

## Major, trace and rare earth element geochemistry of coal and oil shale in the Yuqia area, Middle Jurassic Shimengou Formation, northern Qaidam Basin

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**Abstract.** Coal and oil shale in the Middle Jurassic Shimengou Formation of the northern Qaidam Basin (China) have been characterized and compared using total organic carbon (TOC) content, oil yield, and proximate as well as major, trace and rare earth element (REE) and X-ray powder diffraction (XRD) analyses.

The results show that coal is represented by lignite and bituminous coal and oil shale is of medium quality. In both coal and oil shale, Si, Al, K, Ti and Na originate from a mixed clastic sedimentary component comprised of clay minerals, quartz and feldspars. In coal, rare earth elements (REEs) are related to phosphate minerals, whereas those in oil shale have inorganic affinities and are mainly associated with clay minerals and quartz. REEs in coal and oil shale are of terrigenous origin. Both coal and oil shale in the Yuqia area are possibly the products of source rocks that have experienced moderate chemical weathering during a warm and humid climate, and they have similar source rocks of felsic volcanic and sedimentary rocks.

**Keywords:** Yuqia oil shale and coal, trace and rare earth elements, Middle Jurassic, Qaidam Basin.

### 1. Introduction

Coal and oil shale are found to coexist in many basins in China, such as Huadian [1], Meihe [2], Fushun [3], Ordos [4], Huangxian [5], etc. On the

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basis of occurrence and the size of reserves, a comprehensive exploration and development of these rocks can be carried out to improve the production efficiency, at the same time reducing the production costs. Many investigators have conducted a series of comparative studies on coexisting coal and oil shale [3, 6–8]. The characteristics of coal and oil shale depend on their contents of organic components (macerals) as well as minerals and other inorganic constituents (mineral matter) [9, 10]. The contents of some of the major and trace mineral–inorganic elements are closely related to the mineral content of clastic sedimentary rocks [11–16]. Rare earth elements (REEs) have the qualities of chemical stability, coherent behavior during different geochemical processes and predictable patterns of fractionation [17, 18]. As a result, trace and rare earth elements combined with major elements are widely used to study the paleoenvironment, paleoclimate, provenance and tectonic setting of clastic sedimentary rocks [19–23].

The Shimengou Formation in the Middle Jurassic Yuqia area is the main stratum of coexisting coal and oil shale. Some researchers have studied coal [24, 25] and oil shale [26, 27] seams separately with respect to quality, modes of occurrence of formation, and metallogenic regularities, but studies of their inorganic geochemistry, provenance and tectonic setting are rare. This article aims to compare coal and oil shale in the Yuqia area, Middle Jurassic Shimengou Formation, in terms of quality, and analyze their inorganic geochemistry, e.g. the modes of occurrence of major, trace and rare earth elements, as well as the provenance.

## 2. Geological setting

The Yuqia area is located in the central part of the northern Qaidam Basin in a long and narrow NE-trending zone. It is bordered by the Dakendaban Mountains in the north and east, and the Lvliang Mountains in the south (Fig. 1). The Lower Jurassic strata are missing in the Yuqia area.

The Upper Jurassic section consists of the Hongshuigou Formation and the Caishiling Formation. The Hongshuigou Formation is mostly composed of greyish-green and purplish-red siltstone and mudstone with fine sandstone interbedded. The Caishiling Formation is chiefly comprised of gray siltstone interbedded with conglomerate in the lower part.

The Middle Jurassic section consists of the Dameigou Formation and the Shimengou Formation. The former is primarily composed of gray sandy conglomerate, coarse-to-medium-grained sandstone and coal seams with abundant carbonaceous mudstone interbedded. The Shimengou Formation is the target layer, including the Coal-bearing Member and the Shale Member. Gray and black siltstone, mudstone and gray coarse-to-fine-grained sandstone are the main sediments and multilayered coal seams are found in the Coal-bearing Member. Black coals are filled with pyrite particles and the main

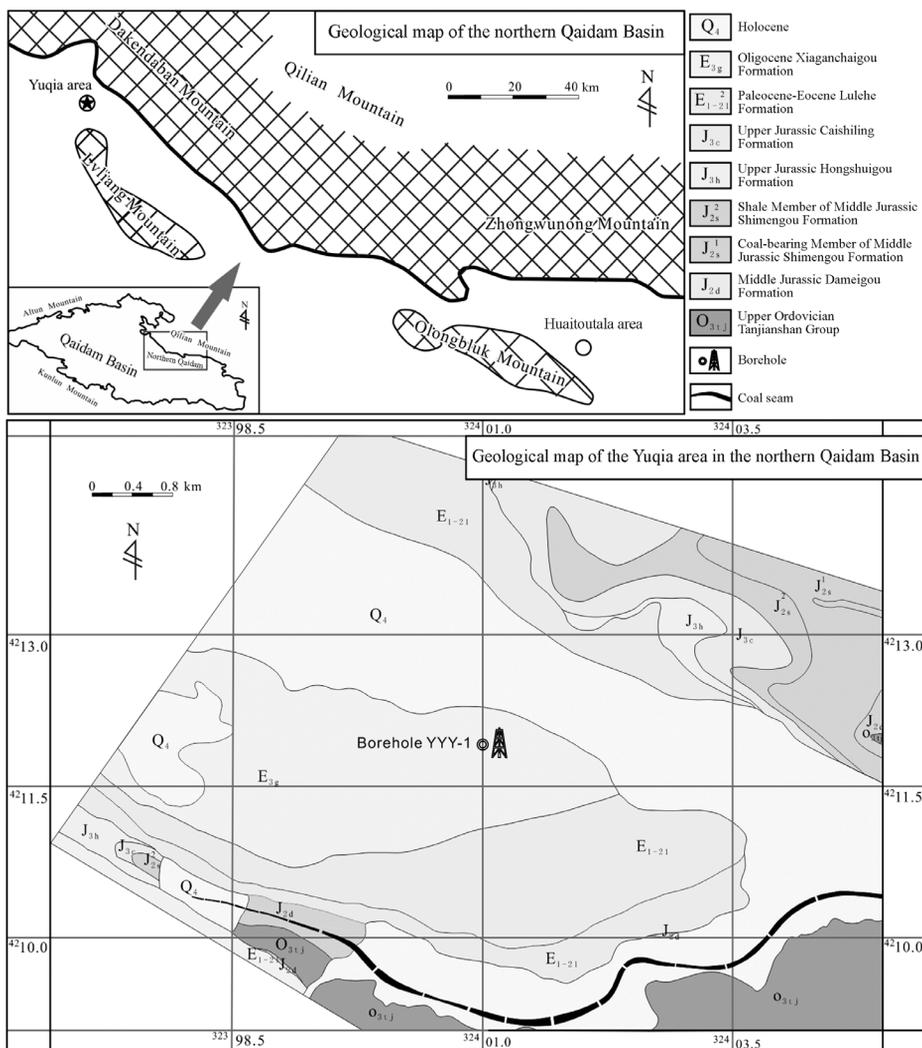


Fig. 1. Geological map of the Yuqia area in the Qaidam Basin.

depositional environments of the Coal-bearing Member are delta fronts and swamps. The Shale Member mainly consists of dark gray siltstone, mudstone and dark brown shale and oil shale. A shallow-to-deep lake is thought to be the main depositional environment. Large amounts of carbonate interlayers, siderite concretions, and ostracode and lamellibranch fossils are contained in oil shale. Laminations are highly developed in the Shale Member [24–28].

### 3. Materials and methods

Seven samples of coal from the Coal-bearing Member and twenty-three samples of oil shale from the Mudstone Member (Fig. 2) were collected to determine their total organic carbon (TOC) and total sulfur (TS) contents, trace, rare earth and major elements, and oil yield, as well as carry out proximate and X-ray powder diffraction (XRD) analyses.

#### 3.1. Total organic carbon, total sulfur, oil yield and proximate analysis

The total organic carbon and total sulfur contents as well as oil yield were determined and proximate analysis (including moisture and volatile matter contents, ash yield, and calorific value) was performed in the Key Laboratory for Oil Shale and Coexisting Minerals Mineralization & Exploration and Exploitation, Changchun of Jilin Province, China. The TOC and TS contents were analysed using a LECO CS-230, following the Chinese standard GB/T 19145-2003 [29] and ASTM standard D3177-02 (2007) [30], respectively. Oil yield was determined using low-temperature carbonization furnaces, following the Chinese Petroleum Chemical Industry Standard SH/T 0508-92 [31]. The moisture and volatile matter contents, ash yield, and calorific values were determined following the ASTM standards D3173-11 (2011), D3175-11 (2011), D3174-11 (2011) and D5865-13 (2013) [32–35]. The moisture content was calculated after the samples had been heated at a temperature of 105 °C until constant mass. Ash yield and volatile matter content were both determined using a muffle furnace X1-2000. The volatile matter content was calculated by the reduced proportion minus water content after the samples had been heated in the absence of air. The calorific value was determined using a DC5015 calorimeter.

#### 3.2. Major, trace and rare earth element analyses

Major, trace and rare earth elements were determined in the Analytical Laboratory of Beijing Research Institute of Uranium Geology. 25 to 50 mg samples were analyzed using the NexION300D inductively coupled plasma mass spectrometry (ICP-MS), following the technique described by Dai et al. [16]. Major elements contained in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  were identified using X-ray fluorescence (XRF) spectrometers AB104L, AL104 and AxiosmAX, following the analytical methods described by Kimura [36] and Dai et al. [16]. The analytical uncertainty was usually lower than 5%.

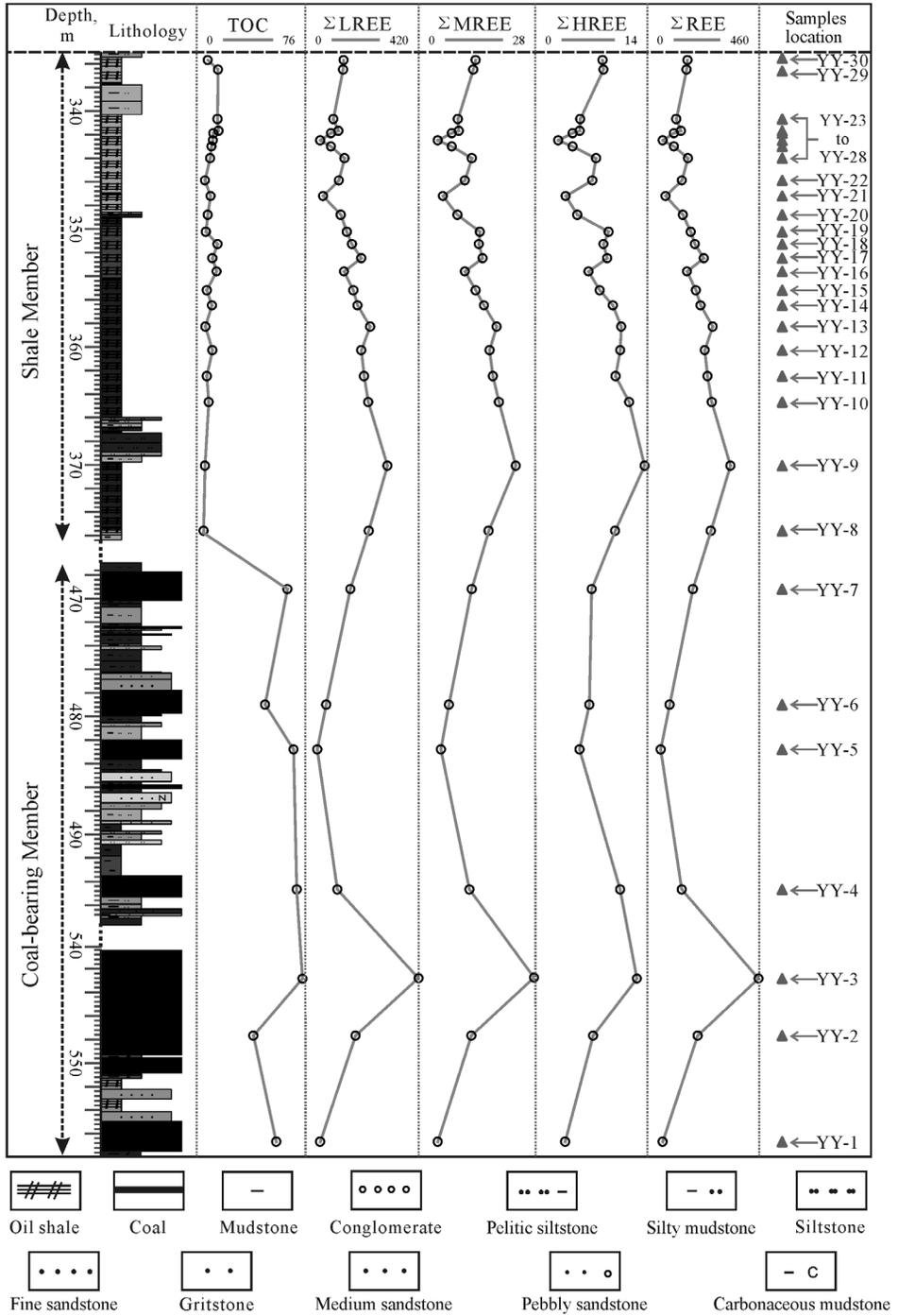


Fig. 2. Vertical distribution of REEs and samples location.

### 3.3. X-ray powder diffraction analysis

X-ray powder diffraction analysis was also performed in the Analytical Laboratory of Beijing Research Institute of Uranium Geology, following the method provided by Ward et al. [37, 38] and Ruan and Ward [39]. The Panalytical X'Pert PRO X-ray diffractometer was used to record X-ray spectrograms. Each mineral has a specific XRD pattern and the intensity of the characteristic peak in the spectrum positively correlates with the content of a mineral in the sample which can be determined through this relationship.

## 4. Results

### 4.1. Quality characterization of coal and oil shale

Coal in the Middle Jurassic Yuqia area can be classified into lignite and bituminous coal based on the Chinese national standard GB/T 5751-2009 [40]. The average content of TOC and TS are 60.00 wt% and 1.03%, respectively. The ash yield, water and volatile matter contents and calorific value are 30.81%, 3.84%, 35.64% and 19.43 MJ/kg, respectively (Table 1).

Oil shale in the Middle Jurassic Yuqia area has average TOC and TS contents of 9.21 wt% and 0.41%, respectively. Its oil yield is 6.43 wt%, ash yield 74.75%, water and volatile matter contents are 2.28% and 23.47%, respectively, and the calorific value is 4.25 MJ/kg (Table 1). The Yuqia area oil shale belongs to medium-quality oil shales [28].

### 4.2. Minerals in coal and oil shale

The mineralogical composition of coal samples from the Middle Jurassic Yuqia area comprises mainly clay minerals (29.2–76.4%) and quartz (10.2–30.6%). Some pyrite (3.6–26.6%), calcite (1.5–34%) and siderite (14.2%) can also be found in the coal samples. Kaolinite (52–100%) is the main component of clay minerals, and some samples also contain illite (25–36%) and an illite-smectite mixed layer (12–21%) (Table 2). The minerals in oil shale are chiefly clay minerals (25.5–72.1%), quartz (11.1–45%) and calcite (2.1–52.6%). In some oil shale samples aragonite may be quite abundant (15.9–51.6%), and some contain siderite (3.4–16.8%), plagioclase (5.6–8.5%) and dolomite (14.9%). The clay minerals in the the oil shale samples are primarily illite (14–52%), kaolinite (5–48%), an illite-smectite mixed layer (12–73%) and chlorite (4–11%), while in some samples smectite is present in high amounts, 56–75% (Table 2).

**Table 1. TOC content, oil yield and proximate analysis of coal and oil shale in the Middle Jurassic Yuqia area of the Qaidam Basin**

Sample No.	Lithology	TOC, wt%	TS, wt%	OY, wt%	A <sub>ad</sub> <sup>ad</sup> wt%	W <sub>ad</sub> <sup>ad</sup> wt%	V <sub>daf</sub> <sup>daf</sup> wt%	Q <sub>daf</sub> <sup>daf</sup> MJ/kg
YY-1	Coal	55.95	0.47	nd	42.94	2.96	30.42	16.20
YY-2	Coal	40.02	0.41	nd	35.02	4.68	37.46	18.30
YY-3	Coal	74.10	0.71	nd	21.60	4.46	44.40	29.33
YY-4	Coal	70.21	0.65	6.99	31.66	4.85	34.86	19.02
YY-5	Coal	67.90	1.80	nd	28.35	1.40	10.13	13.57
YY-6	Coal	48.10	2.37	9.30	29.63	3.86	59.32	18.80
YY-7	Coal	63.70	0.77	nd	26.48	4.67	32.87	20.80
Average		60.00	1.03	8.15	30.81	3.84	35.64	19.43
YY-8	Oil shale	4.15	0.19	4.02	83.54	1.59	14.77	1.87
YY-12	Oil shale	8.22	0.18	4.13	82.02	2.12	14.53	3.33
YY-13	Oil shale	6.41	0.12	4.35	84.14	2.59	13.26	2.39
YY-16	Oil shale	13.70	0.24	8.03	76.52	2.05	21.45	6.16
YY-18	Oil shale	8.85	0.22	4.67	81.00	2.76	15.62	3.56
YY-22	Oil shale	11.45	0.55	8.17	68.40	2.19	29.35	5.36
YY-24	Oil shale	10.70	0.16	9.17	62.90	1.96	35.18	4.69
YY-25	Oil shale	11.45	0.55	8.50	63.28	2.87	39.33	5.61
YY-27	Oil shale	15.35	1.49	10.20	70.75	3.74	27.55	7.31
YY-28	Oil shale	6.10	0.34	5.68	73.92	1.86	24.27	3.54
YY-30	Oil shale	4.97	0.46	3.79	75.74	1.38	22.84	2.92
Average		9.21	0.41	6.43	74.75	2.28	23.47	4.25

Note: nd denotes no data; TS denotes total sulfur; OY denotes oil yield; A denotes ash yield; W denotes moisture content; V denotes volatile matter; Q denotes calorific value; ad denotes air dried basis; daf denotes dry and ash-free basis.

**Table 2. Minerals present in coal and oil shale samples collected from borehole YYY-1 in the Yuqia area, Qaidam Basin**

Sample No.	Lithology	Relative content of minerals, [ $\omega(B)/10^{-2}$ ]				
		Quartz	Plagioclase	Calcite	Dolomite	Aragonite
YY-1	Coal	23.6	–	–	–	–
YY-2	Coal	–	–	–	–	–
YY-3	Coal	28.5	–	–	–	–
YY-4	Coal	10.2	–	34	–	–
YY-5	Coal	30.6	–	–	–	–
YY-6	Coal	–	–	–	–	–
YY-7	Coal	18.3	–	1.5	–	–
YY-8	Oil shale	30.7	–	–	–	–
YY-9	Oil shale	44.9	–	–	–	–
YY-10	Oil shale	27.9	–	–	–	–
YY-11	Oil shale	41.3	–	–	–	–
YY-12	Oil shale	38.9	–	–	–	–
YY-13	Oil shale	31.4	–	–	–	–
YY-14	Oil shale	37.4	–	–	–	–
YY-15	Oil shale	38.8	5.6	–	–	–
YY-16	Oil shale	43.1	8.5	–	–	–
YY-17	Oil shale	45	6.3	–	–	–
YY-18	Oil shale	31.8	–	13.8	–	–
YY-19	Oil shale	31.3	–	32.8	–	–
YY-20	Oil shale	41.4	–	–	–	–
YY-21	Oil shale	11.1	–	39	–	15.9
YY-22	Oil shale	14.4	–	52.6	–	–
YY-23	Oil shale	13.7	–	2.1	–	51.6
YY-24	Oil shale	13	–	18.8	14.9	27.8
YY-25	Oil shale	27.8	–	15.5	–	–
YY-26	Oil shale	18.2	–	19.2	–	–
YY-27	Oil shale	38.6	–	–	–	–
YY-28	Oil shale	14.9	–	39.8	–	–
YY-29	Oil shale	32.5	–	6.2	–	–
YY-30	Oil shale	16.8	–	37.5	–	–

Note: – denotes not determined.

Continuation of Table 2.

Relative content of minerals, [ $\omega(B)/10^{-2}$ ]			Relative content of clay minerals, [ $\omega(B)/10^{-2}$ ]				
Siderite	Pyrite	Clay minerals	Smectite	Illite/ smectite	Illite	Kaolinite	Chlorite
–	–	76.4	–	12	28	60	–
–	–	–	–	–	–	100	–
–	–	71.5	–	14	26	60	–
–	26.6	29.2	–	–	–	100	–
14.2	–	55.2	–	12	36	52	–
–	–	–	–	–	–	100	–
–	3.6	76.6	–	21	25	54	–
11.9	–	57.4	–	28	31	32	9
–	–	55.1	4	22	36	30	8
–	–	72.1	–	19	46	26	9
–	–	58.7	–	22	45	24	9
3.4	–	57.7	–	17	52	22	9
–	–	68.6	–	49	21	22	8
3.7	–	58.9	–	12	35	48	5
–	–	55.6	–	46	24	20	10
–	–	48.4	–	40	25	35	–
–	–	48.7	–	26	40	23	11
–	–	54.4	–	30	41	29	–
–	–	35.9	–	46	34	16	4
–	–	58.6	–	29	46	19	6
8.3	–	25.7	–	73	22	5	–
–	–	33	72	–	14	10	4
–	–	32.6	56	–	26	18	–
–	–	25.5	75	–	17	8	–
–	–	56.7	–	35	39	26	–
13.7	–	48.9	–	44	27	29	–
–	–	61.4	–	22	37	41	–
7.9	–	37.4	–	45	31	24	–
16.8	–	44.5	–	17	45	29	9
10.8	–	34.9	–	23	35	34	8

### 4.3. Rare earth element concentrations and normalized patterns

#### 4.3.1. Rare earth element concentrations

A total of 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were analyzed. They were classified into light REEs (LREEs – La, Ce, Pr, Nd, Sm), medium REEs (MREEs – Eu, Gd, Tb, Dy) and heavy REEs (HREEs – Ho, Er, Tm, Yb, Lu), based on the grouping by Seredin and Dai [17] and Dai et al. [18]. The total concentration of REEs ( $\Sigma$ REE) of Yuqia coal is 172.77  $\mu\text{g/g}$  on average, which is higher than the respective average figure for Chinese coals (117.7  $\mu\text{g/g}$  [41]), US coals (54  $\mu\text{g/g}$  [42]) and coals worldwide (60  $\mu\text{g/g}$  [43]). The total concentration of LREEs ( $\Sigma$ LREE) of Yuqia coal is 45.87–417.60  $\mu\text{g/g}$  (average 153.27  $\mu\text{g/g}$ ), constituting about 89% of  $\Sigma$ REE. The concentration of HREEs ( $\Sigma$ HREE) is 3.75–12.72  $\mu\text{g/g}$  (7.70  $\mu\text{g/g}$  on average), making up only 4% of  $\Sigma$ REE, whereas the average concentration of MREEs ( $\Sigma$ MREE) is 11.80  $\mu\text{g/g}$  (4.63–27.48  $\mu\text{g/g}$ ), accounting for about 7% of  $\Sigma$ REE.

The Shimengou Formation oil shale has an average REE concentration of 183.36  $\mu\text{g/g}$ , which is higher than the upper continental crust (UCC) average 146.40  $\mu\text{g/g}$  [44] and the North American Shale Composite (NASC) average 173.20  $\mu\text{g/g}$  [45]).  $\Sigma$ LREE of Shimengou oil shale is 56.11–304.90  $\mu\text{g/g}$  (average 162.19  $\mu\text{g/g}$ ) and makes up 88% of  $\Sigma$ REE, being higher than the average for Chinese oil shales (61.48  $\mu\text{g/g}$  [46]) and Australian oil shales (63.00  $\mu\text{g/g}$  [47]).  $\Sigma$ HREE is 2.88–13.69  $\mu\text{g/g}$  (average 7.93  $\mu\text{g/g}$ ) and makes up only 4% of  $\Sigma$ REE, which is also higher than Chinese oil shales average (6.71  $\mu\text{g/g}$  [46]) but lower than Australian oil shales average (14.40  $\mu\text{g/g}$  [47]). The total average concentration of MREEs ( $\Sigma$ MREE) of Shimengou oil shale, 13.24  $\mu\text{g/g}$  (4.70–23.34  $\mu\text{g/g}$ ), is similar to that of coal, and also forms about 7% of  $\Sigma$ REE.

#### 4.3.2. Chondrite-normalized patterns

REE abundances in coal and oil shale are normalized to chondrite (Fig. 3) and similar distribution trends are displayed for all samples. The average ratios of  $\Sigma$ LREE/ $\Sigma$ HREE (L/H) for coal and oil shale are 19.91 and 20.45, respectively, showing LREE enrichment and HREE deficit [48, 49]. The average values of  $(\text{La}/\text{Yb})_{\text{N}}$ ,  $(\text{Ce}/\text{Yb})_{\text{N}}$ ,  $(\text{La}/\text{Sm})_{\text{N}}$  and  $(\text{Gd}/\text{Yb})_{\text{N}}$  for coal are 8.12, 5.65, 4.59 and 1.25, respectively, and for oil shale 8.31, 6.07, 3.92 and 1.43, respectively. All these values are in agreement with LREE enrichment and HREE deficit figures given above. For comparison, LREEs in oil shale are more enriched than in coal [17].

All the chondrite-normalized patterns have shown a certain degree of negative Eu anomaly and negligible Ce anomaly (the average values of  $\text{Eu}/\text{EuN}^*$  for coal and oil shale are 0.60 and 0.67, respectively, and  $\text{Ce}/\text{CeN}^*$  are 0.94 and 0.96, respectively ([48]; Table 3; Fig. 3). Compared with oil shale, coal has shown a higher degree of Ce abnormality.

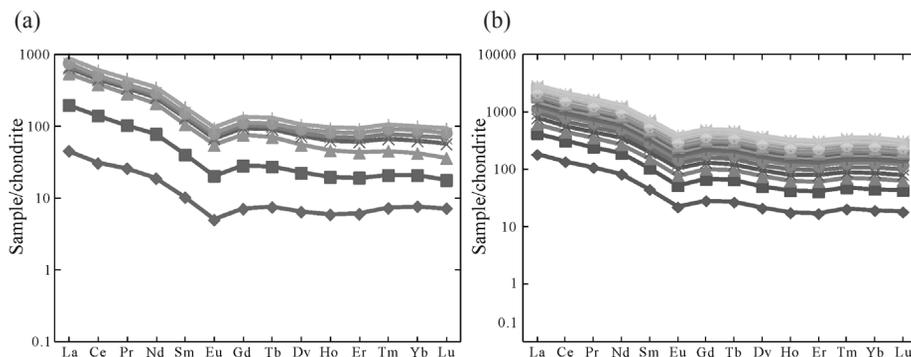


Fig. 3. Chondrite-normalized patterns for: a) coal, b) oil shale.

## 5. Discussion

### 5.1. Modes of occurrence of major elements

#### 5.1.1. Modes of occurrence of major elements in coal

$\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$  and  $\text{Na}_2\text{O}$  in coal are highly correlated with ash yield (the coefficients are 0.72–0.84) and between themselves (Table 4). The major elements Si, Al, Mg, K, Ti and Na are related to detrital minerals such as quartz and clays [51–53], indicating that they originate from a mixed clay assemblage.

$\text{SiO}_2$ ,  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  have a very strong positive correlation with ash yield ( $R^2 \geq 0.72$ ) (Table 4). Si is mostly contained in quartz and aluminosilicate minerals, which are the major components of ash [36, 54].  $\text{Al}_2\text{O}_3$  is present in aluminosilicate minerals, and  $\text{K}_2\text{O}$  is related to illite, which is contained in K-bearing clay minerals in the form of interlayer cations [36, 55]. The strong correlation of these compounds with ash yield indicate the enrichment of clay minerals and quartz in the samples. Most samples have relatively low ratios of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  (0.44–0.60; Table 5), suggesting the quartz source of Si besides clay minerals [2, 53]. These values agree with the amounts of quartz, kaolinite, illite and an illite-smectite mixed layer determined by XRD in coal (Table 2).

Mg might be related to carbonate minerals or Mg-bearing clay minerals (via illite and an illite-smectite mixed layer and montmorillonite [36, 56]). In the Yuqia area, MgO in coal has exhibited a high positive correlation with ash yield (0.79), indicating its possible relation to illite and an illite-smectite mixed layer (Table 2). Ti mainly occurs in titanium oxide and is correlated with organic matter and clay minerals [57–59]. The correlation coefficients of 0.90 for  $\text{TiO}_2\text{-Al}_2\text{O}_3$ , 0.78 for  $\text{TiO}_2\text{-ash yield}$  and 0.55 for  $\text{TiO}_2\text{-TOC}$  give evidence of the strong positive relationship between the components. Na is mostly present in alkali feldspar or clay minerals other than in porewater

**Table 3. Rare earth element concentrations of Yuqia coal and oil shale,  $\mu\text{g/g}$** 

Sample No.	Lithology	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
YY-1	Coal	14.10	24.80	3.11	11.30	2.04	0.37	1.84	0.35	2.07	0.43	1.26	0.23	1.60	0.23
YY-2	Coal	46.90	89.70	9.35	35.70	6.03	1.14	5.50	0.94	5.16	0.99	2.77	0.44	2.75	0.34
YY-3	Coal	108.00	196.00	21.80	78.60	13.20	2.55	12.50	2.03	10.40	1.91	4.98	0.79	4.46	0.58
YY-4	Coal	33.40	49.10	6.43	25.70	4.75	0.93	4.76	0.92	5.64	1.25	3.72	0.69	4.33	0.66
YY-5	Coal	9.64	21.70	2.53	9.92	2.08	0.38	1.93	0.41	2.67	0.60	1.86	0.36	2.39	0.38
YY-6	Coal	24.20	34.60	3.62	13.80	2.55	0.52	2.62	0.54	3.61	0.79	2.36	0.44	2.80	0.41
YY-7	Coal	38.10	78.20	9.41	35.90	6.62	1.16	5.74	0.98	4.93	0.92	2.56	0.45	2.75	0.41
Average		39.19	70.59	8.04	30.13	5.32	1.01	4.98	0.88	4.93	0.98	2.79	0.49	3.01	0.43
YY-8	Oil shale	56.00	109.00	12.80	48.90	8.85	1.61	7.30	1.25	6.71	1.25	3.53	0.65	3.98	0.57
YY-9	Oil shale	73.00	141.00	16.20	62.90	11.80	2.20	10.00	1.79	9.35	1.78	4.93	0.86	5.32	0.80
YY-10	Oil shale	57.70	105.00	12.80	49.70	9.27	1.87	8.23	1.42	7.82	1.45	4.27	0.70	4.69	0.64
YY-11	Oil shale	53.10	98.90	12.00	46.60	8.79	1.78	7.82	1.27	6.98	1.27	3.64	0.59	4.04	0.53
YY-12	Oil shale	51.60	93.50	11.30	44.00	8.43	1.68	7.43	1.22	6.80	1.30	3.76	0.63	4.37	0.60
YY-13	Oil shale	59.10	109.00	13.00	49.80	9.56	1.78	8.16	1.41	7.41	1.40	3.85	0.67	4.23	0.63
YY-14	Oil shale	47.70	88.90	10.40	39.80	7.49	1.47	6.72	1.14	6.36	1.20	3.48	0.59	3.92	0.55
YY-15	Oil shale	42.80	80.60	9.67	38.00	7.02	1.30	6.04	1.03	5.37	1.02	2.88	0.51	3.20	0.47
YY-16	Oil shale	35.30	66.40	7.71	30.10	5.63	1.13	4.76	0.82	4.44	0.88	2.38	0.42	2.63	0.40
YY-17	Oil shale	52.20	95.60	11.20	42.40	7.71	1.61	6.76	1.10	5.95	1.06	3.18	0.54	3.76	0.49
YY-18	Oil shale	40.60	80.30	9.34	35.90	6.89	1.51	6.12	1.04	5.79	1.10	3.14	0.51	3.36	0.43
YY-19	Oil shale	36.00	70.40	8.54	33.90	6.61	1.36	5.91	1.10	6.34	1.20	3.28	0.60	3.61	0.52
YY-20	Oil shale	31.80	59.70	7.33	28.10	5.04	0.97	4.12	0.68	3.54	0.65	1.84	0.32	2.15	0.31
YY-21	Oil shale	16.20	30.00	3.47	13.60	2.57	0.61	2.37	0.42	2.44	0.48	1.41	0.22	1.50	0.20
YY-22	Oil shale	30.00	57.70	6.50	25.80	4.99	1.04	4.53	0.82	4.78	0.95	2.59	0.45	2.76	0.38
YY-23	Oil shale	33.40	68.10	7.75	31.40	5.98	1.29	5.35	0.96	5.18	1.01	2.76	0.49	2.93	0.43
YY-24	Oil shale	21.90	46.40	5.02	19.60	3.71	0.81	3.34	0.59	3.28	0.61	1.71	0.28	1.82	0.27
YY-25	Oil shale	13.50	26.10	2.95	11.40	2.16	0.46	1.96	0.37	1.91	0.38	1.02	0.18	1.15	0.15
YY-26	Oil shale	23.50	44.00	5.23	20.20	3.82	0.75	3.41	0.61	3.22	0.63	1.69	0.29	1.82	0.27
YY-27	Oil shale	29.60	56.50	6.81	26.30	4.95	0.97	4.25	0.72	3.79	0.72	2.03	0.35	2.17	0.31
YY-28	Oil shale	25.50	48.00	5.56	21.40	4.15	0.87	3.78	0.67	4.18	0.72	2.00	0.33	2.28	0.30
YY-29	Oil shale	33.30	64.70	7.51	29.60	5.98	1.26	5.27	0.95	5.69	1.07	3.42	0.47	3.20	0.41
YY-30	Oil shale	32.90	65.60	7.76	30.50	5.97	1.32	5.52	1.00	5.92	1.10	3.09	0.51	3.33	0.43
Average		38.99	74.15	8.73	33.91	6.41	1.29	5.62	0.97	5.36	1.01	2.86	0.48	3.14	0.44
Chondrite		0.31	0.81	0.12	0.60	0.20	0.07	0.26	0.05	0.32	0.07	0.21	0.03	0.21	0.03

Note:  $\Sigma\text{LREE}$  – total content of light rare earth elements ( $\Sigma\text{LREE} = \text{La} + \text{Ce} + \text{Pr} + \text{Nd} + \text{Sm}$ );  $\Sigma\text{MREE}$  – total content of medium rare earth elements ( $\Sigma\text{MREE} = \text{Eu} + \text{Gd} + \text{Tb} + \text{Dy}$ );  $\Sigma\text{HREE}$  – total content of heavy rare earth elements ( $\Sigma\text{HREE} = \text{Ho} + \text{Er} + \text{Tm} + \text{Yb} + \text{Lu}$ );  $\Sigma\text{REE}$  – total content of rare earth elements ( $\Sigma\text{REE} = \Sigma\text{LREE} + \Sigma\text{MREE} + \Sigma\text{HREE}$ );  $L/H = \Sigma\text{LREE}/\Sigma\text{HREE}$ ;  $N$  – chondrite-normalized;  $\text{Eu}/\text{Eu}_N^* = \text{Eu}_N/(\text{Sm}_N \times \text{Gd}_N)^{1/2}$ ,  $\text{Eu}_N$ ,  $\text{Sm}_N$  and  $\text{Gd}_N$  represent the chondrite-normalized value;  $\text{Ce}/\text{Ce}_N^* = \text{Ce}_N/(\text{La}_N \times \text{Pr}_N)^{1/2}$ ,  $\text{Ce}_N$ ,  $\text{La}_N$  and  $\text{Pr}_N$  represent the chondrite-normalized value [50].  
Data source: Chondrite [45].

Continuation of Table 3.

$\Sigma$ LREE	$\Sigma$ MREE	$\Sigma$ HREE	$\Sigma$ REE	L/H	(La/Lu)N	(La/Yb)N	(Ce/Yb)N	(La/Sm)N	(Gd/Yb)N	Eu/EuN*	Ce/CeN*
55.35	4.63	3.75	63.73	14.76	5.93	5.94	4.00	4.46	0.92	0.59	0.89
187.68	12.74	7.29	207.71	25.74	13.35	11.50	8.42	5.02	1.61	0.61	1.02
417.6	27.48	12.72	457.8	32.83	18.02	16.33	11.34	5.28	2.25	0.61	0.96
119.38	12.25	10.65	142.28	11.21	4.90	5.20	2.93	4.54	0.88	0.60	0.80
45.87	5.39	5.59	56.85	8.21	2.46	2.72	2.34	2.99	0.65	0.59	1.05
78.77	7.29	6.8	92.86	11.58	5.71	5.83	3.19	6.12	0.75	0.62	0.88
168.23	12.81	7.09	188.13	23.73	8.99	9.34	7.34	3.71	1.68	0.58	0.98
153.27	11.8	7.7	172.77	19.91	8.48	8.12	5.65	4.59	1.25	0.60	0.94
235.55	16.87	9.98	262.4	23.60	9.51	9.49	7.07	4.08	1.47	0.62	0.97
304.9	23.34	13.69	341.93	22.27	8.83	9.25	6.84	3.99	1.51	0.62	0.98
234.47	19.34	11.75	265.56	19.95	8.72	8.29	5.78	4.02	1.41	0.66	0.92
219.39	17.85	10.07	247.31	21.79	9.70	8.86	6.32	3.90	1.56	0.66	0.93
208.83	17.13	10.66	236.62	19.59	8.32	7.96	5.52	3.95	1.37	0.65	0.92
240.46	18.76	10.78	270	22.31	9.08	9.42	6.65	3.99	1.55	0.62	0.94
194.29	15.69	9.74	219.72	19.95	8.39	8.20	5.85	4.11	1.38	0.64	0.95
178.09	13.74	8.08	199.91	22.04	8.81	9.02	6.50	3.93	1.52	0.62	0.94
145.14	11.15	6.71	163	21.63	8.54	9.05	6.51	4.05	1.45	0.67	0.96
209.11	15.42	9.03	233.56	23.16	10.31	9.36	6.56	4.37	1.45	0.69	0.94
173.03	14.46	8.54	196.03	20.26	9.14	8.15	6.17	3.80	1.46	0.72	0.98
155.45	14.71	9.21	179.37	16.88	6.70	6.72	5.03	3.51	1.32	0.67	0.96
131.97	9.31	5.27	146.55	25.04	9.93	9.97	7.16	4.07	1.54	0.66	0.93
65.84	5.84	3.81	75.49	17.28	7.84	7.28	5.16	4.07	1.27	0.77	0.95
124.99	11.17	7.13	143.29	17.53	7.64	7.33	5.39	3.88	1.32	0.67	0.98
146.63	12.78	7.62	167.03	19.24	7.52	7.69	6.00	3.60	1.47	0.70	1.01
96.63	8.02	4.69	109.34	20.60	7.85	8.11	6.58	3.81	1.48	0.71	1.05
56.11	4.7	2.88	63.69	19.48	8.71	7.91	5.86	4.03	1.37	0.69	0.98
96.75	7.99	4.7	109.44	20.59	8.42	8.71	6.24	3.97	1.51	0.64	0.95
124.16	9.73	5.58	139.47	22.25	9.24	9.20	6.72	3.86	1.57	0.65	0.95
104.61	9.5	5.63	119.74	18.58	8.23	7.54	5.43	3.96	1.33	0.67	0.96
141.09	13.17	8.57	162.83	16.46	7.86	7.02	5.22	3.59	1.32	0.69	0.97
142.73	13.76	8.46	164.95	16.87	7.40	6.66	5.08	3.56	1.33	0.71	0.98
162.19	13.24	7.93	183.36	20.45	8.55	8.31	6.07	3.92	1.43	0.67	0.96
2.04	0.7	0.55	3.29	3.71	1.00	1.00	1.00	1.03	1.00	1.01	0.99

**Table 4. The correlation coefficients ( $R^2$ ) between  $\Sigma$ REE, total sulfur, TOC, and major and rare earth elements of Yuqia coal**

	TOC	S <sup>T</sup>	Ash	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>T</sup>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	Ti <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	$\Sigma$ REE	Th	U	Li	Be	Sc	V	Cr	
TOC	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
S <sup>T</sup>	-0.18	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Ash	0.14	-0.34	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
SiO <sub>2</sub>	0.49	-0.57	0.81	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Al <sub>2</sub> O <sub>3</sub>	0.27	-0.36	0.72	0.91	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Fe <sup>T</sup>	-0.51	0.84	-0.26	-0.65	-0.44	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
MgO	0.51	-0.56	0.79	1.00	0.92	-0.65	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
CaO	-0.06	0.96	-0.14	-0.42	-0.27	0.86	-0.41	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Na <sub>2</sub> O	0.59	-0.69	0.74	0.97	0.81	-0.78	0.97	-0.54	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□
K <sub>2</sub> O	0.45	-0.56	0.84	1.00	0.91	-0.63	0.99	-0.42	0.97	1.00	□	□	□	□	□	□	□	□	□	□	□	□
MnO	-0.16	0.98	-0.20	-0.46	-0.26	0.90	-0.46	0.98	-0.61	-0.46	1.00	□	□	□	□	□	□	□	□	□	□	□
Ti <sub>2</sub> O	0.55	-0.57	0.78	1.00	0.90	-0.68	1.00	-0.42	0.98	0.99	-0.47	1.00	□	□	□	□	□	□	□	□	□	□
P <sub>2</sub> O <sub>5</sub>	-0.74	0.34	-0.49	-0.56	-0.24	0.44	-0.56	0.19	-0.67	-0.57	0.32	-0.57	1.00	□	□	□	□	□	□	□	□	□
$\Sigma$ REE	-0.36	0.49	-0.55	-0.38	-0.01	0.43	-0.35	0.29	-0.51	-0.40	0.42	-0.38	0.72	1.00	□	□	□	□	□	□	□	□
Th	-0.04	0.17	-0.24	0.11	0.44	0.01	0.14	0.05	-0.02	0.07	0.16	0.12	0.53	0.84	1.00	□	□	□	□	□	□	□
U	-0.20	0.26	-0.10	0.13	0.50	0.18	0.15	0.14	-0.04	0.11	0.26	0.12	0.51	0.86	0.95	1.00	□	□	□	□	□	□
Li	0.65	-0.56	0.63	0.95	0.84	-0.70	0.95	-0.46	0.96	0.94	-0.51	0.95	-0.67	-0.30	0.15	0.14	1.00	□	□	□	□	□
Be	-0.26	-0.60	0.46	0.25	0.12	-0.39	0.22	-0.46	0.29	0.27	-0.49	0.25	0.05	-0.60	-0.41	-0.45	0.01	1.00	□	□	□	□
Sc	-0.20	-0.39	0.59	0.54	0.64	-0.32	0.53	-0.27	0.45	0.54	-0.24	0.54	0.26	-0.11	0.25	0.24	0.28	0.71	1.00	□	□	□
V	0.02	-0.63	0.69	0.73	0.72	-0.58	0.72	-0.49	0.68	0.73	-0.49	0.73	-0.02	-0.32	0.12	0.09	0.51	0.75	0.95	1.00	□	□
Cr	0.44	-0.33	0.30	0.74	0.86	-0.55	0.77	-0.31	0.67	0.70	-0.27	0.76	-0.08	0.25	0.72	0.64	0.76	-0.09	0.50	0.57	1.00	□
Co	-0.06	0.61	0.19	-0.19	-0.15	0.56	-0.20	0.77	-0.28	-0.18	0.72	-0.18	0.15	-0.16	-0.21	-0.18	-0.39	0.17	0.22	0.03	-0.29	□
Ni	0.07	-0.25	0.87	0.70	0.69	-0.22	0.68	-0.04	0.60	0.71	-0.08	0.69	-0.16	-0.43	-0.06	0.00	0.44	0.63	0.85	0.85	0.39	□
Cu	-0.22	0.02	-0.44	-0.08	0.22	-0.04	-0.05	-0.20	-0.14	-0.10	-0.06	-0.08	0.54	0.87	0.89	0.85	0.04	-0.45	0.01	-0.07	0.51	□
Zn	-0.12	-0.19	0.21	0.04	-0.01	-0.15	0.03	-0.03	0.04	0.03	-0.06	0.07	0.26	-0.38	-0.20	-0.32	-0.21	0.81	0.69	0.61	-0.04	□
Ga	0.46	-0.37	0.93	0.93	0.80	-0.41	0.91	-0.18	0.88	0.94	-0.25	0.91	-0.69	-0.53	-0.15	-0.05	0.84	0.23	0.42	0.59	0.49	□
Rb	0.62	-0.48	0.64	0.90	0.77	-0.60	0.90	-0.39	0.91	0.90	-0.45	0.89	-0.75	-0.32	0.05	0.10	0.97	-0.09	0.13	0.37	0.63	□
Sr	-0.47	0.58	-0.43	-0.37	0.03	0.55	-0.35	0.40	-0.53	-0.38	0.53	-0.39	0.76	0.98	0.80	0.87	-0.35	-0.53	-0.02	-0.27	0.19	□
Mo	-0.60	0.13	0.23	0.12	0.42	0.31	0.12	0.00	-0.05	0.16	0.11	0.05	0.38	0.55	0.47	0.70	0.06	-0.18	0.22	0.10	0.21	□
Cd	-0.70	-0.46	0.33	0.19	0.32	-0.14	0.17	-0.54	0.13	0.23	-0.45	0.13	0.35	0.09	0.11	0.25	0.05	0.49	0.52	0.50	0.08	□
In	0.45	-0.45	0.58	0.90	0.92	-0.57	0.91	-0.41	0.85	0.89	-0.41	0.89	-0.44	-0.01	0.41	0.44	0.95	-0.11	0.33	0.50	0.85	□
Sb	0.15	-0.67	0.91	0.83	0.68	-0.57	0.81	-0.49	0.83	0.85	-0.55	0.81	-0.46	-0.67	-0.29	-0.23	0.66	0.70	0.69	0.85	0.35	□
Cs	0.65	-0.47	0.61	0.89	0.77	-0.60	0.90	-0.38	0.90	0.89	-0.44	0.88	-0.75	-0.30	0.08	0.12	0.98	-0.13	0.11	0.35	0.66	□
Ba	-0.49	0.57	-0.38	-0.34	0.07	0.56	-0.31	0.40	-0.51	-0.34	0.53	-0.35	0.75	0.97	0.80	0.88	-0.33	-0.51	0.01	-0.24	0.21	□
W	-0.33	-0.02	-0.36	-0.57	-0.73	0.21	-0.59	-0.13	-0.45	-0.54	-0.14	-0.60	-0.11	-0.19	-0.62	-0.54	-0.46	-0.07	-0.67	-0.61	-0.81	□
Tl	-0.28	0.58	-0.06	-0.57	-0.66	0.72	-0.59	0.64	-0.57	-0.53	0.58	-0.60	-0.05	-0.28	-0.68	-0.55	-0.64	-0.02	-0.42	-0.53	-0.89	□
Pb	0.41	-0.48	0.31	0.76	0.85	-0.65	0.79	-0.47	0.72	0.73	-0.43	0.78	-0.12	0.20	0.67	0.59	0.80	-0.04	0.48	0.59	0.98	□
Bi	0.40	-0.55	0.11	0.63	0.68	-0.70	0.65	-0.61	0.64	0.60	-0.57	0.64	-0.18	0.24	0.60	0.52	0.76	-0.19	0.20	0.36	0.86	□
Nb	0.54	-0.50	0.80	0.97	0.85	-0.58	0.97	-0.36	0.95	0.97	-0.42	0.96	-0.71	-0.41	0.01	0.06	0.96	0.10	0.34	0.55	0.64	□
Ta	0.65	-0.33	0.55	0.86	0.80	-0.50	0.87	-0.26	0.84	0.85	-0.30	0.86	-0.66	-0.13	0.25	0.28	0.96	-0.26	0.10	0.30	0.74	□
Zr	0.47	-0.63	0.84	0.97	0.83	-0.69	0.96	-0.44	0.96	0.97	-0.50	0.97	-0.56	-0.54	-0.04	-0.05	0.87	0.45	0.63	0.82	0.64	□
Hf	0.55	-0.55	0.80	1.00	0.89	-0.65	1.00	-0.41	0.98	0.99	-0.46	0.99	-0.63	-0.40	0.07	0.09	0.97	0.20	0.46	0.67	0.72	□

Note: Fe<sup>T</sup> represents total Fe.



[2, 36, 53]. Na<sub>2</sub>O in coal has a relatively strong positive correlation with ash yield, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO and TiO<sub>2</sub> ( $R^2 \geq 0.74$ ) (Table 4), indicating the existence of Na-bearing clay minerals and an illite-smectite mixed layer or minor alkali feldspar. In addition, the TOC content in coal is also positively correlated with SiO<sub>2</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O and Ti<sub>2</sub>O (0.45–0.59; Table 4), giving evidence of that clay minerals in coal have some affinity for organic matter. The above results suggest the dominance of clay minerals in the inorganic fraction of coal samples.

Fe is chiefly present in siderite, pyrite, ferrous sulfate and iron oxide, and it is commonly related to pyrite in high-sulfur coal [36, 60]. This is also the case with the coal of the studied area. The TS content in coal has a solid positive correlation with Fe<sup>T</sup> ( $R^2 = 0.84$ ) (Fig. 4a), while pyrite is present in some samples (Table 2). CaO and MnO have a strong positive correlation between themselves ( $R^2 = 0.98$ ) (Fig. 4b), and both are highly correlated with Fe<sup>T</sup> and S (0.86–0.98) (Table 4), implying that Mn in coal is related to calcite, and Ca and Mn in calcite are associated with pyrite.

### 5.1.2. Modes of occurrence of major elements in oil shale

SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and TiO<sub>2</sub> in oil shale are relatively strongly correlated with ash yield (0.50–0.63) and also each other (Table 6). This suggests their origin from a mixed clay assemblage, similarly to coal. Oil shale samples have relatively low ratios of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> below 0.40 (Table 5), indicating the presence of quartz in addition to clay minerals. This result complies with the amount of quartz contained in oil shale samples (Table 2). Unlike coal, TiO<sub>2</sub> in oil shale has a negative correlation with TOC (–0.26), suggesting that Ti in oil shale is only associated with clastic minerals and has no affinity for organic matter.

Na<sub>2</sub>O in oil shale has a strong positive correlation with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and TiO<sub>2</sub> (0.72–0.87; Table 6), indicating that clay minerals are responsible for the generation of Na. The content of Na<sub>2</sub>O in oil shale (average 0.47 wt%) is higher than in coal (average 0.16 wt%) (Table 5), which proves that besides clay minerals, also plagioclase (Table 2) contributes to the abundance of Na.

The CaO content in oil shale (average 12.51 wt%) is much higher than in coal (average 0.96 wt%) (Table 5), and the contribution of dolomite, aragonite and plagioclase to the presence of Ca in oil shale cannot be ignored (Table 2). Ca is considered to occur in not just one form and it can be present in carbonate and organic associations [36, 51]. The positive correlation between CaO and MgO (0.42) (Fig. 4c) in oil shale indicates the contribution of dolomite. It is worth noting that Ca-bearing fossils such as bivalves and ostracods are present in the Yuqia oil shale in high amounts [27] and are responsible for the abundance of Ca in oil shale samples.

Fe<sup>T</sup> in oil shale exhibits no relationship with total sulfur, but has a relatively strong positive correlation with ash yield (0.55), which demonstrates the

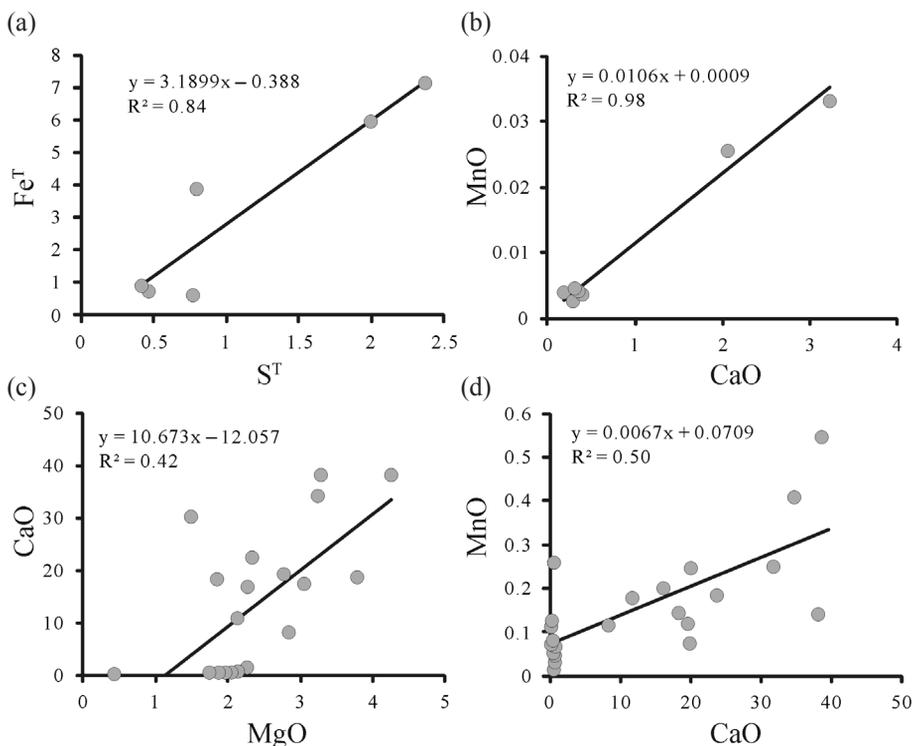


Fig. 4. Correlation diagrams of selected elements in coal and oil shale samples.

affinity of Fe for clay minerals besides siderite. MnO in oil shale has a positive correlation with  $Fe^T$  (0.35) and CaO (0.50) (Fig. 4d), suggesting that Mn in oil shale is associated with carbonate minerals.  $P_2O_5$  in oil shale has a relatively strong positive correlation with CaO (0.71) and MnO (0.43), which gives evidence of the important role of carbonate minerals in the rich generation of P.

## 5.2. Affinities of trace elements

### 5.2.1. Affinities of trace elements in coal

In the Yuqia coal, the elements Li, Sc, V, Ni, Ga, Rb, In, Sb, Cs, Nb, Ta, Zr and Hf are strongly correlated with ash yield ( $\geq 0.55$ ; Table 4), indicating the prevailing inorganic affinities of these elements. All of these elements, except Sc, have a good correlation with  $SiO_2$ ,  $Al_2O_3$ , MgO,  $Na_2O$ ,  $K_2O$  and  $Ti_2O$  ( $\geq 0.60$ ; Table 4), suggesting their association also with clay minerals in coal. It should be noted that Li, Rb, Cs, Nb, Ta, and Hf are also positively correlated with TOC ( $\geq 0.54$ ), which points towards a certain degree of organic affinity of these elements.

Cr, Pb and Bi show a relatively weak correlation with ash yield (0.30, 0.31 and 0.11, respectively; Table 4). At the same time, their correlation coefficients with TOC are relatively high (0.44, 0.41 and 0.40, respectively),

**Table 5. Major component concentrations in Yuqia coal and oil shale**

Sample No.	Lithology	SiO <sub>2</sub> , wt%	Al <sub>2</sub> O <sub>3</sub> , wt%	Fe <sup>T</sup> , wt%	MgO, wt%	CaO, wt%	Na <sub>2</sub> O, wt%	K <sub>2</sub> O, wt%	MnO, wt%	Ti <sub>2</sub> O <sub>3</sub> , wt%	P <sub>2</sub> O <sub>5</sub> , wt%	LOI, wt%	FeO, wt%	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	CIA
YY-1	Coal	28.42	15.00	0.75	0.48	0.39	0.23	1.04	0.004	0.50	0.04	52.54	0.62	0.53	88.80
YY-2	Coal	1.44	1.19	0.34	0.13	0.30	0.10	0.04	0.003	0.04	0.11	96.16	0.22	0.83	76.92
YY-3	Coal	12.75	6.75	0.98	0.29	0.31	0.18	0.44	0.004	0.25	0.15	77.56	0.37	0.53	87.33
YY-4	Coal	3.12	1.87	4.05	0.17	0.19	0.15	0.14	0.004	0.05	0.13	89.99	0.16	0.60	81.89
YY-5	Coal	8.11	6.12	6.02	0.22	2.01	0.14	0.20	0.026	0.12	0.21	76.65	0.25	0.75	90.03
YY-6	Coal	3.72	1.79	7.12	0.18	3.22	0.14	0.13	0.033	0.08	0.09	83.46	0.17	0.48	74.67
YY-7	Coal	8.90	3.94	0.46	0.25	0.34	0.18	0.28	0.004	0.19	0.08	84.98	0.10	0.44	81.79
Average		9.49	5.24	2.82	0.25	0.96	0.16	0.32	0.011	0.18	0.12	80.19	0.27	0.59	83.06
YY-8	Oil shale	47.11	28.42	1.36	0.33	0.16	0.15	1.16	0.005	0.97	0.04	19.83	0.29	0.60	94.36
YY-9	Oil shale	53.77	20.88	4.47	1.84	0.35	0.50	2.62	0.127	0.78	0.10	14.36	2.18	0.39	83.68
YY-10	Oil shale	53.89	19.33	4.97	1.92	0.39	0.58	2.69	0.077	0.72	0.11	15.10	3.74	0.36	81.73
YY-11	Oil shale	53.85	19.17	4.71	1.84	0.54	0.62	2.45	0.131	0.72	0.10	15.75	3.33	0.36	81.27
YY-12	Oil shale	53.39	18.53	6.17	1.91	0.48	0.67	2.47	0.269	0.68	0.10	15.04	4.54	0.35	80.76
YY-13	Oil shale	54.95	18.89	4.26	1.95	0.54	0.63	2.39	0.061	0.65	0.09	15.43	1.95	0.34	81.17
YY-14	Oil shale	24.13	7.92	6.05	4.25	39.62	0.26	1.11	0.562	0.32	1.35	14.32	0.19	0.33	79.36
YY-15	Oil shale	51.78	17.82	4.56	1.90	0.49	0.68	2.24	0.034	0.66	0.09	19.48	1.80	0.34	80.83
YY-16	Oil shale	49.64	14.92	4.27	1.87	0.79	0.80	2.04	0.071	0.62	0.29	24.24	2.04	0.30	77.72
YY-17	Oil shale	51.52	17.18	4.62	2.05	0.67	0.74	2.35	0.052	0.71	0.17	19.68	3.56	0.33	78.89
YY-18	Oil shale	20.02	5.75	5.26	3.25	35.62	0.23	0.75	0.426	0.24	0.98	27.22	0.35	0.29	78.55
YY-19	Oil shale	41.44	10.65	4.18	2.16	11.70	0.53	1.36	0.187	0.41	0.46	26.33	2.00	0.26	76.84
YY-20	Oil shale	54.14	17.14	4.33	2.26	0.80	0.80	2.52	0.031	0.70	0.15	17.05	1.87	0.32	76.90
YY-21	Oil shale	21.10	4.99	3.73	1.49	31.73	0.36	0.73	0.249	0.20	1.59	33.30	2.66	0.24	71.81
YY-22	Oil shale	25.13	8.48	3.75	2.34	23.74	0.35	1.07	0.175	0.30	0.50	33.60	1.52	0.34	78.69
YY-23	Oil shale	29.18	9.30	5.36	1.85	19.57	0.44	1.22	0.120	0.35	0.74	31.29	1.45	0.32	77.10
YY-24	Oil shale	26.62	7.58	2.63	3.84	19.47	0.44	1.12	0.068	0.29	0.17	37.46	1.95	0.28	74.10
YY-25	Oil shale	22.31	4.06	3.89	3.28	38.11	0.33	0.51	0.132	0.19	0.56	26.60	1.03	0.18	71.24
YY-26	Oil shale	37.17	12.99	6.42	2.84	8.29	0.42	1.63	0.117	0.42	0.22	28.90	4.42	0.35	80.53
YY-27	Oil shale	49.87	14.95	4.15	1.69	0.81	0.75	2.02	0.069	0.59	0.27	22.80	2.07	0.30	77.85
YY-28	Oil shale	29.25	10.81	5.41	2.26	18.23	0.32	1.35	0.145	0.32	0.17	31.13	4.06	0.37	81.09
YY-29	Oil shale	24.70	9.96	5.60	3.04	16.08	0.26	1.21	0.199	0.39	0.20	37.79	3.42	0.40	82.10
YY-30	Oil shale	22.82	9.27	5.87	2.82	19.94	0.25	1.10	0.247	0.36	0.22	36.54	3.49	0.41	82.06
Average		39.03	13.43	4.61	2.30	12.53	0.48	1.66	0.155	0.50	0.38	24.49	2.34	0.34	79.51

Note: LOI denotes loss on ignition.

and with  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{Ti}_2\text{O}$  high (0.60–0.86; Table 4), giving evidence of their significant contribution to clay mineral affinities. Co, Sr, Ba and Tl have a high positive correlation with total S and  $\text{Fe}^{\text{T}}$  (0.55–0.72; Table 4), demonstrating their affinities for pyrite present in coal.

### 5.2.2. Affinities of trace elements in oil shale

In the Yuqia oil shale, the correlation coefficients of Th, Li, Be, Sc, V, Co, Ni, Zn, Ga, Rb, Cd, In, Cs, W, Tl, Pb, Bi, Ta, Zr and Hf with ash yield are all positive and relatively high ( $R^2 = 0.50$ – $0.73$ ), while those with TOC are negative ( $R^2 = -0.52$  to  $-0.24$ ) (Table 6), indicating the predominantly inorganic affinities of these elements. Besides, all the above elements are highly correlated with  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{TiO}_2$  ( $R^2 \geq 0.50$ ; Table 6), demonstrating the important role of clay minerals in the formation of these elements. Pb also has a positive correlation with  $\text{Fe}^{\text{T}}$  (0.41; Table 6), suggesting that siderite might have been the carrier of Pb in oil shale.

Cr, Cu, Sb and Nb exhibit a positive correlation with ash yield (0.34–0.45) and a negative correlation with TOC ( $-0.44$  to  $-0.13$ ) (Table 6). The correlation coefficients of these elements, except Sb, with  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{Ti}_2\text{O}$  are high (0.57–0.96; Table 6), demonstrating their affinities for clay minerals. Sb has a relatively good correlation with  $\text{Fe}^{\text{T}}$  ( $R^2 = 0.47$ ) and Mn ( $R^2 = 0.33$ ). As discussed above, the amount of Mn in oil shale is controlled by calcium carbonate and siderite, but Sb shows no correlation with CaO ( $R^2 = 0.01$ ), thus, we can conclude that the Sb amount in oil shale is mainly controlled by siderite. Mo has a positive correlation with both CaO ( $R^2 = 0.32$ ) and  $\text{P}_2\text{O}_5$  ( $R^2 = 0.71$ ), proving the affinity of P for carbonate minerals and its possible presence mainly in carbonate minerals.

### 5.3. Affinities of REEs

REEs in coal and oil shale have different characteristics. In coal,  $\Sigma\text{REE}$  is highly correlated with  $\text{P}_2\text{O}_5$  ( $R^2 = 0.72$ ) and MnO ( $R^2 = 0.42$ ), suggesting the possible occurrence of REEs in phosphate minerals.  $\Sigma\text{REE}$  in coal also correlates positively with total sulfur (0.49),  $\text{Fe}^{\text{T}}$  (0.43) and MnO (0.42) as well as Sr (0.98) and Ba (0.97) (Table 4). As demonstrated above, Ca, Mn, Sr and Ba in coal are all associated with pyrite and have exhibited the affinities of REEs with pyrite in coal.

$\Sigma\text{REE}$  in oil shale has a negative correlation with TOC ( $R^2 = -0.43$ ), but a positive correlation with ash yield ( $R^2 = 0.82$ ),  $\text{SiO}_2$  ( $R^2 = 0.74$ ),  $\text{Al}_2\text{O}_3$  ( $R^2 = 0.83$ ),  $\text{Na}_2\text{O}$  ( $R^2 = 0.42$ ),  $\text{K}_2\text{O}$  ( $R^2 = 0.78$ ) and  $\text{Ti}_2\text{O}$  ( $R^2 = 0.81$ ) (Table 6). This gives evidence of inorganic affinities of REEs in oil shale and their association primarily with clay minerals and quartz.

REEs typically originate from seawater and terrigenous substances [2]. The chondrite-normalized Ce anomaly ( $\text{Ce}_N/\text{Ce}_N^*$ ) is often used as a signature

**Table 6. The correlation coefficients ( $R^2$ ) between  $\Sigma$ REE, total sulfur, TOC, and major and rare earth elements of Yuqia oil shale**

	TOC	S <sup>T</sup>	Ash	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>T</sup>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	Ti <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	$\Sigma$ REE	Th	U	Li	Be	Sc	V	
TOC	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
S <sup>T</sup>	-0.09	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Ash	0.12	-0.28	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
SiO <sub>2</sub>	-0.29	-0.13	0.50	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Al <sub>2</sub> O <sub>3</sub>	-0.27	-0.29	0.63	0.95	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Fe <sup>T</sup>	0.35	-0.01	0.55	0.03	0.19	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
MgO	0.27	-0.02	-0.30	-0.48	-0.42	-0.06	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□	□
CaO	0.15	0.18	-0.56	-0.96	-0.96	-0.17	0.42	1.00	□	□	□	□	□	□	□	□	□	□	□	□	□
Na <sub>2</sub> O	-0.15	0.01	0.24	0.87	0.72	-0.17	-0.44	-0.82	1.00	□	□	□	□	□	□	□	□	□	□	□	□
K <sub>2</sub> O	-0.25	-0.24	0.51	0.97	0.99	0.12	-0.42	-0.96	0.79	1.00	□	□	□	□	□	□	□	□	□	□	□
MnO	0.11	0.08	0.12	-0.52	-0.46	0.35	-0.01	0.50	-0.60	-0.50	1.00	□	□	□	□	□	□	□	□	□	□
Ti <sub>2</sub> O	-0.26	-0.24	0.53	0.96	0.98	0.11	-0.43	-0.96	0.80	0.98	-0.48	1.00	□	□	□	□	□	□	□	□	□
P <sub>2</sub> O <sub>5</sub>	0.00	0.18	-0.47	-0.55	-0.66	-0.25	-0.30	0.71	-0.34	-0.62	0.43	-0.61	1.00	□	□	□	□	□	□	□	□
$\Sigma$ REE	-0.43	-0.35	0.82	0.74	0.83	0.10	-0.41	-0.72	0.42	0.78	-0.20	0.81	-0.52	1.00	□	□	□	□	□	□	□
Th	-0.38	-0.27	0.61	0.79	0.89	0.16	-0.32	-0.80	0.50	0.86	-0.27	0.89	-0.61	0.94	1.00	□	□	□	□	□	□
U	-0.28	-0.12	0.12	0.17	0.27	0.09	-0.16	-0.16	-0.11	0.20	0.19	0.27	-0.07	0.50	0.53	1.00	□	□	□	□	□
Li	-0.30	-0.34	0.70	0.88	0.95	0.19	-0.37	-0.89	0.61	0.93	-0.31	0.95	-0.64	0.92	0.96	0.46	1.00	□	□	□	□
Be	-0.41	-0.27	0.62	0.90	0.95	0.09	-0.45	-0.86	0.62	0.94	-0.32	0.93	-0.54	0.93	0.95	0.39	0.97	1.00	□	□	□
Sc	-0.38	-0.26	0.73	0.86	0.93	0.15	-0.43	-0.84	0.56	0.90	-0.28	0.91	-0.59	0.96	0.96	0.47	0.97	0.97	1.00	□	□
V	-0.47	-0.22	0.51	0.77	0.87	0.11	-0.42	-0.74	0.48	0.84	-0.28	0.85	-0.52	0.92	0.95	0.46	0.91	0.94	0.95	1.00	□
Cr	-0.28	-0.06	0.45	0.84	0.87	0.09	-0.38	-0.83	0.70	0.88	-0.39	0.91	-0.56	0.81	0.90	0.35	0.90	0.89	0.90	0.90	0.90
Co	-0.25	-0.05	0.55	0.71	0.75	0.23	-0.31	-0.74	0.56	0.73	-0.21	0.80	-0.53	0.80	0.89	0.45	0.85	0.79	0.85	0.85	0.84
Ni	-0.33	-0.11	0.59	0.70	0.74	0.25	-0.49	-0.66	0.49	0.72	-0.03	0.76	-0.35	0.86	0.89	0.48	0.84	0.84	0.88	0.88	0.88
Cu	-0.44	-0.07	0.37	0.76	0.81	0.05	-0.28	-0.75	0.57	0.82	-0.37	0.85	-0.56	0.84	0.95	0.45	0.88	0.88	0.89	0.89	0.93
Zn	-0.36	-0.21	0.58	0.90	0.95	0.14	-0.36	-0.88	0.62	0.93	-0.38	0.94	-0.62	0.90	0.96	0.46	0.98	0.97	0.96	0.94	0.94
Ga	-0.36	-0.23	0.57	0.89	0.95	0.16	-0.39	-0.87	0.62	0.94	-0.36	0.94	-0.62	0.89	0.96	0.41	0.98	0.98	0.97	0.96	0.96
Rb	-0.32	-0.22	0.50	0.95	0.97	0.09	-0.42	-0.92	0.76	0.98	-0.45	0.97	-0.60	0.82	0.90	0.28	0.95	0.96	0.93	0.90	0.90
Sr	0.06	0.15	-0.36	-0.69	-0.72	-0.18	0.31	0.70	-0.50	-0.70	0.20	-0.69	0.52	-0.47	-0.52	-0.20	-0.67	-0.64	-0.58	-0.51	-0.51
Mo	-0.18	-0.01	-0.22	-0.21	-0.29	-0.12	-0.35	0.32	-0.04	-0.28	0.07	-0.25	0.71	-0.20	-0.23	0.07	-0.27	-0.24	-0.28	-0.17	-0.17
Cd	-0.52	-0.26	0.58	0.73	0.82	0.09	-0.37	-0.70	0.40	0.78	-0.19	0.81	-0.48	0.96	0.97	0.60	0.92	0.93	0.94	0.96	0.96
In	-0.39	-0.19	0.53	0.85	0.92	0.10	-0.35	-0.83	0.57	0.89	-0.36	0.89	-0.62	0.87	0.95	0.45	0.95	0.95	0.95	0.95	0.95
Sb	-0.13	-0.14	0.34	0.01	0.14	0.47	-0.37	0.01	-0.16	0.09	0.33	0.10	0.11	0.37	0.30	0.32	0.20	0.20	0.30	0.36	0.36
Cs	-0.35	-0.34	0.62	0.90	0.96	0.15	-0.41	-0.87	0.62	0.95	-0.34	0.92	-0.61	0.87	0.92	0.36	0.95	0.96	0.95	0.91	0.91
Ba	-0.27	0.04	0.13	0.38	0.30	-0.15	-0.20	-0.32	0.46	0.35	-0.29	0.40	-0.07	0.45	0.48	0.18	0.39	0.39	0.43	0.44	0.44
W	-0.35	-0.31	0.57	0.89	0.93	0.10	-0.44	-0.86	0.69	0.93	-0.33	0.93	-0.57	0.86	0.93	0.37	0.95	0.94	0.93	0.90	0.90
Tl	-0.37	-0.40	0.50	0.38	0.48	0.33	-0.38	-0.34	0.17	0.45	0.26	0.48	-0.14	0.58	0.58	0.29	0.60	0.57	0.52	0.50	0.50
Pb	-0.24	-0.29	0.65	0.47	0.66	0.41	-0.14	-0.55	0.16	0.60	-0.03	0.64	-0.58	0.82	0.89	0.56	0.79	0.72	0.79	0.82	0.82
Bi	-0.24	-0.28	0.63	0.43	0.63	0.36	-0.05	-0.51	0.10	0.56	-0.08	0.59	-0.63	0.79	0.86	0.53	0.75	0.69	0.76	0.81	0.81
Nb	-0.33	-0.14	0.45	0.90	0.93	0.12	-0.38	-0.89	0.71	0.94	-0.37	0.96	-0.60	0.84	0.94	0.37	0.96	0.95	0.93	0.92	0.92
Ta	-0.28	-0.18	0.50	0.87	0.92	0.19	-0.37	-0.86	0.65	0.92	-0.30	0.94	-0.60	0.84	0.95	0.43	0.97	0.94	0.93	0.91	0.91
Zr	-0.36	-0.11	0.61	0.86	0.92	0.27	-0.42	-0.83	0.57	0.91	-0.22	0.90	-0.58	0.88	0.95	0.44	0.94	0.96	0.95	0.92	0.92
Hf	-0.45	-0.07	0.51	0.88	0.92	0.13	-0.39	-0.86	0.61	0.91	-0.36	0.90	-0.59	0.86	0.92	0.36	0.92	0.96	0.94	0.94	0.94

Note: Fe<sup>T</sup> represents total Fe.



of seawater, and both LREEs and HREEs are enriched in seawater [61]. This shows that both coal and oil shale have negligible chondrite-normalized Ce anomalies and display similar traits of LREE enrichment and HREE deficit (Table 3; Fig. 3), which excludes seawater as a source of REEs. As a whole, similar vertical trends of  $\Sigma$ REE,  $\Sigma$ LREE and  $\Sigma$ HREE are exposed (Fig. 2), which points to the same controlling factors of REEs in coal and oil shale. In addition, the Yuqia coal and oil shale also reveal similar normalized distribution patterns (Fig. 3), which provides good evidence for the same REE origin and formation process of these rocks [62, 63]. The chondrite-normalized curves of coal and oil shale have a negative Eu anomaly, which is likely inherited from their source rocks [64, 65], implying that REEs in both coal and oil shale originate from terrigenous substances. Moreover,  $\Sigma$ REE in oil shale has a good positive correlation with terrigenous elements Th ( $R^2 = 0.94$ ), Li ( $R^2 = 0.92$ ), Be ( $R^2 = 0.93$ ), Sc ( $R^2 = 0.96$ ), V ( $R^2 = 0.92$ ) and Zn ( $R^2 = 0.90$ ), but a negative correlation with some typical non-terrigenous elements such as Sr ( $R^2 = -0.47$ ). This may be a sign of the terrigenous origin of REEs in oil shale, while in coal, they have no significant positive correlation with terrigenous trace elements.

## 5.4. Weathering and provenance

### 5.4.1. Source area weathering

The chemical index of alteration (CIA) reflects the weathering degree of rocks and paleoclimate and is calculated using the molecular proportions of the following compounds:  $CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$ , where  $CaO^*$  is the amount of  $CaO$  incorporated in the silicate fraction of the rock, while the molecular proportions are calculated by dividing the amount of the compounds by their relative atomic mass. The CIA value of 50–65 indicates a cold and dry climate during low chemical weathering, CIA of 65–85 is indicative of a warm and humid climate during moderate chemical weathering, whereas its value between 85 and 100 signifies a hot and humid climate during strong chemical weathering [66, 67]. The average value of CIA for coal is 83.06 and for oil shale 79.51 (Table 5). These figures demonstrate that both coal and oil shale in the Yuqia area are possibly the products of source rocks that have experienced moderate chemical weathering during a warm and humid climate.

The  $Al_2O_3$  vs  $(Na_2O + CaO^*)$  vs  $K_2O$  (A-CN-K) ternary plot is also used to deduce chemical weathering trends [66, 69, 70]. Both coal and oil shale have displayed distribution trends that are approximately parallel to the A-CN axis; with the increase of the value of CIA, coal and oil shale tend to be distributed closer to the A-K axis (Fig. 5a). All the samples are located within the area of illite and kaolinite-chlorite. This aluminum-rich composition results from enhanced chemical weathering [70–72], while the finding is in agreement with

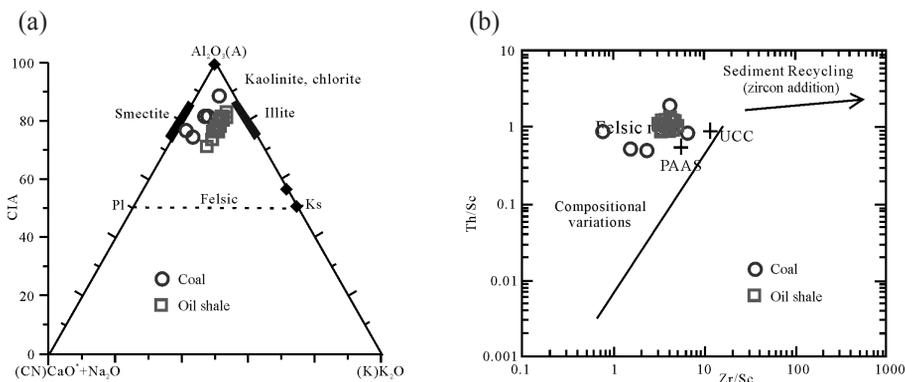


Fig. 5. A-CN-K and Zr/Sc-Th/Sc diagrams for coal and oil shale samples (base map sources: a) [66]; b) [67]).

the XRD results for tested clay minerals (Table 2). The Yuqia coal and oil shale are closely and densely distributed (Fig. 5a), suggesting their uniform weathering process.

#### 5.4.2. Provenance and source of REEs

The depositional process such as mineral sorting might change the abundance of some minerals, thus causing the enrichment of specific elements [73]. The ratio of Th/Sc has remained stable during the sediment recycling process [68], and Zr/Sc has not been influenced by the later hydrothermal alteration [74], so, both can be used to reflect the compositional changes, mineral sorting and heavy mineral content of source rocks [68]. Most samples are plotted in the diagram of Zr/Sc vs Th/Sc close to PAAS and UCC (Fig. 5b), indicating that the component contents of the samples are controlled by the source rocks. Both coal and oil shale are distributed above the line of compositional variations (Fig. 5b), suggesting their generation from felsic source rocks. The diagrams of La/Th vs Hf, Th/Sc vs La/Sc and La/Yb vs  $\Sigma$ REE can mirror the source rocks of sedimentary rocks [75–78]. The samples have a mixed provenance of felsic and basic volcanic rocks and felsic sedimentary rocks (Fig. 6).

The REE abundance can also be used to infer the source of sedimentary rocks [68, 73, 79]. Commonly, felsic source rocks have relatively high ratios of LREE/HREE and negative Eu anomalies when normalized to chondritic meteorites, whereas mafic source rocks display relatively low LREE/HREE ratios and no Eu anomalies [44, 73, 80]. At the same time, the chondrite-normalized patterns and parameters indicate that both coal and oil shale samples are characterized by LREE enrichment and HREE deficit.

The geochemical composition within the sediment-source region is one of the important factors controlling the Ce and Eu anomalies [18, 81–84].

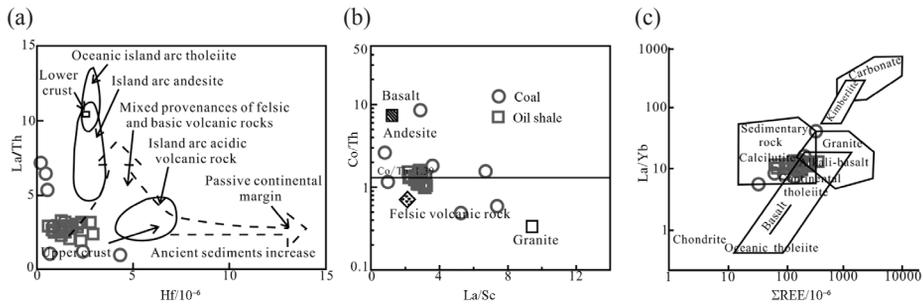


Fig. 6. Diagrams of source rocks (base map sources: a) [77]; b) [75]; c) [78]).

Sediment source regions dominated by felsic or felsic-intermediate rocks are characterized by weakly negative Ce and negative Eu anomalies [64, 65]. The weak negative Ce anomalies may also be caused by oxidation and in-situ precipitation of  $Ce^{4+}$  during weathering in the sediment-source region [18]. In the latter region, felsic terrigenous input has sometimes a lower  $(La/Lu)_N$  ratio compared to sedimentary terrigenous source regions [18, 85]. The strongly negative Eu (average 0.60) (Table 3) and weakly negative Ce anomalies (average 0.94) (Table 3) of coal indicate the felsic or felsic-intermediate source rocks mixed with sedimentary rocks. Oil shale has weakly negative Ce (average 0.96) and Eu anomalies (average 0.67) (Table 3) and relatively high  $(La/Lu)_N$  ratios (average 8.55), suggesting the pronounced sediment terrigenous input differently from coal. Summarizing the above results, we infer that the Yuqia coal and oil shale have similar source rocks of felsic volcanic and sedimentary rocks.

## 6. Conclusions

1. This study discussed and compared the inorganic geochemistry, provenance and tectonic setting of oil shale and coal in the Yuqia area of the Qaidam Basin, China. Coal is mainly represented by lignite and bituminous coal, and oil shale mostly belongs to medium-quality oil shales. In the chondrite-normalized patterns, both coal and oil shale exhibit LREE enrichment and HREE deficit with negative Eu and negligible Ce anomalies.
2. In both coal and oil shale, Si, Al, K, Ti and Na originate from a mixed clastic sedimentary component comprised of clay minerals, quartz and feldspars. In coal, Mg is mainly correlated with illite and an illite-smectite mixed layer, Ti is correlated with organic matter and clay minerals, Fe is mainly present in pyrite, Mn is related to calcite, and Ca and Mn are associated with pyrite. Trace elements Li, Rb, Cs, Nb, Ta and Hf are associated with

both organic matter and clay minerals and Co, Sr, Ba and Tl have strong affinities for pyrite. In oil shale, Ti has only an inorganic affinity, whereas Na has another source, potentially plagioclase. Mn is associated with carbonate minerals, P is related to carbonate minerals and Ca is associated with carbonate minerals and Ca-bearing fossils. Most trace elements are related to clay minerals. Li, Co, Ni, Ga, Cs, Pb, Bi and Ta might also have the carrier of siderite; Cr, Cu and Nb have clay-mineral affinities; Sb is mainly controlled by siderite, but Mo has good affinities for carbonate minerals.

3. In coal, REEs are related to phosphate minerals, while REEs in oil shale have inorganic affinities and are mainly associated with clay minerals and quartz. The REEs in coal and oil shale are of terrigenous origin. Coal and oil shale are possibly the products of source rocks that have experienced moderate chemical weathering during a warm and humid climate; they both have similar source rocks of felsic volcanic and sedimentary rocks.

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