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EDITED BY

Umar Ashraf,
Yunnan University, China

REVIEWED BY

Santosh Kumar Rai,
Wadia Institute of Himalayan Geology, India
Hassan Nasir Mangi,
China University of Mining and Technology, China
Shifeng Dai,
China University of Mining and Technology,
Beijing, China

*CORRESPONDENCE

Jing Li
✉ jingli@cug.edu.cn

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Significant contribution of seawater infiltration and hydrothermal activity on lithium enrichment in the Ceshui Formation coal of the LianShao Coalfield, Hunan Province, South China

Jing Li^{1*}, Yuan Wang¹, Han Zhang^{1,2}, Amina Wumaier³,
Xinguo Zhuang¹, Xavier Querol⁴, Natalia Moreno⁴
and Baoqing Li¹

¹Key Laboratory of Tectonics and Petroleum Resources of Ministry of Education, China University of Geosciences, Wuhan, China, ²Changsha Nonferrous Metallurgical Design and Research Institute Co., Ltd., Changsha, Hunan, China, ³Urumqi Geological Brigade, Geological Bureau, Xinjiang Uyghur Autonomous Region, Urumqi, China, ⁴Institute of Environmental Assessment and Water Research, Instituto De Diagnostico Ambiental Y Estudios Del Agua, Consejo Superior de Investigaciones Cientificas (ID/EA-CSIC), Barcelona, Spain

The Ceshui Formation is one of the most important coal-bearing formation of the Lower Carboniferous in China, especially in South China. This study investigates the mineralogical and geochemical characteristics of the Lower Carboniferous Ceshui Formation coal from the studied area, Lianshao Coalfield, Hunan Province, with special emphasis on significant lithium enrichment in the studied area. The Ceshui Formation bituminous from the Toudi open-pit mine is characterized by medium-low ash yield, low volatile matter yield and low sulfur content. Minerals occurring in the coal are mainly composed of kaolinite, tobelite and calcite, followed by quartz, anatase, ankerite, microcline, siderite and illite, with a trace amount of pyrite. Compared with the average values in worldwide coals, Li is significantly enriched in the Ceshui Formation coals in the studied area, occurring mainly in kaolinite and secondarily in chlorite. The closer to the roof and floor, the higher the concentration of Li. The concentration of Li₂O in coal ashes exceeds the Extraction Standard for Li₂O in coal-bearing strata, presenting a promising metallogenic potential. The enrichment of Li in the Toudi coals is primarily derived from the supply of terrigenous sediment provenance and strongly influenced by its interaction with infiltrated seawater and hydrothermal fluids. The sediment provenance of the terrigenous clastic was derived from the Li-rich granite in the Xuefeng Oldland to the northeast of Lianshao coalfield. The Ceshui Formation coal in the studied area was formed in a

marine-influenced transitional sedimentary environment, and Li from Li-rich granitic debris was more readily enriched in coal seams during slow sea regressive process. The infiltration of hydrothermal fluids and interaction with Li-bearing terrestrial material further promoted Li enrichment in the Toushi coals.

KEYWORDS

lithium enrichment in coal, infiltration of seawater, hydrothermal fluids, Ceshui Formation coals, Toushi open-pit coal mine

1 Introduction

Lithium is an important critical metal resource that has been intensively utilized in battery storage, new energy technologies, and other strategic emerging industries. Lithium deposits primarily occur in pegmatites, brines, and sedimentary rocks (e.g., clays, bauxites) (Benson et al., 2017; Kesler et al., 2012; Liu et al., 2017; Wang et al., 2020; Yu et al., 2019). Under certain geological conditions, the concentrations of several critical metal elements, including Li, Ge, Ga, U, Nb, Ta, Zr, Hf, Rb, Cs and rare earth elements and Y (REY), in some coals or coal combustion byproducts are comparable to, or even much higher than their cut-off grades in conventional ore deposits, forming new-type coal-host critical metal deposits (Dai and Finkelman, 2018; Dai et al., 2024; Seredin and Dai, 2012; Seredin et al., 2013; Zhao et al., 2022).

Lithium has been found enriched (5 times higher than the world average content) in coals from several coal coalfields worldwide, some of which are even considered as coal-host Li deposits (e.g., Seredin and Tomson, 2008; Dai et al., 2012a; Li et al., 2016; Sun et al., 2013, 2022b; Zhao et al., 2019a, b; Zhou et al., 2021; Shao et al., 2022; Di et al., 2023; Sun et al., 2023; Hou et al., 2023; Jiu et al., 2023; Liu et al., 2024). Globally, highly-elevated Li concentration (up to 3000 $\mu\text{g/g}$) in coal deposits was first reported in the Krylovsk and Verkhne-Bikinsk coal basins in Russian Far East in the 1980s (Seredin and Tomson, 2008), and also found in the Appalachian bituminous and Pennsylvania anthracites from the United States (Lin et al., 2018; Hower et al., 2021). In China, Li enrichment has been continuously found in coals from the Haerwusu and Guanbanwusu Surface Coal Mine, Jungar Coalfield, Inner Mongolia (Dai et al., 2008, 2012a), the Antaibo open pit coal mine, Pingshuo mining area in Shanxi Province (Sun et al., 2013), the Jincheng Coalfield, Qinshui Basin (Zhao et al., 2019a), and the Caotang mine, Chongqing Coalfield (Zhou et al., 2021). The content of Li_2O in the coal ashes from these coal mines is higher than that of the marginal grade for conventional deposits (0.2%; DZ/T 0203-2002, 2002), presenting a high economic potential for Li recovery.

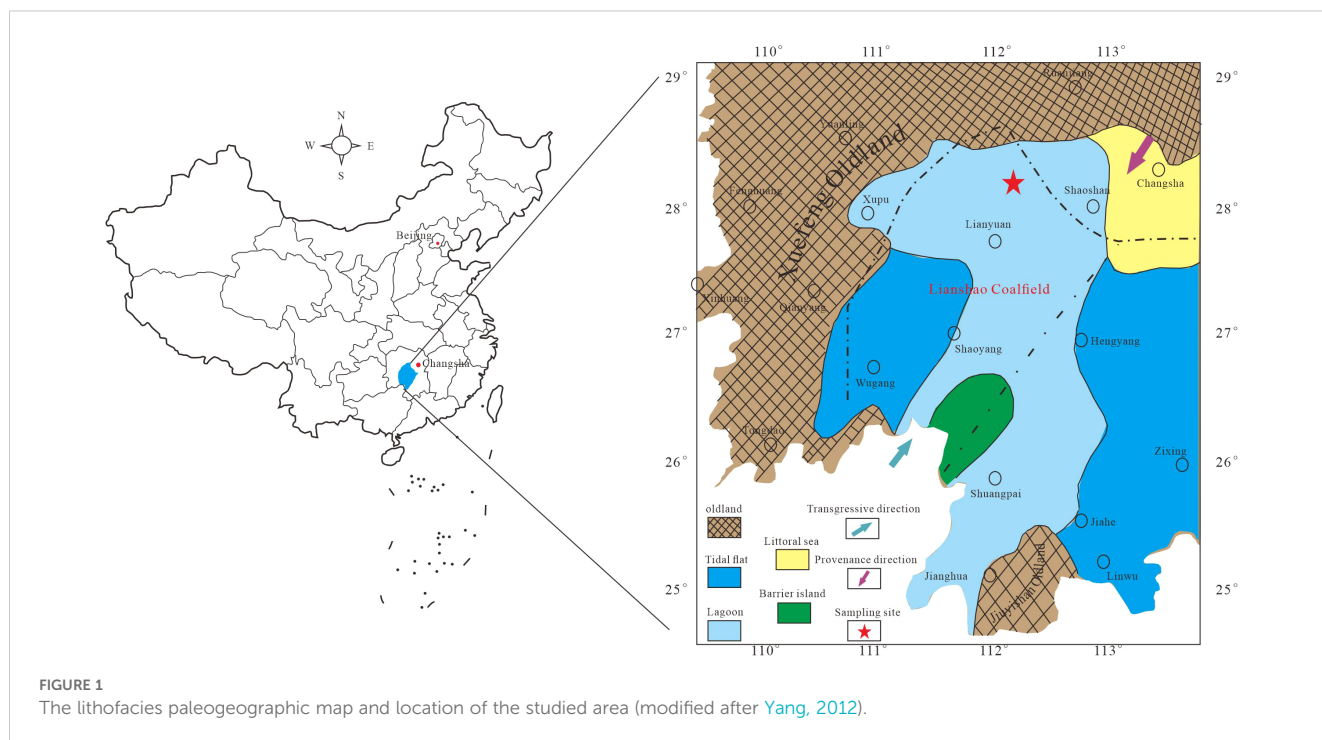
Nonetheless, due to the low atomic number of Li, it is extremely difficult to fully illustrate its modes of occurrence and enrichment mechanism in coal. Previous studies have shown that Li in coal generally occurs in clay minerals such as kaolinite, illite, chlorite,

and/or cookeite (Dai et al., 2012a, 2021; Finkelman et al., 2018; Sun et al., 2022a; Yuan et al., 2024; Zhang et al., 2024; Zhao et al., 2018, 2022; Zhou et al., 2021; Zou et al., 2020). Lithium enrichment in coals is generally thought to have been derived from detrital materials migrated from the sediment-source region into the peat bog during the syngenetic process, and further enriched in coals during the epigenetic stages (Dai et al., 2022, 2024; Sun et al., 2022b; Zhao et al., 2022). In addition, highly elevated Li concentration in some coals is attributed to the activities of hydrothermal solutions (e.g., Dai et al., 2012a; Zhao et al., 2019a, 2022; Zhou et al., 2021). Several researches have emphasized that the migration and leaching of felsic-intermediate rocks from sediment provenance and the tonsteins (volcanic ash) by (acidic) groundwater or hydrothermal solutions are responsible for the enrichment of Li in coals (Dai et al., 2014a; Hower et al., 2016; Karayigit et al., 2021; Zhang et al., 2023a, b; Zhao et al., 2022).

The LianShao Coalfield is one of the most important coalfields in Hunan Province, South China, and the Ceshui Formation is the primary coal-bearing strata in the Lianshao Coalfield. He (2008) reported that Li concentration is relatively high (up to 269 $\mu\text{g/g}$) in the Ceshui Formation coal of the Lianshao Coalfield, but the modes of occurrence and enrichment origin of Li was not investigated. Based on systematical mineralogical and geochemical analyses of the Ceshui Formation coals from the Toushi open-pit coal mine, Lianshao Coalfield, this paper aims to find out the modes of occurrence Li in coal and to elaborate the enrichment origins of Li in the studied coals, which is of great economic and environmental significance for the efficient and clean use of the Ceshui Formation coals, especially in the current situation of insufficient coal reserves in the region.

2 Geological setting

The Lianshao Coalfield is located in the central and western part of the Changsha-Shaoyang fault depression in the South China fold belt, and the Toushi open-pit coal mine is situated in the Lianyuan coal-bearing sag in the north of the LianShao Coalfield (Figure 1). The LianShao Coalfield is trending along the NE-NNE direction, and is composed of a series of relatively continuous tight anticline



and short axial syncline from north to south, accompanied by overthrust faults (Yang, 2012).

The coal-bearing strata in the coalfield include the Lower Carboniferous Ceshui Formation (C_{1c}) and the Upper Permian Longtan Formation (P_{3l}). The Ceshui Formation is the main coal-bearing strata in the study area, which conformably underlies the Lower Carboniferous Zimenqiao Formation (C_{1z}), and overlies the Lower Carboniferous Shidengzi Formation (C_{1s}). The Ceshui Formation was predominantly composed of detrital sediments of the bay lagoon facies (Figure 1, Yang, 2012), and is divided into the Lower (C_{1c}^1) and Upper (C_{1c}^2) Members (Figure 2a). The lowermost Upper Member is primarily composed of siliceous consolidated quartz conglomerate and quartz sandstone, and the rest of the Upper Member consists mainly of clayey mudstone, limestone, siltstone, sandy mudstone interbedded with quartz sandstone and coal streak, with an average thickness of 65 m. The Lower Member is the main coal-bearing member and averages 50 m in total thickness, which is mainly made up of siltstone, sandy mudstone, mudstone, quartz sandstone, and 1 to 7 coal seams, with siderite bed occurring in the lowermost. The Nos. 3 and 5 coals are main minable coal seams in the coalfield, with an average thickness of 15 m and 4.5 m, respectively in the Toushi open-pit mine.

The Longtan Formation is also divided into the Lower (P_{3l}^1) and Upper (P_{3l}^2) Members. The Upper Member (P_{3l}^2) is the coal-bearing member, which is primarily composed of quartz sandstone, sandy mudstone, silty mudstone, carbonaceous mudstone and coal seams, with a total thickness of 34–160 m. The Lower member (P_{3l}^1) is mainly distributed in the south of the coalfield, and is composed of feldspathic quartz sandstone interbedded with carbonaceous streak, sandy mudstone with siderite bed, fine sandstone and mudstone, with a total thickness of 40–448 m.

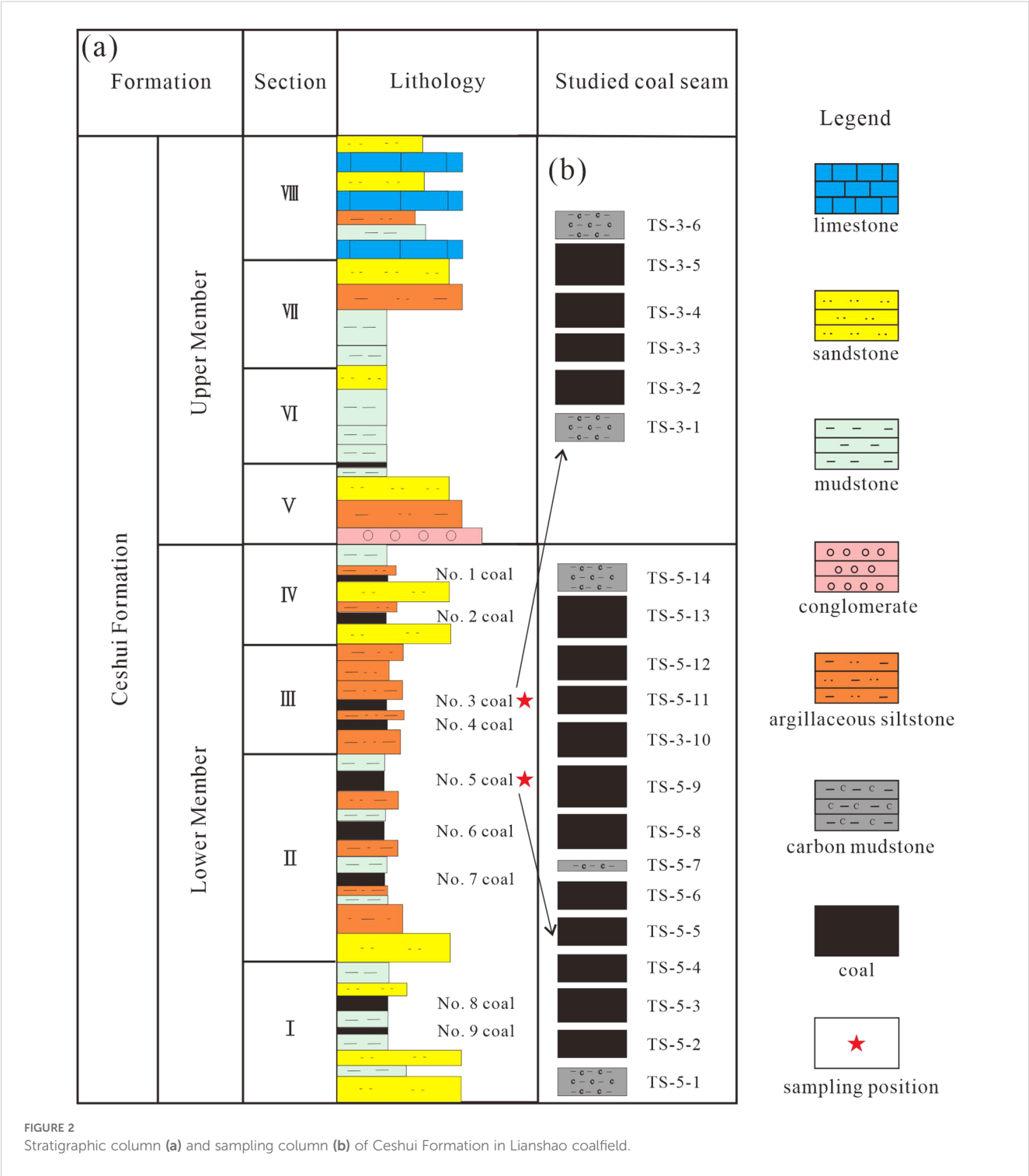
3 Sampling and analytical methods

A total of twenty bulk coal and associated non-coal rock samples, were collected using channel profile sampling method along the working surfaces of the Nos. 3 (one roof, one floor, and four coal samples) and 5 (one roof, one parting, nine coal, and three floor samples) coal seams in the Toushi open-pit mine, LianShao Coalfield. The samples were respectively numbered as TS-3-1 to TS-3-6, and TS-5-1 to TS-5-14 from bottom to top along the working surfaces of Nos. 3 and 5 coal seams (Figure 2b).

The samples were ground using a tungsten carbide mill to pass through 80-mesh sieves for proximate analysis and pass through 200-mesh for mineralogical and geochemical analysis.

Proximate analysis, including the determination of moisture, ash and volatile matter of the collected samples, was conducted using a LECO TGA-601 analyzer following the International Standards Organization (ISO) (2013); International Standards Organization (ISO) (2010a) and International Standards Organization (ISO) (2010b) standards (International Standards Organization (ISO), 2010a, b, 2013). Total sulfur contents were determined using a 5E-8S/AII analyzer based on the ASTM Standard D3177-02 (2007).

Mineral components were determined by X-ray powder diffraction (XRD) technique using a Bruker D8 A25 Advance diffractometer with monochromatic Cu $K\alpha_1$ radiation. Each XRD pattern was recorded over a 2θ interval from 4 to 60°, with a step size of 0.019°, and a counting time of 0.1 s/step, and then the XRD pattern was interpreted by Jade 6.5 software. Thereafter, following the instructions elaborated by Ward et al. (2001) and Dai et al. (2015), the semi-quantitative content of minerals was obtained by Siroquant™, a commercial software package developed by Taylor (1991) based on the principles of diffractogram analysis proposed



by Rietveld (1969). The morphology of minerals and the distribution of some elements were observed by a QUANTA 840 scanning electron microscope in conjunction with an energy dispersive X-ray spectrometer (SEM-EDX).

To further investigate the modes of occurrence of Li, a high-Li sample (TS-5-5) was selected for HR-TEM (Talos™ F200X) observation, which was crushed to <1 μm using an agate mortar and pestle and dispersed in alcohol. Then, an ultrasonic sound

suspension instrument was used to separate samples in alcohol and pipette them onto a lacy carbon film supported by a Cu grid. The HR-TEM point and lattice resolutions were <0.25 nm and 0.12 nm, respectively. The main elemental compositions of nano-minerals with unknown phases were determined by EDS (Super-X G2), which allows for semi quantitative analysis of all elements greater than atomic number 4. The calibration of possible Li-bearing nano-mineral under HR-TEM was conducted following the method

elaborated by Yuan et al. (2024). The diffraction pattern indices, including the interplanar spacing (D_m) and angle of the crystal plane (θ_m) in the selected sample (TS-5-5) were measured using the fast Fourier transformation (FFT) patterns (interplanar spacings, angles, and diffraction patterns). The measured diffraction pattern indices of a selected mineral were then compared to its standard data from the Inorganic Compound Powder Diffraction File (PDF) database of the International Center for Diffraction Data (ICDD) (2024), to identify the mineral. The PDF data of standard minerals was modeled by simulation single-crystal diffraction (SSCD) pattern, and the measured and standard data were compared under a specific zone axis (U V W) (Chen et al., 2022). The detailed calibration and calculation methods, as well as error restrictions are as follows: (1) the standard data on interplanar spacing (D_s) are selected and compared with the measured interplanar spacing (D_m), and all $|D_s - D_m|$ values must be less than 0.01 nm. (2) the crystal face indices and zone axis (U V W) must conform with the equation $(h_1, k_1, l_1) + (h_2, k_2, l_2) = (h_3, k_3, l_3)$ ($h_1k_1l_1$, $h_2k_2l_2$, and $h_3k_3l_3$ are the crystal faces of d_{s1} , d_{s2} , and d_{s3} respectively), and $h_3U + k_3V + l_3W = 0$. (3) The monoclinic system standard angle of the crystal plane (θ_s) was calculated using the following formula: $\cos\theta_s = \frac{d_1d_2}{\sin^2\beta} \left[\frac{h_1h_2}{a^2} + \frac{k_1k_2\sin^2\beta}{b^2} + \frac{l_1l_2}{c^2} - \frac{(l_1h_2 + h_1l_2)\cos\beta}{ac} \right]$, where a , b , c are three groups of edge lengths and α , β , γ are the intersecting angles, and the $|\theta_s - \theta_m|$ values must be less than 3° .

The contents of major element oxides were determined using an X-ray fluorescence spectrometer (XRF). As for the trace element concentrations, prior to determination, about 100 mg of each sample were first subjected to a two-step acid-digestion method, which involves at first the extraction with HNO_3 , followed by a dissolution of the residue with mixtures of HF : HNO_3 : HClO_4 (Querol et al., 1997). The resulting solutions were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, X-Series II Thermo) for most trace elements. Digestion of international reference materials (South African coal reference material, SARM-19) and blanks was also carried out following the same procedure to check the accuracy of the digestion and analytical methods. The analytical precision was better than $\pm 2.5\%$ for Cr, Ba, Pr, Gd and Th; better than $\pm 5.0\%$ for Be, V, As, Y, Nd, Dy, Er and Pb; and better than $\pm 10.0\%$ for the remaining trace elements.

4 Results

4.1 Basic coal characterization

The results of proximate analysis, total sulfur content and random vitrinite reflectance of the Nos. 3 and 5 coals are given in the Appendix Table A1. The Nos. 3 and 5 coals are characterized by extremely-low-moisture contents, medium to high ash yields, and low-sulfur contents according to the Chinese Standard MT/T 850-2000 (2000), Chinese Standard GB/T 15224.1 (2010) and the classification by Chou (2012). The volatile matter yields and random vitrinite reflectance of the Nos. 3 and 5 coals indicate a coal rank of low volatile bituminous coal (ASTM D388-12, 2012).

4.2 Mineralogical characteristics

As shown in Appendix Table A2, minerals in the No. 3 coal from the Toudi mine is dominated by kaolinite (avg. 72.4% on organic-free basis) and tobelite (avg. 22.6%), with minor amounts of quartz (avg. 3.0%), calcite (avg. 2.3%), ankerite (avg. 1.0%), and anatase (avg. 0.5%). By contrast, minerals in the No. 5 coal are primarily composed of kaolinite (avg. 62.9% on organic-free basis), tobelite (avg. 27.6%) and illite (avg. 14.8%), with minor amounts of calcite (avg. 8.8%), ankerite (avg. 4.5%), pyrite (avg. 3.3%), and quartz (avg. 3.0%). In addition, although below the XRD detection limit, trace amounts of chlorite and paragonite were identified by the SEM-EDS, and the former occurs as fracture infillings, while the latter as cell infillings (Figure 3).

It is obvious that kaolinite and tobelite are the primary minerals in both the No. 3 and No. 5 coals (Figure 4). Kaolinite is the most abundant mineral, which occurs as fracture-fillings (Figure 3a), cell-fillings (Figure 3b) and as matrix along the organic matter (Figure 3c). The former two forms reflect an authigenic origin, while the latter form reflects a terrigenous origin for kaolinite formation. Tobelite in the studied coals was found occurring as cell-infillings (Figure 3a) and fracture-infillings (Figures 3d-f), indicating an authigenic origin as well. Apatite was found occurring as subhedral crystals (Figures 3c-g), and in some cases coexists with tobelite (Figures 3e, f), indicating an authigenic origin.

4.3 Geochemical characteristics

4.3.1 Major element oxides

The concentrations of major element oxides and trace elements of the Nos. 3 and 5 coals from the Toudi open-pit mine are shown in Table 1. The major element oxides of the No. 3 coal are dominantly SiO_2 and Al_2O_3 , ranging from 11.9% to 28.7% (avg. 21.5%, on a whole coal basis) and 8.1% to 16.0% (avg. 12.9%), respectively (Table 1). The major element oxides of the No. 5 coal are also primarily SiO_2 (2.2-26.3%, avg. 14.8%) and Al_2O_3 (2.0-14.6%, avg. 8.6%). Compared to the average values of common Chinese coals reported by Dai et al. (2012b), the Nos. 3 and No. 5 coals both have relatively higher concentrations of SiO_2 , Al_2O_3 , K_2O , MgO and TiO_2 , and the No. 5 coal also has relatively higher CaO content. The roof, parting, and floor samples of the Nos. 3 and 5 coals are dominantly composed of SiO_2 (avg. 53.9% and 56.0%, respectively) and Al_2O_3 (avg. 22.1% and 18.6%, respectively), followed by minor proportion of K_2O , Fe_2O_3 , TiO_2 , MgO , CaO , Na_2O , P_2O_5 , and MnO (on a whole rock basis; Table 1).

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the Nos. 3 and 5 coals respectively range from 1.48 to 1.80 (avg. 1.65), and 1.10 to 2.08 (avg. 1.58), slightly higher than those of average Chinese coals (1.42; Dai et al., 2012b) and the theoretical value of kaolinite (1.18), tobelite (1.35), and similar to that of illite (1.57). This indicates that the major host of Si and Al is kaolinite, illite, and tobelite, which are the primary minerals in coal, whereas quartz is an additional host of Si in some coal samples. The elevated CaO in some coal samples of the No. 5 coal seam reflects the high proportion of carbonate minerals in the studied samples (e.g., calcite, Table A2).

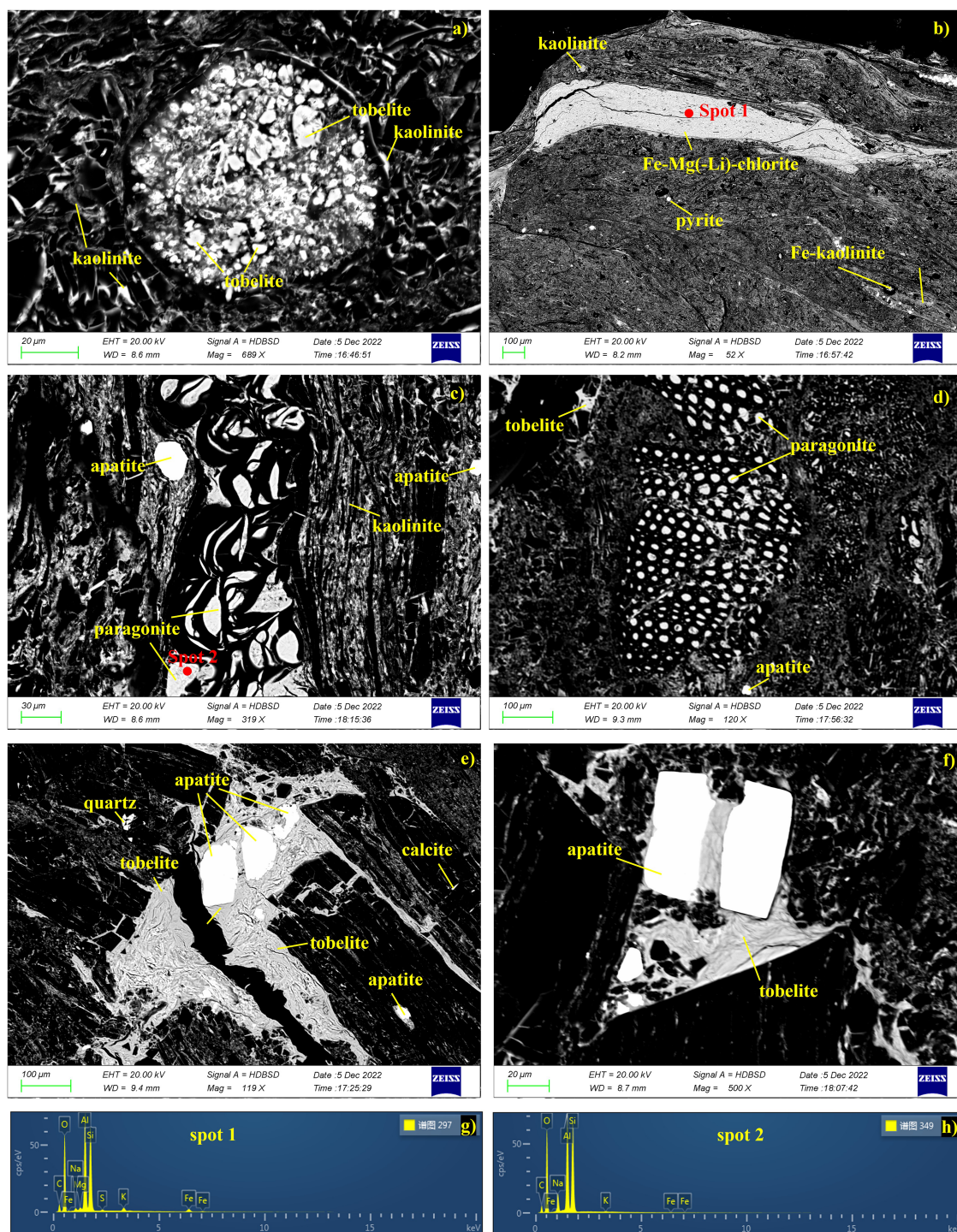


FIGURE 3

SEM back-scattered electron images of minerals in the Toudi coals. (a) tobelite and kaolinite in cell cavities and fissure in TS-5-12; (b) fracture-filling chlorite and granular pyrite in TS-5-12; (c) kaolinite distributed in the matrix and cell-filling paragonite in TS-5-12; (d) fracture-filling tobelite and cell-filling paragonite in TS-5-12; (e) fine quartz particles and coexistence of metasomatic altered apatite and tobelite in TS-5-12; (f) metasomatic altered apatite and tobelite in TS-5-12; (g) EDS spectral for Spot 1 in (b); (h) EDS spectral for Spot 2 in (c).

4.3.2 Trace elements

Concentration coefficient (CC, ratio of the average elemental concentration in investigated coals vs. that in common world hard coals), proposed by Dai et al. (2015), is widely used to evaluate the enrichment degree of trace elements in coal (Dai et al., 2015).

Compared with the common world hard coals (Ketris and Yudovich, 2009), the Nos. 3 and 5 coals in the Toudi mine are significantly enriched in Li (Figure 5), with CC up to 17.8 and 13.4, and average Li concentration as high as 214 μg/g and 160 μg/g (on a whole-coal basis), respectively. In addition, the No. 3 coal is also

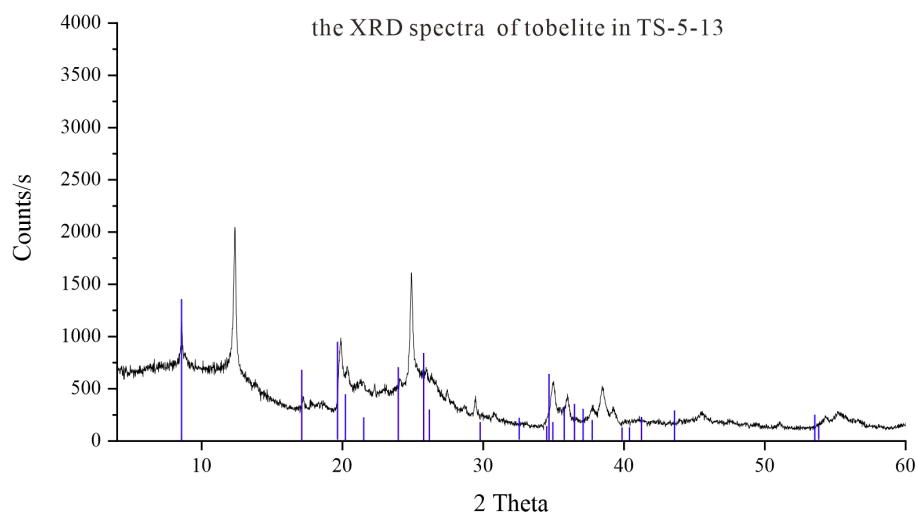


FIGURE 4
The XRD spectra of tobelite in TS-5-13.

enriched in V (CC = 5.6), Cr (CC = 5.6), Sm (CC = 5.4), and Th (CC = 5.1), and the No. 5 coal is enriched in Pb (CC = 5.5), Sm (CC = 5.2), and Co (CC = 5.0). Manganese is depleted in the Nos. 3 and 5 coals (CC < 0.5; Figure 5), and Zn, Rb, Sr, Ba and Lu in the Nos. 3 and 5 coals are relatively close to the average values of world hard coals ($0.5 < CC < 2$; Figure 5). The remaining elements are slightly enriched in the Nos. 3 and 5 coals in the Toushi mine ($2 < CC < 5$).

4.3.3 Rare earth elements and yttrium

The concentration of total rare earth elements and Y (Σ REY) in the Nos. 3 and 5 coals ranges from 112 $\mu\text{g/g}$ to 459 $\mu\text{g/g}$, and 41 $\mu\text{g/g}$ to 620 $\mu\text{g/g}$, with an average of 276 $\mu\text{g/g}$ and 241 $\mu\text{g/g}$, respectively, which is 3–4 times higher than the average (68.6 $\mu\text{g/g}$) for common worldwide coals (Ketris and Yudovich, 2009). With respect to non-coal parting, roof, and floor samples, the REY concentration in roof and floor samples from the No. 3 coal are 276 $\mu\text{g/g}$ and 269 $\mu\text{g/g}$, respectively, similar to that in No. 3 coal. The REY concentration in roof sample (105 $\mu\text{g/g}$) from the No. 5 coal is relatively lower than that in No. 5 coal, and those in the parting and floor samples are slightly higher than the average in No. 5 coal (Table 2).

Normalized to REY concentration in the upper continental crust (UCC, Taylor and McLennan, 1985), REY is correspondingly classified to light REY (L-type, LREY; $\text{La}_N/\text{Lu}_N > 1$), medium REY (M-type, MREY; $\text{La}_N/\text{Sm}_N < 1$ and $\text{Gd}_N/\text{Lu}_N > 1$), or heavy REY (H-type, HREY; $\text{La}_N/\text{Lu}_N < 1$) enrichment pattern (Seredin and Dai, 2012). According to this classification, the REY enrichment patterns for both Nos. 3 and 5 coal samples are predominantly of L-M type with the exception of TS-5-5 (L type, Table 2). Unlike in the Nos. 3 and 5 coals, the REY enrichment patterns in the non-coal roof and floor samples are primarily of M-H-type and H-type, but the parting of the No. 5 coal (TS-5-7) is characterized by L-type enrichment pattern (Table 2).

As pointed out by Dai et al. (2016) and Yan et al. (2018), Eu concentrations can be interfered by high concentrations of Ba (Ba/Eu ratio > 1000) during analysis using a quadrupole-based ICP-MS,

for example, interference by $^{135}\text{Ba}^{16}\text{O}$ and $^{134}\text{Ba}^{16}\text{OH}$ to ^{151}Eu , and $^{137}\text{Ba}^{16}\text{O}$ and $^{136}\text{Ba}^{16}\text{OH}$ to ^{153}Eu . Nonetheless, the Ba/Eu ratio in the samples investigated in this study are less than 1000, indicating that there is no interference of Ba concentration to Eu concentration (Figure 6d), consequently, the Eu concentrations determined are correct. The average δEu values of the Nos. 3 and 5 coal are 0.54 and 0.50, respectively (Table 2), both showing a remarkable negative anomaly. The roof and floor samples from No. 3 coal seam show weak positive Eu anomaly, and the roof samples from No. 5 coal seam show no obvious Eu anomaly. With respect to Gd anomaly, the roof, floor, and parting samples from Nos. 3 and 5 coal seams present no obvious or weak negative Gd anomalies, while the Nos. 3 and 5 coal show remarkable Gd anomalies (Table 2). With respect to Ce anomaly, the coal and non-coal rock samples all present weak to obvious negative Ce anomalies.

5 Discussion

5.1 Modes of occurrence of elevated Li in the coals

Lithium in coal has been found predominantly presenting an inorganic affinity, occurring in clay minerals (e.g., kaolinite, chlorite, illite, and cookeite), or to a lesser extent in micas and tourmaline (Dai et al., 2021, 2023, 2024; Di et al., 2023; Zhao et al., 2022; Zhang et al., 2024). For instance, the elevated Li in coals from the Guanbanwu mine, Jungar Coalfield (Inner Mongolia, Dai et al., 2012a), the Caotang and Daping mine, Yudongnan Coalfield (Chongqing, Zhou et al., 2021; Zou et al., 2023) and from the Jincheng Coalfield, Qinshui Basin, Shanxi (Zhao et al., 2022) occurs in cookeite or other Li-bearing chlorite group minerals. By contrast, Li in coals from the Antaibao mine, Ningwu Coalfield (Sun et al., 2022a; Di et al., 2023) and the Donggou mine, Chongqing (Zou et al., 2020) mainly occur in kaolinite.

TABLE 1 Concentration of major element oxides (%_w) and trace elements (μg/g) of the Nos. 3 and 5 coal from the Toudi open-pit mine (on whole-coal basis).

Coal seam	No. 3 coal							No. 5 coal														No. 5 avg
Samples	TS-3-1	TS-3-2	TS-3-3	TS-3-4	TS-3-5	TS-3-6	No. 3 avg	TS-5-1	TS-5-2	TS-5-3	TS-5-4	TS-5-5	TS-5-6	TS-5-7	TS-5-8	TS-5-9	TS-5-10	TS-5-11	TS-5-12	TS-5-13	TS-5-14	
SiO ₂	50.3	24.9	20.6	11.9	28.7	57.5	21.5	46.1	49.6	49.6	22.5	26.3	23.9	42.7	3.5	4.0	2.2	8.9	21.7	20.0	92.1	15.8
Al ₂ O ₃	25.6	15.3	12.1	8.1	16.0	18.7	12.9	23.2	23.5	23.6	14.3	14.6	11.5	20.6	2.7	3.6	2.0	5.3	12.3	11.2	1.9	10.1
CaO	0.2	0.4	0.7	0.7	0.2	0.1	0.5	0.2	0.1	0.2	0.6	0.3	0.3	0.2	12.1	0.7	1.6	1.0	0.3	0.6	0.3	1.9
K ₂ O	1.9	0.6	0.6	0.2	0.7	1.6	0.5	1.8	1.9	1.9	0.4	0.7	0.5	1.3	0.5	0.1	0.0	0.2	0.4	0.5	0.1	0.4
Na ₂ O	0.21	0.21	0.13	0.10	0.21	0.22	0.16	0.22	0.26	0.31	0.08	0.16	0.13	0.19	0.88	0.10	0.06	0.12	0.17	0.18	0.04	0.21
Fe ₂ O ₃	1.4	1.0	1.1	0.6	1.2	1.1	1.0	1.4	1.3	1.3	0.8	1.2	1.3	1.0	3.2	0.5	0.4	1.1	2.9	1.0	0.8	1.4
MgO	0.6	0.4	0.3	0.2	0.4	0.4	0.3	0.6	0.6	0.6	0.2	0.4	0.3	0.5	1.5	0.1	0.2	0.1	0.2	0.3	0.1	0.4
TiO ₂	1.1	0.7	0.6	0.3	0.9	0.8	0.6	1.0	1.0	1.0	0.6	1.0	0.6	0.8	0.1	0.2	0.1	0.3	0.6	0.5	0.3	0.5
P ₂ O ₅	0.03	0.14	0.05	0.01	0.03	0.03	0.06	0.04	0.04	0.04	0.01	0.03	0.03	0.04	0.09	0.02	0.01	0.18	0.07	0.02	0.02	0.05
Li	234	296	182	88.0	290	187	214	223	217	222	72.2	209	161	264	188	38.0	9.9	89.1	348	329	6.6	160
Be	3.2	3.7	3.0	2.5	3.4	2.5	3.2	3.4	3.4	3.6	2.3	4.3	2.5	3.5	10.9	0.9	0.0	1.7	3.2	2.8	0.3	3.2
P	150	605	232	31.3	121	133	247	174	157	165	51.7	149	120	166	384	83.5	40.8	788	289	93.6	91.3	222
Sc	25.5	18.9	17.2	12.7	19.0	21.7	17.0	26.2	27.6	26.6	10.2	20.2	16.8	22.1	33.5	5.1	3.0	8.7	12.9	13.3	2.5	13.7
V	166	158	138	95.3	173	132	141	157	164	159	71.6	192	169	139	257	39.2	22.9	68.2	129	132	14.9	120
Cr	150	99.0	89.4	52.4	115	125	89.0	139	146	141	24.2	115	104	122	152	24.6	13.9	40.6	88.9	82.8	72.9	71.7
Mn	35.1	13.2	27.0	22.8	17.7	34.8	20.2	41.2	41.9	34.8	29.0	27.1	25.5	26.7	130	8.2	16.8	8.9	8.3	11.1	15.4	29.4
Co	9.5	17.3	15.6	9.6	16.4	18.6	14.7	8.4	6.7	11.3	21.0	25.7	18.3	8.5	75.2	8.1	6.7	35.5	29.6	7.7	3.1	25.3
Ni	40.3	47.0	41.1	23.7	43.4	37.1	38.8	38.1	36.4	42.7	32.4	48.3	42.0	36.1	131	18.4	11.0	33.8	66.4	34.3	6.7	46.4
Cu	26.0	48.8	42.8	25.7	35.6	23.7	38.2	40.5	42.7	35.4	67.2	71.7	63.6	29.6	134	20.7	12.8	24.7	32.5	24.7	3.9	50.2
Zn	22.2	37.5	12.0	22.6	29.6	32.8	25.4	21.8	23.9	22.9	51.8	43.5	30.7	13.1	136	17.2	8.6	19.5	28.0	17.2	45.0	39.1
Ga	36.4	29.6	23.2	12.9	29.7	27.7	23.8	35.1	34.9	34.9	9.4	29.2	23.8	34.9	40.1	5.3	2.9	15.4	22.0	22.2	2.8	18.9
Rb	97.7	32.0	28.8	10.4	35.7	96.8	26.7	107	104	98.0	18.6	33.6	26.7	73.5	25.6	2.2	0.9	8.0	20.8	24.0	3.2	17.8
Sr	81.7	148	86.1	43.7	75.9	60.9	88.5	86.0	94.3	81.8	50.4	62.1	48.2	75.5	476	50.0	49.6	344	84.8	42.8	21.0	134
Y	39.9	40.3	31.3	17.9	28.8	37.8	29.6	45.1	45.0	39.9	24.0	38.7	34.3	38.0	131	13.7	11.5	23.2	22.8	21.7	17.1	35.7
Zr	236	142	109	54.8	129	190	109	218	237	226	25.8	180	108	223	230	28.8	17.8	49.9	110	107	1019	95.2

(Continued)

TABLE 1 Continued

Coal seam	No. 3 coal							No. 5 coal														No. 5 avg
Samples	TS-3-1	TS-3-2	TS-3-3	TS-3-4	TS-3-5	TS-3-6	No. 3 avg	TS-5-1	TS-5-2	TS-5-3	TS-5-4	TS-5-5	TS-5-6	TS-5-7	TS-5-8	TS-5-9	TS-5-10	TS-5-11	TS-5-12	TS-5-13	TS-5-14	
Nb	22.9	13.2	11.5	5.4	16.8	18.8	11.7	21.6	22.0	21.1	1.6	19.2	11.8	19.0	29.7	3.6	2.7	6.7	11.9	10.7	5.7	10.9
Sn	5.6	4.1	3.2	1.7	4.9	4.3	3.5	5.3	5.6	5.3	<dl	5.1	3.3	4.9	7.7	0.9	0.6	1.8	3.7	3.7	0.9	3.0
Cs	12.6	5.5	4.3	1.4	6.6	13.7	4.4	13.2	12.4	11.9	3.7	5.3	4.5	9.0	0.0	0.0	0.0	1.3	3.7	4.5	0.2	2.5
Ba	305	114	99.4	44.9	136	288	98.5	337	347	308	88.6	123	101	240	159	17.6	10.3	55.8	93.2	93.3	19.0	82.5
La	47.9	88.2	54.6	18.6	51.5	48.0	53.2	58.9	59.5	53.0	24.1	76.1	64.4	67.0	70.1	8.5	4.4	55.5	49.8	24.0	19.1	41.9
Ce	92.0	173	107	37.6	76.2	96.5	98.3	121	121	106	48.1	120	95.4	132	175	15.2	9.2	99.4	77.6	38.9	37.0	75.5
Pr	10.3	20.7	13.1	4.2	10.5	11.7	12.2	13.7	14.2	12.2	5.8	16.4	13.6	15.5	24.4	1.6	1.3	10.6	13.3	7.7	3.9	10.5
Nd	42.1	81.7	49.6	16.6	39.0	43.8	46.7	53.3	53.8	48.9	23.0	59.1	50.6	57.3	108	6.0	5.9	41.9	51.9	32.3	14.1	42.1
Sm	8.5	18.8	11.0	4.4	8.8	10.2	10.8	10.3	10.5	9.3	5.9	11.6	9.9	9.1	33.7	2.0	2.3	9.9	11.0	6.9	2.7	10.4
Eu	1.9	2.6	1.6	<dl	1.4	2.0	1.4	2.0	1.9	1.8	0.9	1.6	1.3	1.2	<dl	<dl	<dl	1.5	1.7	0.8	0.4	0.9
Gd	7.2	11.4	7.2	3.3	5.9	8.1	6.9	8.8	8.3	7.2	4.9	7.8	7.1	6.4	26.5	2.2	2.2	7.0	5.9	4.1	2.4	7.5
Tb	1.2	1.5	1.1	<dl	0.9	1.3	0.9	1.4	1.4	1.2	<dl	1.2	1.1	1.1	<dl	<dl	<dl	0.9	0.8	<dl	0.4	0.5
Dy	7.0	9.1	6.9	4.0	6.5	7.2	6.6	8.3	8.2	7.2	5.4	8.6	7.6	6.9	26.6	2.9	2.3	5.6	5.4	4.8	2.7	7.7
Ho	1.5	1.9	1.5	0.9	1.4	1.4	1.4	1.7	1.7	1.5	1.2	1.9	1.6	1.4	<dl	<dl	<dl	1.1	1.1	1.1	0.6	0.9
Er	4.1	4.4	3.6	2.1	3.4	3.6	3.4	4.7	4.8	4.3	2.6	4.6	3.8	4.0	12.3	1.4	1.1	2.5	2.8	2.7	1.8	3.7
Tm	0.6	1.2	1.0	<dl	1.0	0.6	0.8	0.7	0.7	0.6	<dl	1.3	1.0	0.6	<dl	<dl	<dl	<dl	<dl	<dl	0.3	0.3
Yb	4.1	4.9	4.0	2.4	3.8	3.7	3.8	4.5	4.6	4.2	2.7	5.2	4.1	4.3	12.0	1.6	1.1	2.4	3.2	3.2	2.0	3.9
Lu	0.6	<dl	<dl	<dl	<dl	0.5	<dl	0.7	0.7	0.6	<dl	0.8	<dl	0.6	<dl	<dl	<dl	<dl	<dl	<dl	0.3	0.1
Hf	6.8	4.0	3.3	1.6	3.8	5.4	3.2	6.2	6.6	6.4	<dl	5.2	3.2	6.3	<dl	0.9	0.0	1.5	3.4	3.1	24.3	1.9
Ta	1.8	1.0	0.8	0.0	1.2	1.4	0.7	1.6	1.7	1.6	<dl	1.3	<dl	1.4	<dl	<dl	<dl	<dl	<dl	<dl	0.5	0.1
Pb	16.6	30.1	32.3	27.7	43.5	12.3	33.4	15.9	23.5	17.6	35.4	53.9	47.6	8.6	105	15.4	9.4	46.5	58.7	16.8	10.1	43.2
Th	24.4	21.7	16.0	8.4	20.6	19.9	16.7	22.6	24.5	22.9	7.7	21.3	16.7	22.3	38.0	5.3	3.9	7.3	14.9	11.8	7.8	14.1
U	4.3	6.1	5.2	2.8	5.6	3.3	4.9	4.5	5.1	4.6	3.4	6.7	6.1	4.0	11.0	1.4	0.9	2.7	5.9	4.0	2.6	4.7

<dl, below detection limit.

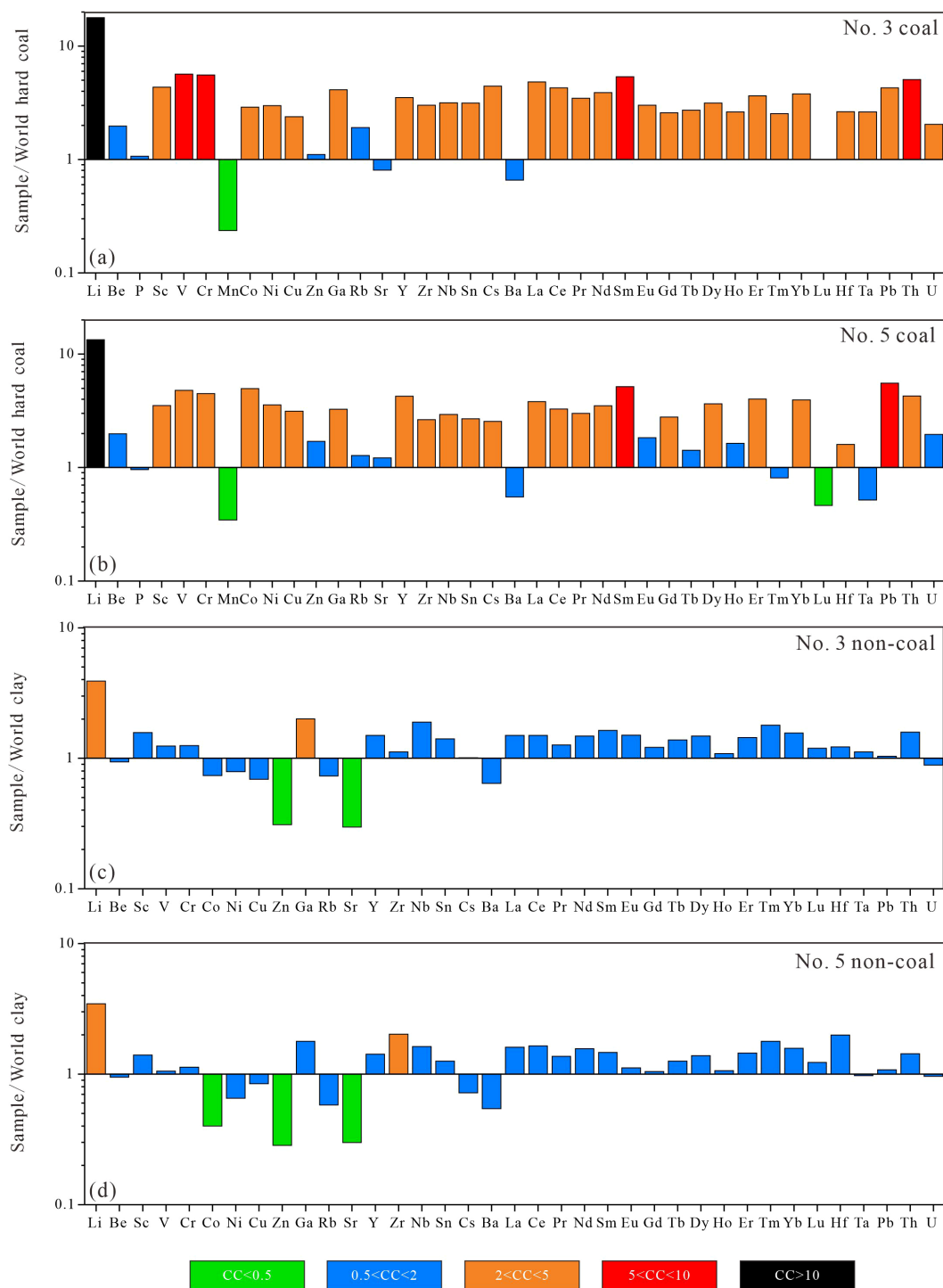


FIGURE 5

Concentration coefficients (CC) of trace elements in the Nos. 3 and 5 coals from the Toudi mine. (a) No. 3 coal; (b) No. 5 coal; (c) No. 3 non-coal; (d) No. 5 non-coal.

In the current research, Li concentration is positively correlated with ash yield ($r=0.62$, Figure 6), which points to a predominant inorganic affinity of Li. Furthermore, Li concentration also presents positive correlation with Al_2O_3 ($r=0.62$) and K_2O content ($r=0.76$, Figure 6), which further indicates that in consistence with previous research, Li in the Toudi coals primarily occurs in aluminosilicate

minerals, especially the K-bearing aluminosilicate minerals. As aforementioned, aluminosilicate minerals in the Toudi coals are dominated by kaolinite, illite, and tobelite. Vertically, Li concentration presents a similar variation trend to kaolinite content, which is higher in coal sections adjacent to the roof, parting and floor of the coal seam (Figure 7). This indicates that

TABLE 2 Concentration (μg/g) of total rare earth elements and yttrium (REY) and geochemical parameters of REY in coal seam samples from the Toushi open-pit mine.

Coal seam	Samples	ΣREY (μg/g)	La _N /Lu _N	La _N /Sm _N	Gd _N /Lu _N	Enrichment type	δEu	δCe	δGd
No. 3 coal	TS-3-1	269	0.84	0.85	0.99	H	1.16	0.94	1.01
	TS-3-2	460	nd	0.70	nd	L-M	0.51	0.92	1.30
	TS-3-3	294	nd	0.74	nd	L-M	0.53	0.91	1.24
	TS-3-4	112	nd	0.63	nd	L-M	nd	0.97	nd
	TS-3-5	239	nd	0.88	nd	L-M	0.58	0.74	1.15
	TS-3-6	276	0.95	0.71	1.26	M-H	1.02	0.93	1.03
No. 5 coal	TS-5-1	335	0.90	0.86	1.06	M-H	0.98	0.97	1.02
	TS-5-2	336	0.92	0.85	1.01	M-H	0.98	0.95	0.96
	TS-5-3	298	0.94	0.85	1.01	M-H	1.01	0.95	0.96
	TS-5-4	149	nd	0.61	nd	L-M	0.51	0.93	3.02
	TS-5-5	356	1.01	0.98	0.82	L	0.49	0.77	1.26
	TS-5-6	296	nd	0.98	nd	L-M	0.45	0.73	1.32
	TS-5-7	345	1.13	1.10	0.86	L	0.76	0.94	0.93
	TS-5-8	620	nd	0.31	nd	L-M	nd	0.99	nd
	TS-5-9	55	nd	0.64	nd	L-M	nd	0.91	nd
	TS-5-10	41	nd	0.29	nd	L-M	nd	0.91	nd
	TS-5-11	262	nd	0.84	nd	L-M	0.54	0.91	1.35
	TS-5-12	247	nd	0.68	nd	L-M	0.57	0.70	1.12
	TS-5-13	148	nd	0.52	nd	L-M	0.43	0.67	2.84
	TS-5-14	105	0.84	0.85	0.99	H	0.68	0.97	1.00

ΣREY, total concentration of rare earth elements and yttrium; *N_N*, normalized to the average REY concentration in the upper crust; L, light rare earth enrichment type; L-M, light-middle rare earth enrichment type; M-H, middle-heavy rare earth enrichment type; H, heavy rare earth enrichment type; δEu=Eu_N/(0.67×Sm_N+0.33×Tb_N); δCe=Ce_N/(0.5×La_N+0.5×Pr_N); δGd=Gd_N/(0.33×Sm_N+0.67×Tb_N); nd, no data.

the hosts of Li in the Toushi coals are mainly kaolinite, and/or to a lesser extent illite and tobelite. Furthermore, fracture-filling chlorite has also been found in the Toushi coals under SEM-EDX (Figure 3b). The EDS data of chlorite shows the occurrence of Fe and Mg and the Al/Si atomic ratio of 1.2 (Figure 3e), pointing to the possible occurrence as chamosite, which may serve as another carrier of Li.

In addition, nanoscale cookeite was further identified in a high-Li sample (TS-5-5) under HR-TEM (Figure 8). As shown in the EDS spectra and elemental composition in Figures 8b, c, the Li-rich TS-5-5 sample is predominantly composed of Al, Si and O. Taking into consideration of the existence of undetectable elements with low atomic number (H, He, Li, Be) and the allowable atomic error range, the Al/Si atomic ratio ranges from 1.11 to 1.66. The Al/Si atomic ratio of cookeite is 1.6, consequently, the EDS data indicates the co-existence of cookeite, kaolinite and organic matter. Comparing the interplanar spacing (*D_m*) and angle of the crystal plane (*θ_m*) in the TS-5-5 sample with those in the standard data (*D_s* and *θ_s*), the values of $|D_m - D_s|$ are all below 0.01nm (0.0048nm, 0.0027nm and 0.0043nm, respectively), and the value of $|\theta_m - \theta_s|$ is 2.56°(<3°), which indicates that nanoscale cookeite (pdf 45-1476) occurs in the TS-5-5 coal sample from Toushi open-pit mine (Table 3). As a consequence, Li occurs predominantly in kaolinite and secondarily occurs in Li-bearing chlorite group minerals, e.g.,

chlorite and cookeite in the Cushui Formation coals from the Toushi open-pit mine.

5.2 Geological origin of Li enrichment in the coals

5.2.1 Contribution of detrital supply from sediment source region

Elements, such as Al, Ti, Zr, Nb, and REY, are relatively immobile during the weathering, migration, hydrothermal alteration, deposition, diagenesis and/or volcanic process (Hayashi et al., 1997), which makes them effective indicators of the initial provenance (terrigenous clast or volcanic ash) of inorganic matter in coals, tonsteins and other sedimentary rocks (Dai et al., 2014b, 2015, 2017a; Zhao et al., 2019a; Liu et al., 2020; Zhang et al., 2022; Di et al., 2023; among others). For instance, the Al₂O₃/TiO₂ ratios of 3-8, 8-21, and 21-70, represent igneous rocks of mafic, intermediate, and felsic compositions, respectively (Hayashi et al., 1997). As illustrated in Figure 9a, the Al₂O₃/TiO₂ ratios of the coal and non-coal rock samples from the Nos. 3 and 5 coal seams are predominantly higher than 21, indicating that the Nos. 3 and 5 coals most probably have the same sediment source region characterized by felsic-intermediate compositions. In

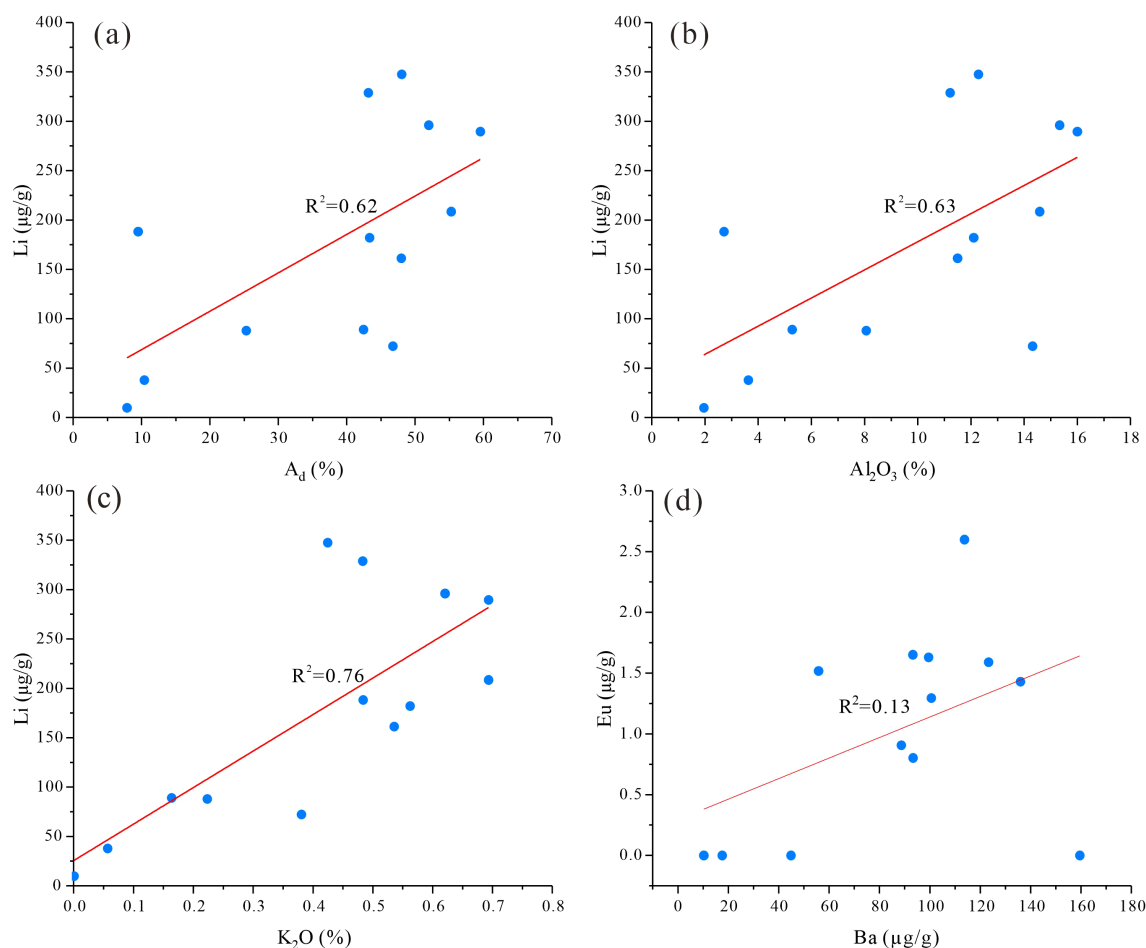


FIGURE 6

Correlation between Li with ash yield (a), Al_2O_3 (b) and K_2O (c) in coals, and correlation between Ba and Eu (d).

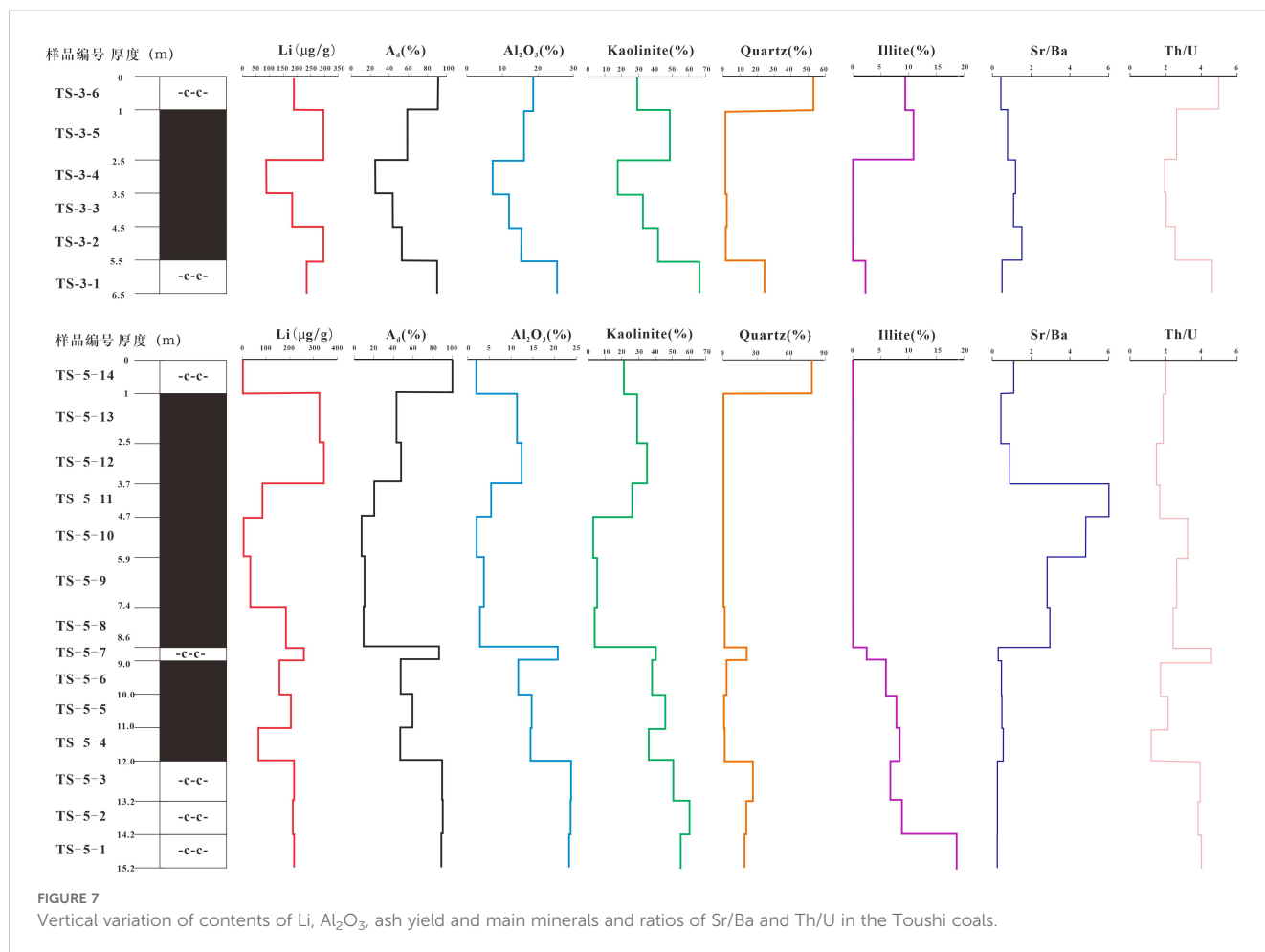
addition, the diagram of Zr/TiO_2 vs. Nb/Y has also been used to discriminate the sediment source of coal and coal-bearing sequences (Liu et al., 2020; Spears, 2012; Zhao et al., 2019a, b), according to which, the sediment provenance of the Toushi coals is of also felsic-intermediate composition (Figure 9b).

The Eu anomalies in coals are commonly inherited from their original inorganic source material (Eskenazy, 1987a, b) and/or attributed to high temperatures coupled with highly reduced environments (Dai et al., 2014a; Dai et al., 2016; Dai et al., 2018a). Specifically speaking, negative Eu anomaly in coals is generally derived from intermediate-felsic source rocks, while positive Eu anomaly is probably ascribed to the influence of mafic igneous rocks or high temperature fluids (Dai et al., 2016). The Nos. 3 and 5 coal are both characterized by remarkable negative Eu anomalies, representing a felsic-intermediate sediment provenance as well.

According to He (2008), the sea regression and deposition of terrigenous debris started since the early stage of the Ceshui Formation in the Lianshao and other coalfields in the central Hunan Region. The Ceshui Formation coal-bearing strata adjacent to the oldland in NE Hunan are characterized by coarse lithology with multi-layer conglomerate and a large total thickness.

Furthermore, the lithology and thickness of the coal measures both become thinner, and the composition maturity, structure maturity and cement structure maturity of clastic minerals in coarser sandstones all become higher from the northeast to the southwest. This indicates that the main sediment source area is located in the northeast while the sea regressed towards the southwest direction. It is concluded that the source rock of the Ceshui Formation coal-bearing sequence was probably the Caledonian granite according to the analyses of isotopic dating and geochemical index such as Co/Ni ratio (He, 2008). Based on the contour maps of the sand-mud ratio, stratigraphic thickness, mudstone thickness percentage and sandstone thickness percentage of the Ceshui Formation coal-bearing sequence in the Lianshao Coalfield, it is further indicated that the terrigenous detrital supply of the Ceshui Formation in the Lianshao Coalfield is mainly sourced from the granite in the Xuefeng Oldland in the northeast of the study area (Figure 1, Yang, 2012).

The enrichment of lithium is enhanced by lower degrees of sub-arc mantle melting and higher extents of intracrustal differentiation (Chen et al., 2020). Arc magmas that traverse thick crust begin with higher initial Li contents due to lower extents of decompression melting and then evolve to higher Li contents through more



extensive intracrustal differentiation. Magmatism and differentiation in continental arcs (e.g., the Andes) usually gives rise to higher lithium content than their island arc counterparts (Chen et al., 2020). Weathering of these enriched source rocks mobilizes and transports such Li into the hydrologic system, ultimately developing Li enrichment in landlocked extensional basins in thickened orogenic settings (Chen et al., 2020). He (2008) reported that the provenance area of Lianshao coalfield has suffered from intensive chemical weathering during the Permo-Carboniferous coal-forming period, and the enrichment of lithium in the Ceshui Formation coal measures was largely ascribed to the weathering products of Li-enriched granite source rocks.

The chemical index of alteration ($\text{CIA} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100\%$, $\text{CaO}^* = \text{CaO} - (10/3 \times \text{P}_2\text{O}_5)$) has been widely used to quantitatively reflect the intensity of chemical weathering, with CIA values of 80–100, 70–80 and 60–70 represent intense weathering under hot and humid tropical climatic conditions, moderate weathering under warm and humid climatic conditions, and weak weathering under cold and dry climatic conditions, respectively (Nesbitt and Young, 1982). However, due to Ca, Na and K are sensitive to leaching during syngenetic and diagenetic process (Dai et al., 2020), the CIA value may not accurately reflect the degree of chemical weathering, in which cases the use of chemical index of weathering ($\text{CIW} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^*$

$+ \text{Na}_2\text{O}) \times 100\%$) can circumvent this problem. If the variation trend of CIW is consistent with that of CIA, it can indicate the accuracy of the CIA (Harnois, 1988). The CIA values of the non-coal rocks in the Toudi mine ranges from 85.3 to 92.9 (avg. 90.9), is consistent with the variation trends of CIW (88.4 to 99.0, avg. 97.3), indicating the reliability of CIA for judging the chemical weathering intensity. Therefore, the CIA and CIW values of the no-coal rocks in the studied area further confirm the intense chemical weathering of granite source rocks during the coal-forming period. The study area is located in fold orogenic belt with complex tectonic movement, concomitant with the generation of more felsic magmas and development of high orogenic uplands (Yang, 2012; Chen et al., 2020). Weathering and leaching of the Li-enriched granitic source rocks from the uplands by surface runoff or groundwater flow transports soluble Li into the peat swamp of confined basins, where it is further concentrated and enriched (Rudnick et al., 2004; Tomascak, 2004; Henchiri et al., 2014; Chen et al., 2020).

5.2.2 Influence of seawater infiltration

Infiltration of seawater and its interaction with Li-bearing terrestrial waters has contributed to Li enrichment in coals from several coalfields (Dai et al., 2018b; Xie et al., 2021). The Sr/Ba ratio is regarded as an empirical indicator of paleosalinity, and is widely

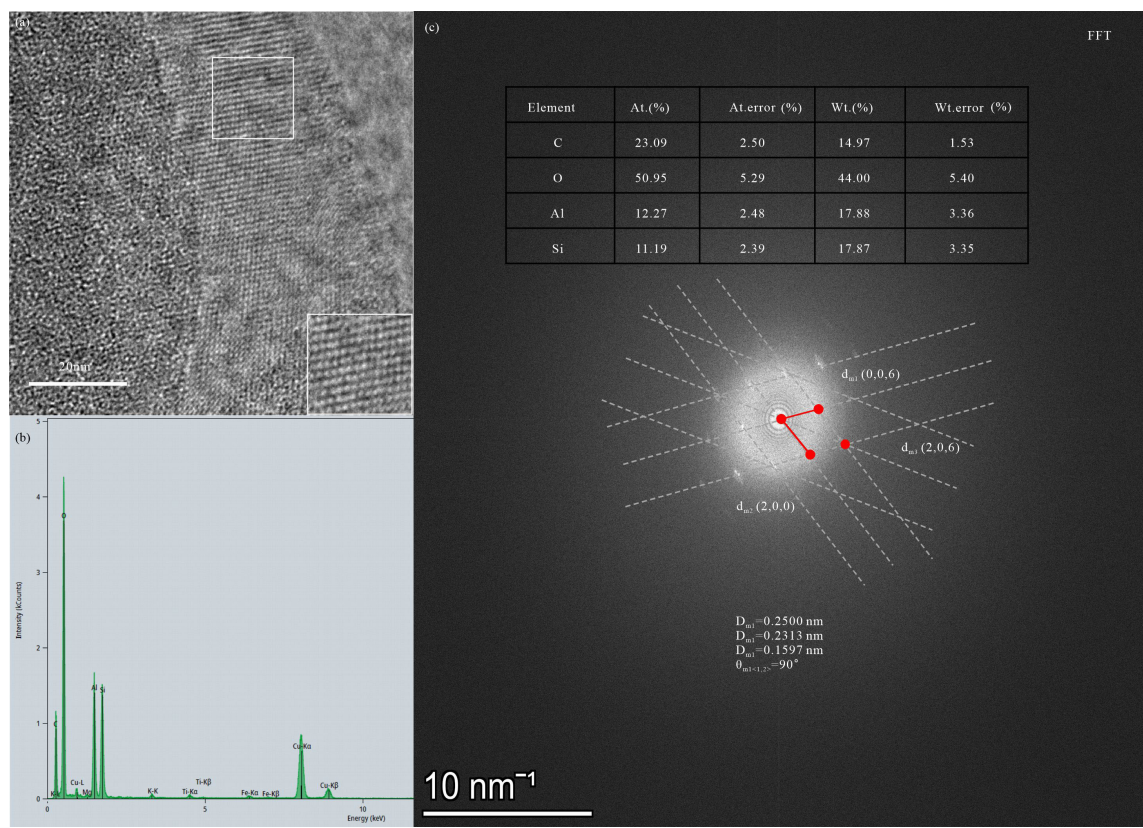


FIGURE 8 Nanoscale cookeite identified in the TS-5-5 coal sample. **(a)** HR-TEM image of nanoscale cookeite identified in TS-5-5 sample; **(b, c)** EDS spectrum and FFT results of selected regions in **(a)**; At, Atomic percentage; At. Error, error range of atomic percentage; Wt, Weight percentage; Wt. error, error range of weight percentage; $d_{m1, 2, 3}$, surface parameters of crystal plane; $+D_{m1, 2, 3}$, interplanar spacing of crystal plane; $\theta_{m1,2,3}$, angle crystal plane.

utilized as a indicator of fresh water or seawater influence in sedimentary environments (Dai et al., 2020; Tribouillard et al., 2006; Zhang et al., 2018). Sr/Ba ratio of 1.0 is used as the boundary for marine/freshwater deposition, with Sr/Ba>1 for seawater deposition, Sr/Ba<1 for freshwater deposition, and 0.6<Sr/Ba<1 for brackish water deposition (Chen et al., 2015b; Dai et al., 2013b, 2013a; Spiro et al., 2019; Yan et al., 2019). In the current research, the Sr/Ba ratios of the Toudou coals fluctuatingly range from 0.5 to 6.2 (avg. 1.8), indicating that the coal seams were intermittently influenced by seawater. The marine influence on the Toudou coals is further indicated by the relatively high content of illite in coals, as infiltration of seawater would favor the transformation of kaolinite into illite and/or montmorillonite (Wei et al., 2020; Zhao et al., 2019b; Zheng et al., 2017). This is

consistent with previous research that the Ceshui Formation coals in the Lianshao Coalfield was predominantly formed in continental and marine transitional sedimentary environment, e.g., bay lagoon and tidal flat, where the peat swamp was mildly marine influenced (Wang et al., 1995; Yang, 2012). It is worth noting that coals formed in seawater-influenced sedimentary environment were usually characterized by high-sulfur content, as seawater sulfate is more available in seawater-influenced environment (Ward et al., 2007; Chou, 2012). However, although formed in marine-influenced environment, the Toudou coals are characterized by low sulfur content (avg. 0.72% and 0.77% in Nos. 3 and 5 coal), which is ascribed to the seawater desalination. The Lianshao coalfield was formed in restricted epicontinental-marine environment, where the seawater was desalinated by the heavy rainfall due to the warm and

TABLE 3 SSCD standard crystal surface parameters and measured values of cookeite in TS-5-5.

Mineral	PDF	Standard crystal surface parameters									Measured value	
			<i>h</i>	<i>k</i>	<i>l</i>	<i>D_s</i> (nm)	<i>θ_s</i> (°)	U	V	W	<i>D_m</i> (nm)	<i>θ_m</i> (°)
Cookeite- <i>I₀₄</i> , B-rich	45-1476	<i>d₁</i>	0	0	6	0.2548	78.30	0	12	0	0.2500	80.86
		<i>d₂</i>	2	0	0	0.2340					0.2313	
		<i>d₃</i>	2	0	6	0.1633					0.1597	

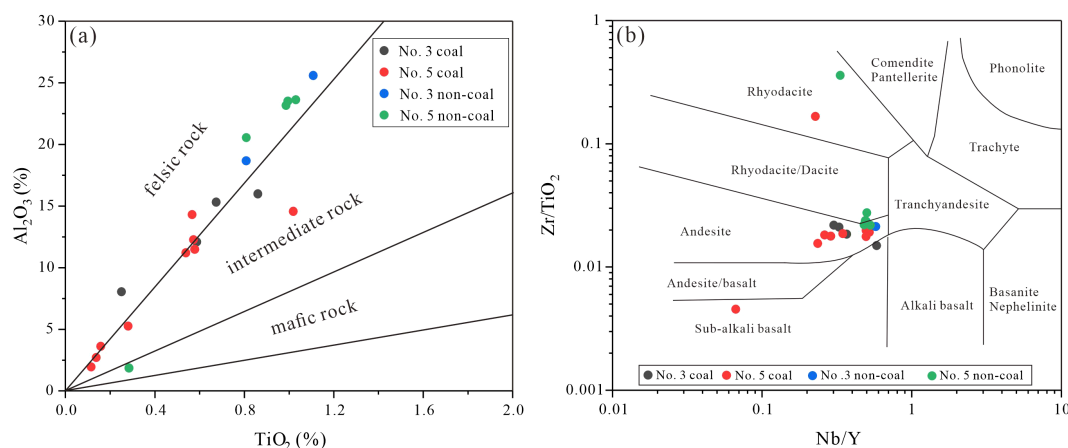


FIGURE 9

Discrimination diagrams of Al_2O_3 vs. TiO_2 (a) and Zr/TiO_2 vs. Nb/Y (b) of the studied samples.

humid climate during the coal formation period (Wang et al., 1995; Yang et al., 1996). In addition, the Ce anomalies of the Toudi coals range from 0.64 to 0.97 (avg. 0.85), and the Th/U ratios from 2.3 to 6.0 (avg. 3.8), both reflecting a relatively anoxic condition in the marine-influenced environment (Wright et al., 1987; Chen et al., 2015a).

As the Sr/Ba ratio is regarded as an empirical of paleosalinity, which is supposed to increase with salinity (Meng et al., 2012; Tao et al., 2017), the vertical variation of Li concentration along with the fluctuation of ash yields and Sr/Ba ratios reflects that Li is highly enriched in coal sections that was formed during slow sea regressive process (Figure 7). This is consistent with previous research that the infiltration of seawater and its interaction with Li-bearing terrestrial materials is favorable for Li enrichment in coals that were formed in the marine-influenced sedimentary environment, especially under the sea regressive background (Dai et al., 2018b; Nechaev et al., 2020; Xie et al., 2021).

5.2.3 Influence of hydrothermal fluids

Magmatic activities frequently occurred in the Lianshao coalfield, among which the Caledonian, Indosinian, and Yanshanian are three predominant large-scale ones. These magmatic activities are characterized by multicyclic granite

intrusion widely distributed in the northeast, east and southern margin of the coalfield (Yang, 2012).

Igneous intrusion is not uncommon in coal beds and coal-bearing sequences. The high-temperature hydrothermal solutions accompanied with the granite intrusion resulted in regional magmatic metamorphism, and subsequently give rise to the high coal rank not only of the Lianshao coals present in this study, but also of coals from other areas (e.g., Dai and Ren, 2007; Finkelman et al., 1998; Sanders et al., 2023; Stewart et al., 2005; Wang et al., 2024a, b; Wang et al., 2023, 2024c). Hydrothermal influences are generally indirectly reflected by several geochemical indicators. e.g., positive Gd anomaly, and Eu anomaly (Ward et al., 1996; Dai et al., 2017a, 2016; Shand et al., 2005). In the current research, almost all the UCC-normalized REY patterns of the studied coal samples show positive Gd anomalies (Table 2, Figure 10), was probably caused by circulation of hydrothermal solutions or acidic waters in the coal-bearing basins (Dai et al., 2016; Di et al., 2023; Johannesson and Zhou, 1997). Furthermore, the influence of hydrothermal solution is also evidenced by the presence of tobelite in the Toudi coals, which may reflect the decomposition of organic nitrogen in the coal during rank advance or hydrothermal alteration, and associated release of aqueous ammonium ions (NH_4^+) into the pore fluids (Daniels and Altaner, 1993; Ward

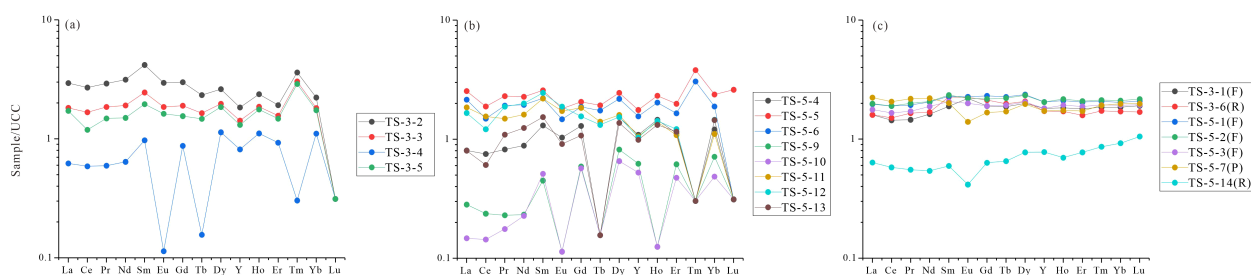


FIGURE 10

UCC-normalized distribution patterns of REY in the studied coal and non-coal rock samples (UCC data are from Taylor and McLennan, 1985). (a) No. 3 coal samples; (b) No. 5 coal samples; (c) non-coal rock samples.

and Christie, 1994; Nieto, 2002; Dai et al., 2012c). The tobelite in coals has been proved to be formed by reaction between kaolinite already present in the coal and NH_4^+ derived from decomposition of the organic matter during hydrothermal alteration at a relatively high temperature (Boudou et al., 2008; Dai et al., 2012c, 2017). Furthermore, the occurrence of fracture-filling chlorite and nanoscale cookeite in the Toushi coals (Figures 3B, 8) is also indicative of hydrothermal activity, which was commonly ascribed to the reaction of kaolinite with Li-bearing solutions or were directly precipitated by Li-bearing fluids, serving as the main carrier of Li in coals (Dai et al., 2012a; Permana et al., 2013; Zhao et al., 2018; Zhou et al., 2021). As a consequence, the elevated Li concentration in the Toushi coals is, at least in part, related to the injection of hydrothermal solutions (submarine hydrothermal fluids or acidic waters).

It is worth noting that apart from Li, V and Cr are also enriched in the Toushi coals, which is indicative of hydrothermal influence as well. Previous research has found that the injection of V-Cr-bearing magmatic hydrothermal solution during coal formation process contributed to the Cr and V enrichment in coals (Brownfield et al., 1995; Wu et al., 2005; Yang, 2012). Dai et al. (2013, 2017b) ascribed the abnormal enrichment of V-Cr-Ni-U element assemblages in organic-rich rocks, e.g., coal and black shale, to submarine hydrothermal activities. In the current study, the terrigenous provenance of the Toushi coals is primarily of intermediate to felsic composition, in which the contents of V, and Cr are much lower than those in basic and ultrabasic rocks (Brownfield et al., 1995). Therefore, the enrichment of V and Cr in the marine-influenced Toushi coals is not derived from the intermediate-felsic terrigenous provenance, but attributed to the submarine hydrothermal activities instead.

5.3 Preliminary assessment of Li resource potential

Lithium is significantly enriched in the Nos. 3 (avg. 214 $\mu\text{g/g}$) and 5 (160 $\mu\text{g/g}$) coals in the Toushi mine, which is much higher than the minimum Li concentration for Li extraction from coal (50 mg/g , Chinese Standard GB/T 41042-2021, 2021). According to GB/T 41042-2021, the Nos. 3 and 5 coals in the Toushi mine both belong to ultra-high to high-Li coals, and present a promising economic potential for Li recovery.

Currently, Li and other critical metals in coal are mostly extracted from coal fly ash, concentrations of critical metals in coal ashes are much more critical for its recovery (Dai et al., 2022). The average content of Li_2O in the Nos. 3 and 5 coals from the Toushi open-pit mine are 0.10% (0.07%–0.12%; on ash basis) and 0.11% (0.03%–0.43%), respectively. The average content of Li_2O in the roof, parting, and floors of the Nos. 3 and 5 coals are 0.05% (0.04–0.06%; on ash basis) and 0.04% (0.01–0.05%), respectively. According to the Extraction Standard for Li_2O in coal-bearing strata proposed by Zhao et al. (2022), the Li_2O content in the coal ashes is higher than the cut-off grade (0.08%), but that in the partings is below this grade. Thus, the Nos. 3 and 5 coal seams from the Toushi

open-pit mine are both considered as promising raw materials for Li recovery.

6 Conclusions

The Nos. 3 and 5 coals of the Ceshui Formation in the Toushi open-pit coal mine, Lianshao Coalfield are characterized by extremely-low-moisture contents, medium to high ash yields, low-sulfur contents, and low volatile matter yields.

The Nos. 3 and 5 coals in the Toushi mine are both significantly enriched in Li, with average Li concentration as high as 214 $\mu\text{g/g}$ and 160 $\mu\text{g/g}$, respectively. In addition, the No. 3 coal is also enriched in V, Cr, Sm, and Th, and the No. 5 coal is enriched in Sm and Pb. Lithium is more elevated in coal portions adjacent to the roof, parting, and floor of the coal seams, occurring in kaolinite, chlorite, and/or nanoscale cookeite. The average content of Li_2O in the coal ashes of the Nos. 3 and 5 coals both exceed the Extraction Standard for Li_2O in coal-bearing strata, indicating that the Nos 3 and 5 coals from the Toushi mine could be taken as promising sources for Li recovery.

The terrigenous detrital supply of the Ceshui Formation in the Lianshao Coalfield is mainly sourced from the granite in the Xuefeng Oldland. Weathering and leaching of the Li-enriched granitic source rocks transports soluble Li into the peat swamp of confined basins, where Li is further concentrated and enriched by the interaction of the Li-bearing terrigenous granitic debris with seawater and hydrothermal fluids infiltrated during the coalification process. The Toushi coals of the Ceshui Formation in the Lianshao Coalfield was predominantly formed in continental and marine transitional sedimentary environment, and Li was much more enriched in the Toushi coals during the sea regressive process due to the interaction of Li-bearing granitic debris with the infiltrated seawater. Furthermore, circulation of hydrothermal solutions (submarine hydrothermal fluids or acidic waters) in the coal-bearing basins and its interaction with Li-bearing granitic terrigenous material further promoted Li enrichment in the Toushi coals.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

JL: Conceptualization, Writing – original draft, Data curation, Investigation, Methodology, Project administration, Resources. YW: Conceptualization, Data curation, Investigation, Methodology, Writing – review & editing. HZ: Investigation, Validation, Writing – review & editing. AW: Validation, Writing – review & editing. XZ: Investigation, Resources, Writing – review & editing. XQ: Validation, Writing – review & editing. NM: Validation, Writing – review & editing. BL: Validation, Writing – review & editing.

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Conflict of interest

Author HZ was employed by the company Changsha Nonferrous Metallurgical Design and Research Institute Co., Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmars.2025.1523669/full#supplementary-material>

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