye**: Investigation, Visualization, Writing—original draft & editing. **Bin Li**: Investigation, Writing—original draft. **Zhiyu Zhang**: Writing—review & editing.

Conflict of interest

These authors declare no competing financial interests.

Ethical standards

This article is a review paper and does not contain any original studies with human participants or animals performed by any of the authors. All referenced data comply with general ethical standards.

Data availability

The relevant data is available from the authors upon reasonable request.

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