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OCCURRENCE AND ENRICHMENT OF TRACE ELEMENTS IN MARINE OIL SHALE (CHINA) AND THEIR BEHAVIOUR DURING COMBUSTION

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Abstract. *The Shengli River-Changshe Mountain oil shale zone represents the potentially largest marine oil shale resource in China. With the aim to have better knowledge of the distribution of trace elements in oil shale, and their behaviour during oil shale combustion and gasification, 28 raw Changliang Mountain oil shale and marl samples, 19 oil shale combustion residue samples and 23 samples of minerals isolated from Changliang Mountain oil shale are studied for trace element content. The oil shale samples from the Changshe Mountain area are characterized by high ash yield (54.69–86.75%) and total organic carbon (TOC) content (2.20–13.44%). The contents of Se, Mo, Cd, As, B, and Ni in raw oil shale samples are 3.78 to 28.44 times their upper continental crust values. The enrichment of an element in oil shale seams may be a function of that association and the origin of oil shale fractions.*

Some trace elements in the Changshe Mountain oil shale show susceptibility to release into the atmosphere, including about 93% Hg and 20–30% As, Ba, Be, Co, Cr, Nb, and Sc. The behaviour and migration of trace elements during oil shale combustion strongly depend on their mode of occurrence in the rock. Based on Pearson's coefficients of correlation between elements, as well as cluster and isolated mineral analyses, the main modes of occurrence of trace elements in marine oil shale are distinguished: 1) clay mineral affined – B, Ba, Be, Cr, Cs, Ga, Hf, Li, Nb, Rb, Sc, Sn, Ta, Th, V, W, Zr, REEs; 2) organic affined – As, Mo, Se; 3) Fe-bearing mineral affined – Bi, Co, Cu, Ni, Pb, U; 4) calcite affined – Cd, Sr and 5) fossil affined – Cd, Zn.

Keywords: *marine oil shale, trace elements, rare earth elements (REEs), Changshe Mountain, fossil remains, minerals.*

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1. Introduction

Oil shale as an alternative energy resource has received much attention lately [1]. In China, oil shale was formed mainly in lacustrine environments. Recently, new marine oil shale zones were found in the Qiangtang basin, northern Tibet, China, including the Bilong Co oil shale zone [2, 3] and the Shengli River-Changshe Mountain oil shale zone [4, 5]. These zones represent the largest marine oil shale resource in China.

In recent years, trace elements emission control during coal combustion has been taken keen interest in [6]. Studies on the elements volatility during the process have shown that their mobility depends on the fuel properties and combustion conditions. These investigations generally suggest that the organic associated trace elements vaporize during coal combustion more easily than those associated with minerals. Oil shale may also contain high concentrations of trace elements [7]. A major application of oil shale is combustion for power generation during which most trace elements are released and redistributed into bottom ash, fly ash and the gaseous phase. Therefore, it is necessary to have knowledge of the concentrations of trace elements in oil shale and their behaviour during oil shale combustion and gasification to control and reduce their emission into the atmosphere. However, very few studies have been done so far on the distribution of trace elements in oil shale, especially in marine oil shale, and their behaviour during oil shale combustion is still quite unclear or not fully understood.

The present study considers in detail the content and distribution of trace elements in Changshe Mountain oil shale found in the northeastern part of the Shengli River-Changshe Mountain oil shale zone. The authors also report trace element contents in oil shale combustion residues, as well as in selected minerals. The main aims of the research are: (1) to evaluate the enrichment of trace elements in marine oil shale; (2) to establish the modes of occurrence of trace elements in marine oil shale; and (3) to determine the volatility of trace elements during oil shale combustion.

2. Geological setting

From north to south, Tibet consists of the Kunlun-Qaidam and Songpan-Ganzi flysch complex, and the Qiangtang and Lhasa terranes, which are separated by the Anyimaqen-Kunlun-Muztagh, Hoh Xil-Jinsha River and Bangong Lake-Nujiang River suture zones, respectively (Fig. 1a) [8]. It is generally accepted that the Paleo-Tethys represented by the present Jinsha River suture opened possibly in the Early Carboniferous period [9] and closed by the Permian-Triassic period [10]. The Mid-Tethys branch between the Lhasa and Qiangtang terranes was open by the Early Jurassic period [10] and closed along the Bangong Lake-Nujiang River suture during the Late Jurassic period [9].

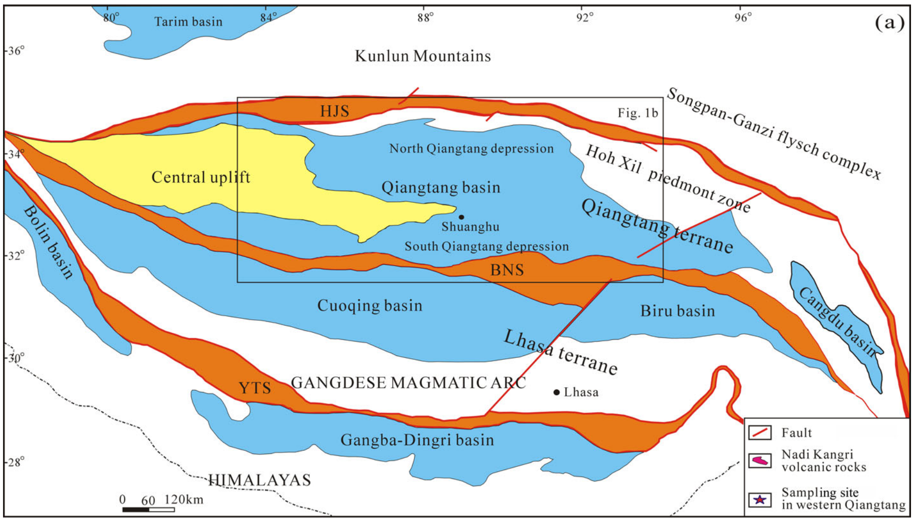


Fig. 1. (a) Map of the Tibetan Plateau showing major terranes (modified from [8]). HJS – Hoh Xil-Jinsha River suture; BNS – Bangong Lake-Nujiang River suture; YTS – Yarlung Tsangpo suture.

The Qiangtang block, bounded by the Hoh Xil-Jinsha River suture zone to the north and the Bangong Lake-Nujiang River suture zone to the south, consists of the North Qiangtang depression, the central uplift and the South Qiangtang depression (Fig. 1b). The Shengli River-Changshe Mountain oil shale zone is located in the southern part of the North Qiangtang depression, northern Tibetan Plateau, China (Fig.1b), comprising Changshe Mountain, Shengli River and Changliang Mountain oil shales (Fig. 1c). The proven reserves of the Shengli River-Changshe Mountain oil shale zone have been

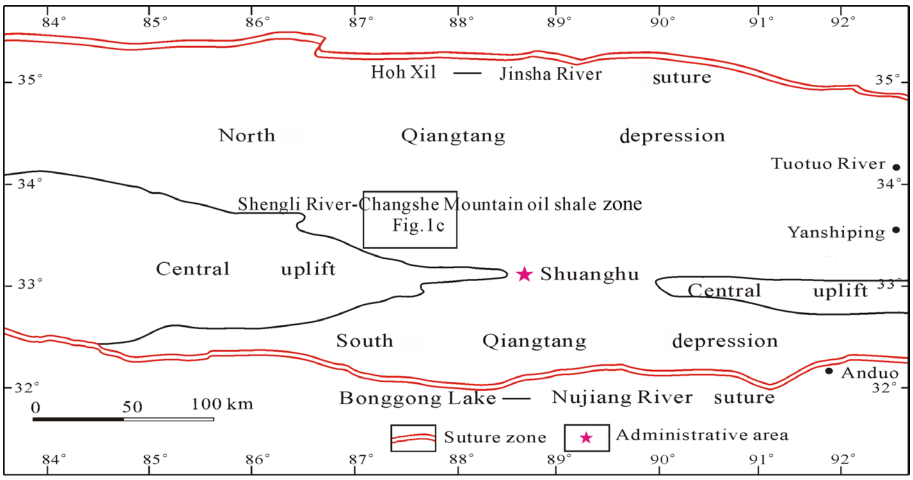


Fig. 1. (b) Generalized map showing the location of the study area (after [4]).

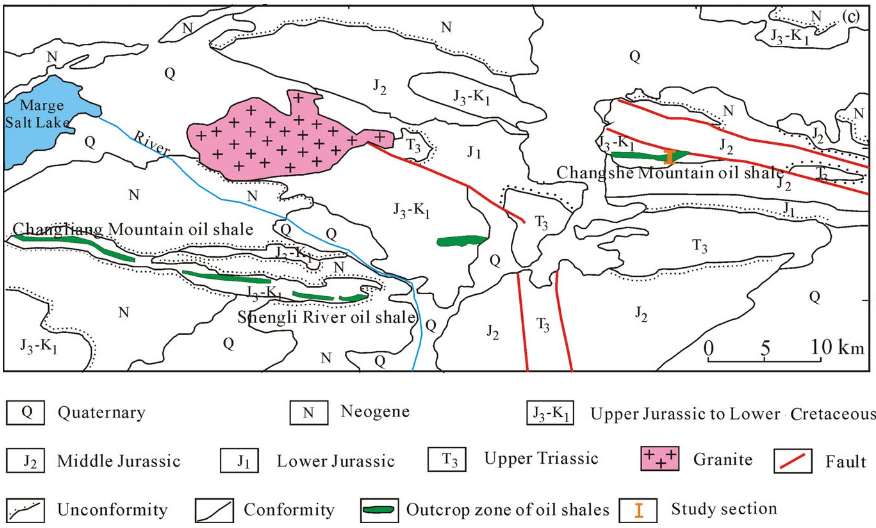


Fig.1. (c) Simplified geological map of the Shengli River area showing the location of the oil shale section (modified from [4]).

estimated to exceed 1.0 × 10^9 tonnes [11], being potentially the largest marine oil shale resource in China.

The Changshe Mountain oil shale is found in the northeastern part of the Shengli River-Changshe Mountain oil shale zone where the Jurassic-Early Cretaceous marine deposits are widely spread [11]. The oil shale, about 11 m in thickness, is exposed for a distance of more than 10 km in an east-west direction. Preliminary isotopic analyses of oil shale samples indicate that the deposition occurred in the Early Cretaceous period [12].

3. Materials and methods

A total of 30 samples, including 19 oil shale and 9 marlstone samples and 2 samples of gastropod fossil remains present in the oil shale seams, were collected from the Changshe Mountain oil shale zone. The study area and sample section locations are shown in Figure 1.

3.1. Geochemical analyses of raw samples

Samples for geochemical analysis were all crushed and ground to less than 200 mesh. The samples were ashed in an open muffle furnace, the temperature being gradually raised to 950 °C. The ash was dissolved in $HClO_4$ and HF, evaporated to dryness and the residue dissolved in hydrochloric acid. In the solution, major elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, P, Mn) were collected applying X-ray fluorescence (XRF) on fused glass beads by using a Rigaku ZSX100e spectrometer at the Analytical Center, Chengdu Institute of Geology and Mineral Resources. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine trace element contents in samples, following the method described in Chinese National Standard DZ/T0223-2001. The samples were digested in a microwave furnace using HNO_3 + HF. The level of detection limit for elements is 0.*n*–*n* × 10^{-12} where *n* = 1–9 [13]. Hg, Se and As were determined by atomic fluorescence spectrometry, using a chemical method according to Chinese standard DZG20.10-1990.

3.2. Organic carbon and organic sulphur analyses

Ash yield was determined at the Coal Field Geological Bureau of Heilongjiang Province, following a Chinese standard method GB/T212-2008. Total organic carbon (TOC) and organic sulphur ($S_{o,\ d}$) were determined at the Organic Geochemistry Laboratory of Exploration & Development Research Institute of PetroChina Huabei Oilfield Company. Pulverized whole-rock samples (2 g) were digested with warm 15% $HClO_4$, and CO_2 was released in the process; this digestion was followed by analyses of TOC and $S_{o,\ d}$, using the Leco analyzer.

3.3. Trace element analysis of combustion residues

The oil shale samples were combusted in an open environment. ICP-MS was used to determine the contents of trace elements in the combustion residues, following the method described in Chinese National Standard DZ/T0223-2001 as discussed above. Hg, Se and As were determined by atomic fluorescence spectrometry, using a chemical method according to Chinese standard DZG20.10-1990.

3.4. Trace element analysis of isolated minerals

In the laboratory, all mineral samples were carefully separated by hand-picking to maximize their purity. After sample preparation, thin and polished sections were made to study mineral "purity" under an optical microscope. ICP-MS was used to analyze the contents of trace elements in isolated minerals, following the method described in Chinese National Standard DZ/T0223-2001 as discussed above. Atomic fluorescence spectrometry was employed to determine As, using a chemical method according to Chinese standard DZG20.10-1990.

The results were statistically treated using the SPSS statistical program. The elemental associations were studied by cluster analysis.

4. Results and discussion

4.1. Oil shale characterization

The TOC content of 19 oil shale samples from the Changshe Mountain area varies from 2.20% to 13.44%, whereas marlstone samples contain 0.38–2.03% TOC (Table 1). The $S_{o,\ d}$ contents in the samples vary between 0.19 and 1.08% and from 0.21 to 0.73%, respectively.

Table 1. Concentrations of organic sulphur, total organic carbon, ash and major elements in Changshe Mountain oil shale and marlstone samples, %

Sample no	Lithology	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	TOC	$S_{o,d}$	A_d
30-1	Marlstone	5.16	1.34	0.52	50.48	0.94	0.28	0.25	0.064	0.028	0.016	0.83	0.26	
30-2	Marlstone	6.33	1.60	0.64	50	0.98	0.36	0.15	0.077	0.031	0.016	0.62	0.25	
30-3	Oil shale	16.34	5.15	2.11	38.82	1.37	1.21	0.3	0.23	0.05	0.019	2.20	0.56	67.08
30-4	Oil shale	21.91	6.55	3.8	30.14	2.58	1.88	<0.04	0.35	0.31	0.035	5.78	0.49	68.85
30-5	Oil shale	1.87	0.76	1.41	47.18	1.02	0.18	0.16	0.034	0.6	0.036	6.30	0.44	54.69
.30-6	Oil shale	2.00	0.68	1.74	47.43	1.21	0.17	0.18	0.031	0.64	0.052	6.36	0.44	55.30
30-7	Oil shale	3.84	1.26	2.71	44.94	1.36	0.3	0.15	0.057	0.8	0.065	6.56	0.45	56.67
30-8	Oil shale	7.53	2.32	1.62	43.42	2.08	0.53	0.17	0.10	0.36	0.033	4.26	0.32	59.03
30-9	Marlstone	7.54	1.99	0.76	48.5	1.00	0.44	0.14	0.092	0.033	0.018	1.25	0.31	
30-10	Marlstone	8.67	2.66	0.96	47.06	1.28	0.59	0.14	0.11	0.033	0.019	1.23	0.48	
30-11	Oil shale	20.99	6.56	2.78	27.32	4.54	1.60	0.18	0.26	0.16	0.028	7.18	0.59	66.00
30-12	Oil shale	17.12	5.25	3.05	30.56	3.68	1.28	0.16	0.21	0.26	0.031	8.41	0.69	63.41
30-13	Oil shale	10.8	3.12	4.24	35.01	1.43	0.72	0.17	0.14	0.91	0.079	13.44	1.08	59.37
30-14	Marlstone	9.52	2.98	1.09	46.37	1.15	0.68	0.15	0.13	0.036	0.024	0.93	0.21	
30-15	Marlstone	6.62	2.14	0.80	49.0	0.98	0.46	0.14	0.094	0.03	0.025	0.85	0.31	
30-16	Oil shale	50.1	18.43	6.15	3.79	1.39	4.78	0.27	0.91	0.33	0.021	3.19	0.19	86.75
30-17	Oil shale	45.28	16.11	5.76	9.03	1.38	4.21	0.27	0.8	0.44	0.026	5.13	0.32	84.20
30-18	Oil shale	41.85	14.01	5.25	14.09	1.28	3.32	0.22	0.66	0.77	0.04	5.34	0.31	82.34
30-19	Oil shale	37.56	12.65	4.62	18.43	1.47	3.19	0.23	0.64	0.36	0.039	4.38	0.30	80.00
30-20	Oil shale	45.53	16.02	5.64	8.47	1.26	4.09	0.31	0.77	0.55	0.025	4.94	0.25	83.36
30-21	Marlstone	14.68	4.23	1.50	35.56	7.29	0.94	0.18	0.23	0.056	0.037	0.38	0.73	
30-22	Oil shale	41.53	14.04	4.19	13.86	1.2	3.59	0.27	0.69	0.29	0.029	3.82	0.23	80.34
30-23	Oil shale	38.04	13.13	4.2	16.95	1.14	3.32	0.28	0.65	0.35	0.033	3.69	0.22	78.71
30-24	Oil shale	34.41	11.81	4.04	21.24	1.08	2.94	0.25	0.58	0.4	0.037	3.12	0.19	77.35
30-25	Oil shale	26.46	8.97	3.34	29.85	0.96	2.2	0.25	0.44	0.46	0.038	3.13	0.21	73.62
30-26	Oil shale	16.56	5.41	2.37	39.35	0.74	1.24	0.2	0.26	0.47	0.043	2.49	0.71	68.50
30-27	Marlstone	9.98	3.15	1.66	45.35	0.61	0.71	0.20	0.15	0.51	0.042	2.03	0.63	
30-28	Marlstone	7.15	2.18	1.18	48.04	0.64	0.48	0.2	0.099	0.48	0.043	1.54	0.44	

TOC – total organic carbon; $S_{o,d}$ – organic sulphur, dry basis; A_d – ash, dry basis.

The Changshe Mountain oil shale samples are characterized by high ash yield, ranging from 54.69% to 86.75% (Table 1), with average shale oil contents remaining between 3.85% and 11.76% [11].

4.2. Enrichment of trace elements in marine oil shale

The concentrations of trace elements in 28 raw Changshe Mountain oil shale and marlstone samples are presented in Tables 2 and 3. On average, the most abundant trace elements in raw oil shale samples are B (7.16–200 ug/g), Ba (52.4–420 ug/g), Cr (8.93–111 ug/g), Cu (17.2–160 ug/g), Rb (6.87–194 ug/g), Sr (176–578 ug/g), V (38.9–123 ug/g), Zn (19.9–425 ug/g) and Zr (6.54–149 ug/g), whereas all the other elements occur in amounts smaller than 100 ug/g. Compared with oil shale samples, the trace element concentrations in marlstone samples from the Changshe Mountain area are a little lower, with an exception of Sr.

The pioneering work of Patterson et al. established that oil shale is enriched with some elements [14]. Enrichment of an element in oil shale may be described by the enrichment factor (EF), which is the ratio of the concentration of an element in sample to its average concentration in the upper continental crust (UCC) [15]. The enrichment factors of trace elements Se, Mo, Cd, As, B and Ni are 28.44, 15.22, 8.46, 7.03, 5.41 and 3.78, respectively. The elements Bi, Co, Cr, Cs, Cu, Li, Ni and V have the enrichment factor > 1.30, while the EF of Ba, Be, Hf, Nb, Sn, Ta, W, Zr and most rare earth elements (REEs) is less than 0.5 and all these elements are therefore considered depleted. The concentrations of all the other elements in the oil shale samples studied are almost similar to their respective UCC values, with the EF between 0.51 and 1.30.

Gluskoter et al. used a value of six times the Clarke value to determine whether coal is enriched with an element [16]. In the present study, we used a value of six times the UCC value to determine element enrichment in oil shale. By these criteria, raw oil shale samples are enriched in Se, Mo, Cd and As. Se is known to have primary affinity for pyrite [17] but can also have many other associations, including clausthalitic and organic [18]. In Changshe Mountain oil shale, the positive relationship (R^2 = 0.63) (Fig. 2) between Se and TOC contents indicates that Se is controlled mainly by organic matter. Mo and As are also correlated with TOC, which is confirmed by the results of cluster analyses grouping these elements with TOC (Fig. 3). In comparison to normal shales, Changshe Mountain oil shale is extremely enriched in organic matter. It is believed that element enrichment in such sediments is associated with the accumulation of elements together with organic matter and sulphides under anoxic conditions [19].

The oil shale samples from the Changshe Mountain area are enriched in Cd. The minerals analysis shows that Cd is abundant in calcite and fossil remains (Tables 2 and 4). The positive relationship (R^2 = 0.32) between Cd and CaO contents further supports the above observations. Therefore, the enrichment of Cd in Changshe Mountain oil shale may be attributed to

Table 2. Trace element contents in raw Changshe Mountain oil shale and marlstone samples, oil shale combustion residues and selected minerals, µg/g

Element	Content in raw samples						Content in combustion residues			Content in selected minerals									UCC value
	Min in OS	Max in OS	MV in OS	Min in marl-stone	Max in marlstone	MV in marl-stone	Min	Max	MV	Min in CMO	Max in CMO	MV in CMO	Min in CF	Max in CF	MV in CF	Min in dolomite	Max in dolomite	MV in dolomite	
As	4.97	19.6	10.5	1.37	15.8	4.46	6.38	17.0	11.6	2.69	23.3	8.44	1.22	3.18	2.08	0.28	0.38	0.33	1.5
B	7.16	200	81.1	13.7	48.7	28.7	11.0	237	99.8	43.8	271	193	< 2.00	12.8	< 7.21	< 2.00	< 2.00	< 2.00	15
Ba	52.4	420	225	31.7	92.9	61.1	68.1	420	234	81.9	403	299	20.0	47.2	34.60	179	266	223	550
Be	0.17	2.74	1.28	0.23	0.81	0.49	0.28	2.99	1.45	0.56	2.79	2.09	0.05	0.06	0.06	< 0.05	< 0.05	< 0.05	3
Bi	0.10	0.37	0.26	0.06	0.10	0.07	0.11	0.47	0.30	0.05	0.41	0.18	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.127
Cd	0.10	6.53	0.83	0.05	0.09	0.07	0.11	12.7	1.34	0.05	1.36	0.23	1.32	4.31	2.65	< 0.05	< 0.05	< 0.05	0.098
Ce	3.84	55.0	28.3	6.53	20.7	11.7	7.03	54.7	31.5	10.5	54.8	38.0	0.58	1.53	0.90	2.77	4.15	3.46	64
Co	8.78	26.4	15.4	6.05	9.82	7.40	6.63	28.1	15.9	1.84	25.7	9.25	2.73	4.87	4.09	1.18	1.67	1.43	10
Cr	8.93	112	63.0	10.1	30.8	19.0	12.1	160	74.3	27.2	168	116	3.19	8.89	5.50	2.76	6.88	4.82	35
Cs	0.47	17.1	6.82	0.85	2.86	1.73	1.02	18.1	7.56	1.75	17.9	10.1	0.07	0.09	0.08	0.12	0.13	0.13	3.7
Cu	17.2	106	67.3	8.83	31.8	14.3	14.1	113	79.9	4.89	119	43.3	6.55	7.61	6.99	3.94	3.97	3.96	25
Dy	0.42	3.32	1.78	0.46	1.46	0.91	0.85	4.37	2.29	0.41	1.78	1.07	0.05	0.16	0.11	0.50	0.84	0.67	3.5
Er	0.27	1.85	1.08	0.25	0.89	0.51	0.48	2.39	1.40	0.37	1.53	1.03	0.10	0.10	0.10	0.22	0.34	0.28	2.3
Eu	0.09	0.80	0.42	0.12	0.37	0.23	0.17	1.01	0.53	0.09	0.39	0.23	< 0.05	< 0.05	< 0.05	0.16	0.25	0.21	0.88
Ga	1.29	24.0	11.2	1.50	5.05	3.02	2.66	28.6	13.5	5.77	28.7	21.3	0.24	0.26	0.25	0.42	0.44	0.43	17
Gd	0.43	3.73	1.93	0.51	1.58	0.99	0.83	4.64	2.42	0.47	1.78	0.94	0.05	0.16	0.09	0.67	1.00	0.84	3.8
Hf	0.14	3.88	1.73	0.33	1.07	0.58	0.38	4.85	2.31	0.94	4.90	3.55	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	5.8
Hg	0.018	0.074	0.04	0.004	0.058	0.03	0.001	0.009	0.004										0.056
Ho	0.09	0.64	0.36	0.08	0.28	0.18	0.17	0.81	0.45	0.10	0.41	0.26	< 0.05	< 0.05	< 0.05	0.09	0.15	0.12	0.8

Table 2. (Continuation)

Element	Content in raw samples						Content in combustion residues			Content in selected minerals									UCC value
	Min in OS	Max in OS	MV in OS	Min in marl-stone	Max in marlstone	MV in marl-stone	Min	Max	MV	Min in CMO	Max in CMO	MV in CMO	Min in CF	Max in CF	MV in CF	Min in dolomite	Max in dolomite	MV in dolomite	
La	2.30	26.5	13.8	3.32	9.97	5.81	4.15	30.7	16.6	6.34	30.6	22.1	0.32	1.03	0.56	1.03	1.50	1.27	30
Li	4.10	53.4	28.4	4.55	12.5	8.24	8.28	59.5	32.0	19.8	64.8	52.8	0.53	1.20	0.77	1.20	1.26	1.23	20
Lu	0.06	0.28	0.18	0.06	0.12	0.08	0.06	0.34	0.20	0.06	0.29	0.20	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.32
Mo	3.78	70.0	22.8	0.66	8.17	2.31	4.93	97.2	29.3	5.99	164	30.8	1.45	9.85	4.33	0.91	3.00	1.96	1.5
Nb	0.56	18.8	8.22	1.52	4.78	2.43	1.22	18.4	8.20	2.88	20.0	13.5	0.11	0.12	0.12	0.16	0.18	0.17	25
Nd	1.73	20.4	11.5	2.85	8.79	5.12	3.52	23.9	14.1	4.37	20.3	13.0	0.20	0.82	0.42	2.12	3.23	2.68	26
Ni	37.8	127	75.6	27.9	47.8	35.3	35.1	152	89.6	19.7	157	65.7	23.1	32.3	28.30	12.4	13.0	12.7	20
Pb	4.28	21.6	12.9	1.95	5.62	3.52	6.46	24.7	15.1	2.41	271	30.7	0.78	2.36	1.36	2.13	2.20	2.17	20
Pr	0.46	5.65	3.06	0.70	2.26	1.31	0.92	6.61	3.87	1.23	6.31	4.25	0.06	0.20	0.11	0.45	0.66	0.56	7.1
Rb	6.87	194	97.6	16.3	55.2	31.6	13.0	253	122	31.4	263	185	1.08	1.60	1.39	1.88	2.10	1.99	112
Sc	2.06	18.8	9.76	2.81	5.63	3.97	2.25	20.8	10.9	2.37	18.5	11.0	0.71	1.74	1.36	0.71	0.86	0.79	11
Se	0.73	2.61	1.42	0.10	1.03	0.34	1.31	4.36	2.11										0.05
Sm	0.37	4.10	2.16	0.56	1.67	1.03	0.76	5.25	2.76	0.68	2.66	1.52	0.06	0.15	0.11	0.59	0.94	0.77	4.5
Sn	0.64	3.63	1.94	0.71	1.20	0.96	0.68	4.8	2.38	1.01	4.74	3.47	0.43	0.64	0.55	0.40	0.50	0.45	5.5
Sr	176	578	307	256	1277	465	223	779	409	33.2	463	135	257	1151	569	148	158	153	350
Ta	0.08	1.33	0.66	0.13	0.35	0.20	0.14	1.72	0.77	0.27	1.81	1.22	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	2.2
Tb	0.07	0.55	0.29	0.07	0.24	0.15	0.13	0.69	0.36	0.06	0.25	0.14	<0.05	<0.05	<0.05	0.08	0.14	0.11	0.64
Th	0.54	13.6	6.17	1.01	3.28	1.82	1.19	16.7	8.10	1.87	13.0	6.26	0.08	0.11	0.09	0.25	0.31	0.28	10.7
Tm	0.05	0.27	0.18	0.06	0.12	0.08	0.06	0.34	0.19	0.06	0.23	0.16	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.33
U	1.26	6.91	3.54	0.50	1.03	0.71	1.43	7.97	4.33	2.08	6.15	4.01	0.18	0.62	0.34	0.32	1.35	0.84	2.8
V	38.9	123	83.7	15.3	39.9	26.9	40.3	177	100	110	221	164	9.50	12.1	10.73	5.16	7.07	6.12	60
W	0.29	1.56	0.86	0.16	0.73	0.31	0.45	1.92	1.07	1.04	2.21	1.86	0.06	0.09	0.07	0.06	0.21	0.14	2
Y	2.89	16.2	9.50	2.86	8.11	5.21	5.16	20.2	11.6	2.48	9.80	6.81	0.41	1.16	0.66	2.61	4.13	3.37	22

Table 2. (Continuation)

Element	Content in raw samples						Content in combustion residues			Content in selected minerals									UCC value
	Min in OS	Max in OS	MV in OS	Min in marl-stone	Max in marlstone	MV in marl-stone	Min	Max	MV	Min in CMO	Max in CMO	MV in CMO	Min in CF	Max in CF	MV in CF	Min in dolomite	Max in dolomite	MV in dolomite	
Yb	0.19	1.83	1.05	0.22	0.73	0.46	0.40	2.27	1.35	0.39	1.82	1.26	0.09	0.09	0.09	0.13	0.2	0.17	2.2
Zn	19.9	425	66.0	5.81	12.9	9.06	18.5	865	105	15.0	396	54.7	34.1	567	238	1.96	3.17	2.57	71
Zr	6.54	149	70.5	14.2	44.1	23.9	14.3	164	74.9	33.9	171	119	1.18	1.38	1.25	1.57	1.63	1.60	190

Min – minimum value; Max – maximum value; MV – mean value; OS – oil shale; CMO – clay minerals and organic matter; CF – calcite and fossil; UCC – upper continental crust (after [15]).

Table 3. Concentrations of trace elements in raw Changshe Mountain oil shale and marlstone samples, µg/g

Sample no/Element	30-1	30-2	30-3	30-4	30-5	30-6	30-7	30-8	30-9	30-10	30-11	30-12	30-13	30-14
As	2.01	15.8	9.41	19.6	11.3	10.0	12.0	5.00	2.80	1.37	8.20	8.56	15.0	2.39
B	13.7	17.1	61.2	84.0	7.88	7.16	15.0	23.0	32.0	30.5	75.0	55.2	29.0	41.4
Ba	48.2	31.7	102	186	52.4	57.3	73.0	99.0	56.0	48.4	235	224	95.0	71.6
Be	0.23	0.31	0.72	1.13	0.17	0.19	0.30	0.40	0.50	0.65	1.10	0.86	0.60	0.59
Bi	0.08	<0.05	0.10	0.33	0.13	0.13	0.20	0.20	<0.05	0.06	0.30	0.33	0.30	0.06
Cd	<0.05	0.05	0.17	0.81	6.53	2.98	2.00	0.80	0.10	<0.05	0.20	0.20	0.40	0.08
Ce	6.53	8.13	17.4	24.6	4.12	3.84	6.80	11.0	11.0	13.5	23.0	21.1	15.0	13.5
Co	6.08	6.05	8.78	15.6	12.1	12.9	13.0	10.0	6.30	6.82	14.0	15.8	17.0	7.80
Cr	10.1	10.9	34.5	51.6	8.93	32.1	13.0	21.0	13.0	29.2	55.0	37.4	25.0	18.9
Cs	0.85	0.92	3.77	5.68	0.62	0.47	1.00	2.10	1.50	1.95	5.50	4.33	2.40	2.13
Cu	8.91	12.4	17.2	66.6	54.5	51.6	59.0	50.0	11.0	9.33	73.0	89.9	85.0	10.2
Dy	0.46	0.59	0.96	1.60	0.47	0.42	0.70	0.80	0.80	1.09	1.40	1.40	1.40	1.01
Er	0.25	0.34	0.61	0.97	0.28	0.27	0.30	0.40	0.40	0.58	0.90	0.83	0.80	0.52
Eu	0.12	0.15	0.23	0.37	0.09	0.11	0.20	0.20	0.20	0.26	0.30	0.33	0.30	0.24
Ga	1.50	1.76	5.89	9.45	1.39	1.29	2.00	3.60	2.50	3.22	8.90	7.56	4.90	3.72
Gd	0.51	0.65	0.98	1.77	0.46	0.43	0.70	0.90	0.90	1.02	1.50	1.59	1.50	1.10
Hf	0.33	0.37	1.2	1.49	0.18	0.14	0.30	0.60	0.60	0.60	1.3.0	1.05	0.6	0.65
Hg	0.023	0.027	0.053	0.059	0.074	0.043	0.029	0.032	0.048	0.015	0.029	0.025	0.046	0.015
Ho	0.08	0.11	0.21	0.32	0.09	0.09	0.10	0.20	0.20	0.21	0.30	0.29	0.30	0.19
La	3.32	3.95	9.09	12.3	2.46	2.30	3.70	5.30	5.10	6.50	12.0	10.2	7.50	6.68
Li	4.55	5.40	16.5	29.1	4.48	4.10	6.40	12.0	10.0	7.99	28.0	24.0	16.0	8.85
Lu	<0.05	<0.05	0.11	0.14	<0.05	<0.05	<0.05	0.10	0.10	0.08	0.10	0.11	0.10	0.08
Mo	0.87	0.97	3.78	20.7	70.0	59.7	50.0	18.0	0.90	0.66	16.0	25.3	52.0	1.61
Nb	1.59	1.52	4.78	6.15	0.64	0.56	1.00	2.20	2.10	2.38	5.40	4.39	2.50	2.79
Nd	2.85	3.49	6.90	9.99	1.79	1.73	2.90	4.60	4.70	6.19	9.20	8.42	6.60	5.64
Ni	27.9	39.5	37.8	67.4	69.2	75.2	73.0	68.0	32.0	32.7	77.0	79.0	78.0	33.0
Pb	1.95	2.00	6.21	15.7	4.72	4.28	6.30	5.80	4.50	3.49	15.0	14.7	14.0	3.40
Pr	0.70	0.93	1.88	2.72	0.47	0.46	0.80	1.20	1.20	1.55	2.50	2.29	1.60	1.50
Rb	16.3	18.3	68.2	96.1	8.89	6.87	13.0	31.0	26.0	34.0	90.0	69.2	360	40.8

Sample no/Element	30-15	30-16	30-17	30-18	30-19	30-20	30-21	30-22	30-23	30-24	30-25	30-26	30-27	30-28	Av in oil shale	Av in marlstone	EF
As	1.45	13.0	15.0	15.0	10.0	13.0	1.47	6.90	7.38	8.10	8.00	6.02	6.90	5.90	10.5	4.45	10.54
B	21.8	200	48.2	126	126	152	48.7	156	139	113	72.0	51.6	30.0	23.4	78.8	28.7	7.88
Ba	43.4	420	341	295	279	336	84.2	327	350	342	295	167	93.0	74.1	225	61.1	0.90
Be	0.46	2.70	2.10	2.00	1.80	2.2	0.81	2.10	1.85	1.80	1.40	1.00	0.50	0.38	1.28	0.49	0.86
Bi	<0.05	0.40	0.40	0.40	0.30	0.40	0.06	0.30	0.27	0.20	0.20	0.14	0.10	0.06	0.26	0.05	4.25
Cd	<0.05	0.10	0.20	0.40	0.20	0.20	0.06	0.10	0.14	0.20	0.10	0.10	0.10	0.07	0.83	0.05	8.46
Ce	11.1	55.0	50.0	45.0	39.0	47.0	20.7	430	42.8	39.0	30.0	20.7	12.0	9.26	28.3	11.7	0.86
Co	6.68	17.0	17.0	26.0	19.0	18.0	8.29	16.0	16.5	16.0	15.0	13.3	9.80	8.80	15.4	7.40	0.53
Cr	15.7	112	111	97.0	91.0	110	30.8	91.0	99.2	84.0	77.0	47.2	23.0	19.0	63.0	19.0	0.34
Cs	1.51	17.0	13.0	9.50	9.40	12.0	2.86	11.0	10.8	9.2.	7.1.	4.33	2.3.0	1.60	6.82	1.73	6.82
Cu	8.83	90.0	80.0	106	64.0	87.0	11.1	69.0	68.0	65.0	58.0	44.7	32.0	25.0	67.3	14.3	0.90
Dy	0.87	2.30	2.60	3.30	2.30	3.00	1.46	2.50	2.58	2.50	2.20	1.64	1.10	0.88	1.78	0.91	0.48
Er	0.48	1.60	1.70	1.80	1.50	1.90	0.89	1.60	1.56	1.50	1.20	0.93	0.70	0.50	1.08	0.51	0.49
Eu	0.21	0.50	0.60	0.80	0.50	0.70	0.37	0.50	0.59	0.60	0.50	0.38	0.30	0.22	0.42	0.23	0.38
Ga	2.60	24.0	20.0	17.0	16.0	20.0	5.05	19.0	17.5	15.0	12.0	7.36	4.00	2.79	11.2	3.02	0.62
Gd	0.95	2.40	2.70	3.70	2.40	3.50	1.58	2.30	2.74	2.80	2.50	1.79	1.20	0.96	1.93	0.99	0.58
Hf	0.48	3.9	3.40	2.70	2.60	3.20	1.07	2.80	2.61	2.30	1.70	1.05	0.70	0.46	1.73	0.58	0.58
Hg	0.004	0.034	0.033	0.029	0.037	0.045	0.033	0.028	0.018	0.027	0.029	0.025	0.019	0.058	0.04	0.03	1.83
Ho	0.17	0.50	0.50	0.60	0.50	0.60	0.28	0.50	0.52	0.50	0.40	0.34	0.20	0.18	0.36	0.18	0.47
La	5.35	27.0	24.0	20.0	19.0	22.0	9.97	21.0	20.7	19.0	15.0	10.6	6.40	5.01	13.8	5.81	0.86
Li	6.05	53.0	47.0	46.0	39.0	50.0	12.5	42.0	38.5	35.0	28.0	20.1	11.0	7.80	28.3	8.24	2.18
Lu	0.06	0.30	0.30	0.30	0.20	0.30	0.12	0.20	0.23	0.20	0.20	0.12	0.10	0.06	0.15	0.06	0.51
Mo	0.82	11.0	13.0	21.0	12.0	16.0	0.83	7.80	8.89	8.90	10.0	8.71	8.20	6.03	22.8	2.31	22.82
Nb	1.92	19.0	16.0	13.0	13.0	15.0	4.78	14.0	13.1	12.0	8.80	5.31	2.90	1.96	8.22	2.43	0.75
Nd	4.82	20.0	19.0	19.0	15.0	19.0	8.79	17.0	17.4	16.0	13.0	8.82	5.40	4.17	11.5	5.12	0.72
Ni	29.6	74.0	76.0	127	87.0	83.0	31.9	77.0	80.9	77.0	74.0	56.7	48.0	43.1	75.5	35.3	0.72
Pb	2.55	22.0	21.0	21.0	15.0	21.0	3.95	14.0	13.7	13.0	10.0	8.07	5.60	4.21	12.9	3.52	1.61
Pr	1.23	5.70	5.30	5.00	4.10	5.00	2.26	4.70	4.66	4.30	3.30	2.30	1.40	1.06	3.06	1.31	0.79
Rb	28.0	194	163	144	141	156	55.2	143	154	150	116	73.6	39.0	27.5	97.6	31.6	3.05

Table 3. (Continuation)

Sample no/Element	30-1	30-2	30-3	30-4	30-5	30-6	30-7	30-8	30-9	30-10	30-11	30-12	30-13	30-14	30-15	30-16	30-17	30-18	30-19	30-20	30-21	30-22	30-23	30-24	30-25	30-26	30-27	30-28	Av in oil shale	Av in marlstone	EF
Sc	2.88	2.81	6.06	8.22	2.06	2.06	2.50	4.10	3.70	4.01	7.40	6.09	4.60	4.47	3.68	19.0	17.0	16.0	14.0	17.0	5.63	15.0	14.1	13.0	10.0	7.51	4.60	3.98	9.76	3.97	0.33
Se	0.10	0.20	0.73	1.67	1.51	1.26	1.70	1.30	0.30	0.16	1.20	1.67	2.60	0.15	0.15	1.30	1.40	1.80	1.30	2.10	0.24	0.90	1.07	1.10	1.20	1.21	1.00	0.8	1.42	0.34	28.44
Sm	0.56	0.66	1.25	1.87	0.42	0.37	0.70	0.80	0.90	1.23	1.60	1.72	1.30	1.13	1.02	3.20	3.50	4.10	2.60	4.00	1.67	3.10	3.07	3.10	2.60	1.72	1.20	0.87	2.16	1.03	0.62
Sn	0.71	0.79	1.30	1.61	0.64	0.65	0.80	1.00	0.90	1.02	1.90	1.58	1.10	1.11	0.93	3.60	3.20	2.70	2.50	3.10	1.20	2.90	2.76	2.40	2.00	1.45	1.10	0.88	1.94	0.96	0.78
Sr	300	321	362	249	578	449	339	325	336	318	206	203	233	256	258	302	291	232	224	248	296	176	244	297	391	477	824	1277	307	465	1.18
Ta	0.19	0.13	0.36	0.47	<0.05	<0.05	0.10	0.20	0.20	0.20	0.40	0.34	0.20	0.22	0.16	1.30	1.20	0.90	0.90	1.10	0.35	1.00	0.94	0.80	0.60	0.38	0.20	0.16	0.59	0.20	0.59
Tb	0.07	0.10	0.15	0.24	0.07	0.07	0.10	0.10	0.10	0.16	0.20	0.23	0.20	0.16	0.15	0.40	0.40	0.60	0.40	0.50	0.24	0.40	0.42	0.40	0.40	0.27	0.20	0.14	0.29	0.15	0.49
Th	1.01	1.11	3.59	5.25	0.60	0.54	0.90	1.90	1.60	1.96	5.00	4.04	2.40	2.10	1.48	14.0	12.0	9.50	9.30	11.0	3.28	10.0	9.32	8.30	6.10	3.77	2.20	1.62	0.17	1.82	1.76
Tm	<0.05	<0.05	0.10	0.14	<0.05	<0.05	<0.05	0.10	0.10	0.08	0.10	0.12	0.10	0.08	0.07	0.30	0.20	0.30	0.20	0.30	0.12	0.20	0.22	0.20	0.20	0.14	0.10	0.07	0.15	0.06	0.47
U	0.51	0.58	1.73	3.84	2.71	2.73	3.40	3.40	0.60	0.73	4.40	5.17	4.50	0.72	0.50	4.20	5.00	6.90	4.30	5.90	0.87	2.30	2.13	2.00	1.60	1.26	1.00	0.88	3.54	0.71	3.89
V	15.3	18.4	54.8	80.2	45.1	38.9	41.0	42.0	24.0	28.2	94.0	85.1	66.0	27.2	20.6	123	115	105	117	118	39.9	109	111	101	82	61.3	37.0	31.3	83.7	26.9	0.36
W	0.16	0.18	0.50	0.72	0.29	0.36	0.40	0.40	0.20	0.28	0.80	0.87	0.60	0.29	0.23	1.60	1.40	1.20	1.20	1.30	0.73	1.20	1.13	1.10	0.80	0.56	0.30	0.31	0.86	0.31	0.86
Y	2.86	3.39	5.50	8.94	3.05	2.89	4.00	4.60	4.200	5.77	7.8	7.68	8.20	5.48	5.08	12.0	12.0	16.0	12.0	15.0	8.11	13.0	13.5	13.0	12.0	9.52	6.70	5.33	9.50	5.21	0.47
Yb	0.22	0.30	0.68	0.93	0.23	0.19	0.30	0.40	0.40	0.53	0.90	0.78	0.70	0.52	0.41	1.80	1.80	1.70	1.40	1.70	0.73	1.60	1.61	1.40	1.10	0.87	0.6	0.46	1.05	0.46	0.48
Zn	5.81	8.78	22.6	70.0	425	134	183	58	6.90	8.74	30.0	21.3	24.0	11.6	9.12	38.0	34.0	31.0	29.0	34.0	12.9	29.0	28.9	24.0	20.0	19.9	11.0	6.92	66.0	9.06	0.83
Zr	14.2	15.8	52.5	63.0	7.99	6.54	12.0	24.0	23.0	23.2	55.0	46.3	29	26.4	18.9	149	125	111	106	122	44.1	109	108	94.0	73.0	46.5	30.0	18.5	70.5	23.9	0.70

Av in oil shale – average element content in oil shale; Av in marlstone – average element content in marlstone; EF – ratio of the concentration of an element in sample to the average concentration of the element in the upper continental crust.

Table 4. Concentrations of trace elements in selected minerals and fossil remains, µg/g

Sample no/Mineral/Fossil/Element	30-3	30-4	30-5	30-6		30-7	30-11		30-12		30-13	30-16	30-17	30-18	30-19	30-20	30-22	30-23	30-24	30-25	30-26	.30-29	30-30	Av in CMO	Av in dolomite	Av in fossil
	CMO	CMO	CMO	CMO	Calcite	CMO	CMO	Dolomite	Dolomite	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	Fossil	Fossil			
As	2.69	5.25	4.06	16.5	1.22	9.96	9.23	0.28	0.38	5.83	23.3	5.07	13.7	12.7	5.90	6.47	7.95	3.56	4.25	4.28	11.2	3.18	1.85	10.5	0.33	2.52
B	230	250	50.7	43.8	<2	67.0	214	<2	<2	138	87.7	258	215	201	227	230	251	271	247	248	239	6.84	12.8	78.8	<2	9.82
Ba	288	275	82.6	81.9	20.0	109	300	266	179	258	153	403	376	370	379	398	351	390	399	363	401	36.6	47.2	225	223	41.9
Be	1.97	1.87	0.69	0.56	0.06	0.95	1.97	<0.05	<0.05	1.62	1.22	2.71	2.62	2.53	2.58	2.69	2.79	2.79	2.73	2.75	2.52	<0.05	0.05	1.28	<0.05	<0.05
Bi	<0.05	0.13	0.16	0.37	<0.05	0.06	0.28	<0.05	<0.05	0.10	0.41	<0.05	0.40	0.29	0.14	0.13	0.20	0.05	0.05	0.07	0.11	<0.05	<0.05	0.26	<0.05	<0.05
Cd	<0.05	0.07	0.19	1.36	2.31	0.18	0.08	<0.05	<0.05	0.07	0.27	0.05	0.25	0.15	<0.05	0.17	0.08	<0.05	<0.05	<0.05	0.06	1.32	4.31	0.83	<0.05	2.82
Ce	43.2	39.2	12.8	10.5	1.53	16.6	41.6	2.77	4.15	36.5	23.0	51.8	54.8	46.6	44.4	50.7	47.6	45.6	46.1	37.0	35.4	0.58	0.59	28.3	3.46	0.59
Co	1.84	2.89	3.71	19.1	2.73	7.83	5.57	1.18	1.67	4.25	21.7	3.97	19.1	25.7	2.54	8.54	14.9	3.10	4.85	5.03	11.9	4.87	4.68	15.4	1.43	4.78
Cr	111	90.6	35.4	27.2	3.19	45.9	84.3	6.88	2.76	71.8	70.9	161	168	163	146	166	149	151	150	142	157	8.89	4.41	63.0	4.82	6.65
Cs	9.86	9.50	2.26	1.75	0.07	3.09	9.30	0.12	0.13	6.79	4.44	15.2	17.9	12.0	13.1	13.1	12.7	13.2	12.9	12.9	11.7	0.09	0.09	6.82	0.13	0.09
Cu	4.89	10.8	27.9	102	7.61	32.1	27.1	3.94	3.97	19.7	94.4	19.3	99.6	119	19.7	41.2	63.9	12.3	20.3	21.8	42.6	6.8	6.55	67.3	3.96	6.68
Dy	1.03	1.01	0.41	0.56	0.16	0.5	0.95	0.50	0.84	0.88	0.81	1.34	1.78	1.33	1.17	1.28	1.38	1.26	1.35	1.17	1.12	<0.05	0.05	1.78	0.67	<0.05
Er	1.00	0.95	0.37	0.40	0.10	0.44	0.94	0.22	0.34	0.77	0.69	1.40	1.53	1.26	1.17	1.32	1.32	1.27	1.32	1.14	1.16	<0.05	<0.05	1.08	0.28	<0.05
Eu	0.24	0.23	0.09	0.13	<0.05	0.14	0.25	0.16	0.25	0.25	0.19	0.28	0.39	0.29	0.23	0.26	0.27	0.20	0.23	0.21	0.19	<0.05	<0.05	0.42	0.21	<0.05
Ga	22.4	20.0	6.81	5.77	0.24	10.2	20.8	0.42	0.44	17.5	12.5	28.4	25.1	25.4	25.6	26.7	26.3	28.7	28.5	26.9	26.1	0.26	0.24	11.2	0.43	0.25
Gd	0.92	0.94	0.47	0.58	0.16	0.54	0.98	0.67	1.00	0.98	0.81	1.10	1.78	1.08	1.05	1.15	1.04	0.88	1.02	0.89	0.79	0.05	0.07	1.93	0.84	0.06
Hf	4.44	3.60	1.27	0.94	<0.05	1.66	3.23	<0.05	<0.05	2.47	1.84	4.90	4.33	4.10	4.52	4.65	4.42	4.69	4.58	4.27	4.06	<0.05	<0.05	1.73	<0.05	<0.05
Ho	0.27	0.24	0.10	0.12	<0.05	0.12	0.24	0.09	0.15	0.21	0.18	0.36	0.41	0.32	0.29	0.32	0.35	0.33	0.33	0.29	0.28	<0.05	<0.05	0.36	0.12	<0.05
La	24.8	22.9	8.08	6.34	1.03	10.1	23.2	1.03	1.50	20.3	13.7	30.6	29.1	25.9	26.9	28.6	26.5	26.9	26.8	23.6	22.6	0.32	0.32	13.8	1.27	0.32
Li	64.8	62.8	23.5	19.8	1.20	33.7	60.1	1.20	1.26	50.9	39.2	60.2	55.8	62.3	57.8	59.6	57.3	59.7	62.2	57.9	63.6	0.53	0.57	28.3	1.23	0.55
Lu	0.21	0.18	0.07	0.06	<0.05	0.08	0.18	<0.05	<0.05	0.14	0.12	0.29	0.29	0.24	0.24	0.26	0.26	0.25	0.26	0.23	0.23	<0.05	<0.05	0.15	<0.05	<0.05
Mo	10.4	15.2	39.1	164	9.85	55.3	18.8	0.91	3.00	23.3	106	5.99	22.4	26.1	7.75	12.8	9.91	7.31	6.35	7.81	15.7	1.68	1.45	22.8	1.96	1.57
Nb	13.9	12.1	3.81	2.88	0.12	5.45	11.0	0.18	0.16	8.79	6.26	20	16.9	16.4	18.3	18.2	17.0	19.2	18.4	17.9	16.4	0.11	0.12	8.22	0.17	0.12
Nd	14.7	12.9	4.88	4.37	0.82	5.92	13.7	2.12	3.23	12.4	8.10	19.1	20.3	16.3	14.7	17.0	16.0	15.5	15.2	12.2	10.5	0.2	0.23	11.5	2.68	0.22
Ni	19.8	27.1	91.2	157	23.1	98.8	50.0	13.0	12.4	43.1	129	19.7	92.3	131	24.1	47.6	78.6	22.1	36.1	39.4	76.3	32.3	29.5	75.5	12.7	30.9

Table 4. (Continuation)

Sample no/Mineral/ Fossil/Element	30-3	30-4	30-5	30-6		30-7	30-11		30-12		30-13	30-16	30-17	30-18	30-19	30-20	30-22	30-23	30-24	30-25	30-26	.30-29	30-30	Av in CMO	Av in dolomite	Av in fossil
	CMO	CMO	CMO	CMO	Calcite	CMO	CMO	Dolomite	Dolomite	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	CMO	Fossil	Fossil			
Pb	3.83	11.4	2.41	271	2.36	14.0	71.5	2.13	2.20	11.8	14.8	4.07	70.0	16.7	7.26	9.92	20.9	3.24	3.91	8.63	7.94	0.94	0.78	12.9	2.17	0.86
Pr	4.68	4.19	1.44	1.23	0.20	1.80	4.39	0.45	0.66	3.97	2.53	6.23	6.31	5.48	4.98	5.77	5.22	5.17	5.1	4.28	3.76	0.06	0.06	3.06	0.56	0.06
Rb	197	175	44.5	31.4	1.08	62.2	177	2.10	1.88	138	85.0	263	249	221	241	259	248	244	248	222	221	1.60	1.50	97.6	1.99	1.55
Sc	9.52	9.09	2.99	2.37	0.71	4.02	9.90	0.71	0.86	7.83	5.66	16.5	18.5	14.8	13.5	16.1	14.5	14.0	14.0	12.5	12.3	1.74	1.63	9.76	0.79	1.69
Sm	1.75	1.66	0.68	0.73	0.15	0.87	1.71	0.59	0.94	1.65	1.16	2.01	2.66	1.79	1.46	1.92	1.71	1.57	1.54	1.30	1.20	<0.05	0.06	2.16	0.77	0.03
Sn	3.68	3.19	1.29	1.01	0.43	1.55	3.66	0.50	0.40	2.81	1.99	4.74	4.18	4.13	4.38	4.32	4.17	4.66	4.56	4.16	3.91	0.64	0.59	1.94	0.45	0.62
Sr	112	109	33.2	59.0	1151	49.8	112	148	158	101	58.4	177	463	216	162	191	121	122	130	106	107	257	298	307	153	278
Ta	1.37	1.14	0.37	0.27	<0.05	0.52	1.04	<0.05	<0.05	0.81	0.56	1.81	1.5	1.44	1.6	1.63	1.59	1.69	1.65	1.52	1.48	<0.05	<0.05	0.59	<0.05	<0.05
Tb	0.14	0.13	0.06	0.08	<0.05	0.07	0.14	0.08	0.14	0.13	0.11	0.17	0.25	0.19	0.15	0.18	0.17	0.16	0.16	0.15	0.14	<0.05	<0.05	0.29	0.11	<0.05
Th	7.43	6.49	1.87	1.91	0.11	2.15	6.73	0.25	0.31	4.68	3.31	9.1	13	7.2	6.71	7.81	8.53	7.34	7.02	5.69	5.62	0.08	0.09	0.17	0.28	0.09
Tm	0.16	0.15	0.06	0.06	<0.05	0.07	0.15	<0.05	<0.05	0.12	0.10	0.23	0.22	0.20	0.18	0.22	0.21	0.22	0.22	0.2	0.19	<0.05	<0.05	0.15	<0.05	<0.05
U	4.15	5.05	4.38	6.15	0.62	3.68	5.05	0.32	1.35	5.92	4.73	2.70	4.75	5.36	4.32	4.02	2.73	2.08	2.49	2.17	2.49	0.22	0.18	3.54	0.84	0.2
V	133	124	133	127	9.5	110	172	5.16	7.07	151	122	204	201	210	199	221	156	174	173	173	174	12.1	10.6	83.7	6.12	11.4
W	1.89	2.01	1.04	1.34	0.09	2.21	1.98	0.21	0.06	1.61	1.38	2.08	1.85	1.78	1.89	2.01	2.07	2.03	2.00	2.21	2.16	0.06	0.07	0.86	0.14	0.07
Y	6.66	6.14	2.48	3.39	1.16	3.34	6.36	2.61	4.13	5.72	4.94	8.56	9.80	8.06	7.53	8.09	8.94	8.52	8.78	8.02	7.32	0.41	0.41	9.50	3.37	0.41
Yb	1.34	1.21	0.44	0.39	0.09	0.51	1.13	0.13	0.20	0.87	0.76	1.82	1.79	1.59	1.46	1.64	1.69	1.55	1.66	1.42	1.38	<0.05	<0.05	1.05	0.17	<0.05
Zn	18.7	19.6	104	396	34.1	88.3	20.4	1.96	3.17	15.0	35.9	20.0	53.5	35.0	19.6	35.7	32.5	20.2	23.2	20.4	26.4	112	567	66.0	2.57	340
Zr	136	111	43.0	33.9	1.18	56.9	106	1.57	1.63	84.9	61.4	171	147	139	159	156	141	158	157	153	132	1.18	1.38	70.5	1.60	1.28

CMO – clay minerals and organic matter;
Av in CMO – average element content in clay minerals and organic matter;
Av in dolomite – average element content in dolomite;
Av in fossil – average element content in fossil remains.

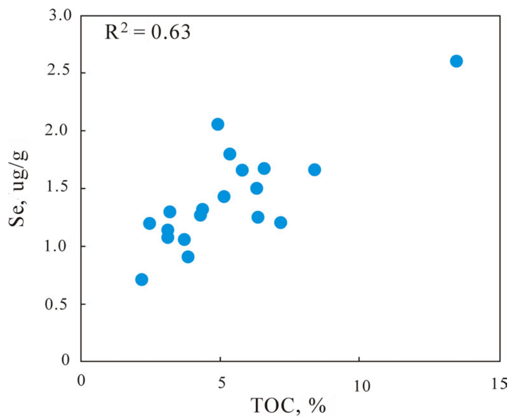


Fig. 2. Correlation between Se and TOC contents in Changshe Mountain oil shale samples.

abundant fossils found in oil shale seams, because Cd is present in the fossils as a micro-nutrient [20].

In the present study, raw Changshe Mountain oil shale samples are also found to have a slightly higher B content. This may be attributed to weathering source rocks, because B is mainly present in clay minerals (Fig. 4). Clearly, the enrichment of an element in oil shale seams may be a function of that association and the origin of various oil shale fractions.

4.3. Modes of occurrence of trace elements in marine oil shale

According to the results of cluster analysis, four element association groups were identified (Fig. 3), referred to as groups A, B, C and D.

Group A includes Ba, V, Sn, Li, W, Be, Ga, B, Sc, Si, Rb, Zr, Hg, Th, Al, K, Nb, Ti, Cr, Cs, and REEs. The correlation coefficients of Ce-Pr (R^2 = 0.998), Nd-Yb (R^2 = 0.996), La-Sn (R^2 = 0.986), Li-W (R^2 = 0.962), Dy-Ho (R^2 = 0.994), Er-Y (R^2 = 0.960), Eu-Gd (R^2 = 0.988), Sm-Tb (R^2 = 0.976), Be-Ga (R^2 = 0.992), Sc-Si (R^2 = 0.992), Rb-Zr (R^2 = 0.974), Hf-Th (R^2 = 0.998), Al-K (R^2 = 0.996) and Nb-Ti (R^2 = 0.998) are all higher than 0.95. Group A can be split into Group A1 and Group A2 (Fig. 3). Group A1 consists of all the REEs, which should be expected to be strongly correlated in sedimentary rocks, plus Ba, V, Sn, Li, W, whereas Group A2 consists of the remainder, including elements that might be expected to be associated with siliciclastic sedimentary rocks.

Group B represents the Bi-Pb-Fe-Co-Ni-U association (Fig. 3). The coefficient of correlation between Bi and Pb (R^2 = 0.914) is the highest within this association. Elements of this group have positive coefficients of correlation with Fe, indicating the prevailing Fe-bearing mineral affinity. Note that Fe and Al exhibit a very strong correlation, especially when the most organic-rich (TOC > 5.5%) samples are plotted separately (Fig. 5). The

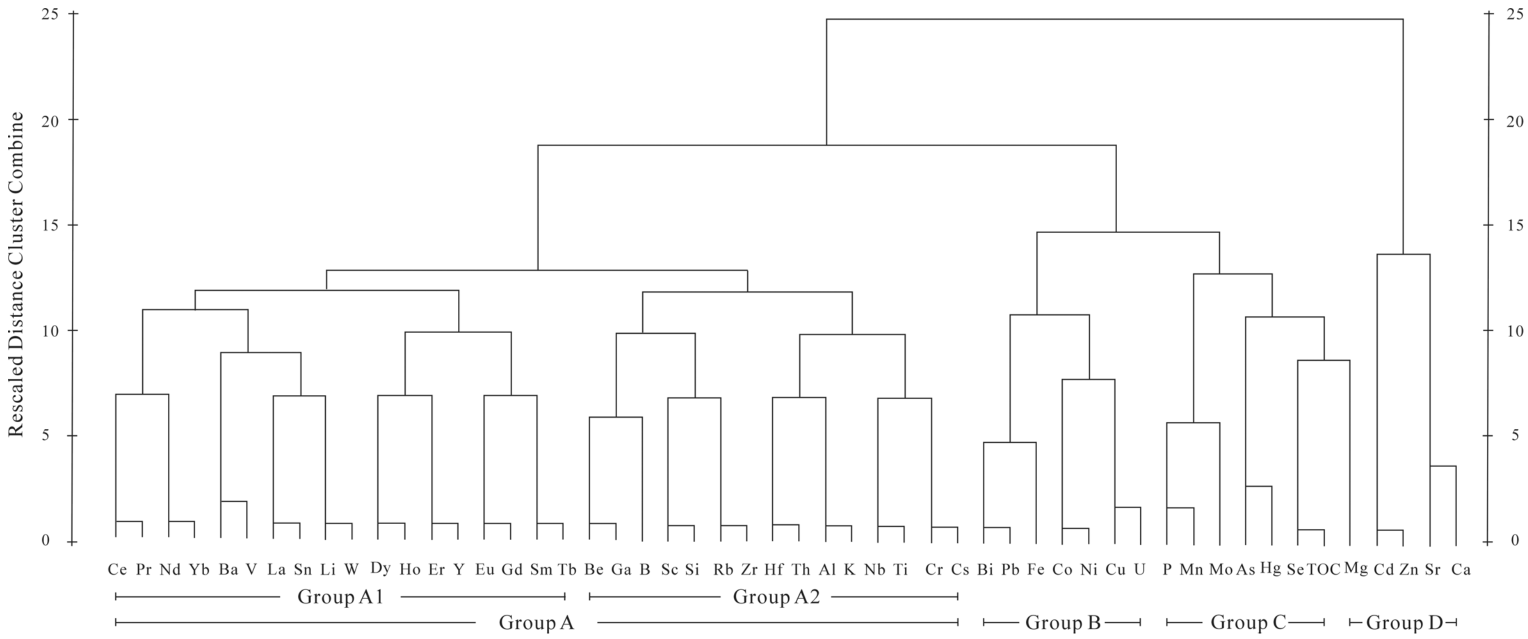
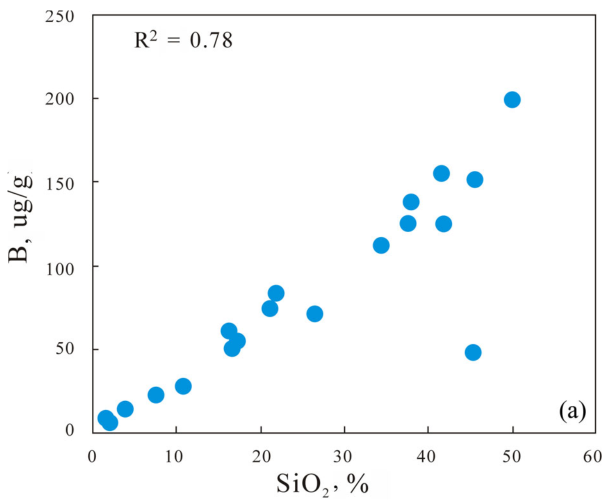


Fig. 3. Dendrogram produced by cluster analysis of analytical results on 19 raw oil shale samples (cluster method, centroid clustering; interval, Pearson's correlation; transform values, maximum magnitude of 1).



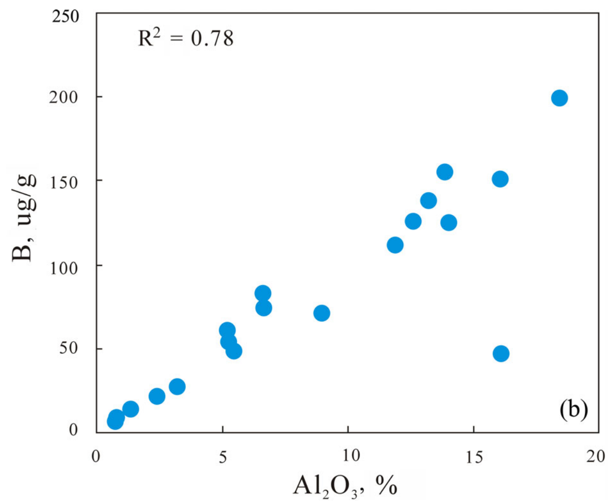


Fig. 4. Plot of the concentration of (a) B vs. SiO_2 and (b) B vs. Al_2O_3 showing the dominance of B in clay minerals.

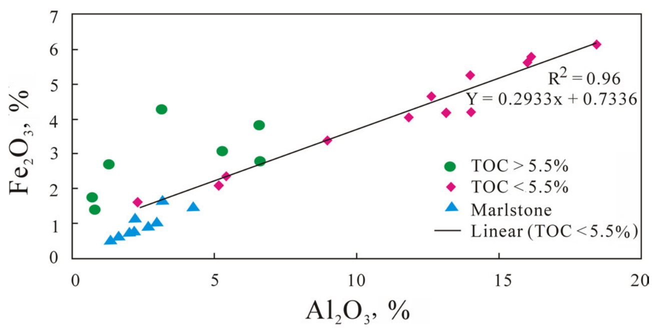


Fig. 5. Relationship between the Al_2O_3 and Fe_2O_3 contents of Changshe Mountain oil shale samples.

average values for clay minerals and organic matter (CMO) indicate that CMO are enriched in U (1.13-fold) and Pb (2.38-fold) relative to oil shale, whereas Co (0.60), Ni (0.87) and Bi (0.63) are slightly depleted. It is difficult to see these as reflecting the same chemical influence, except the influence of Al_2O_3, which reflects detrital input. Pyrite was probably derived from clastic material, along with many other metals, and hence was transferred to the sulfide phase, along with these metals, by diagenesis.

Group C comprises Ph, Mn, Mo, As, Se and Mg, which all have positive coefficients of correlation with TOC content. These elements, together with Hg, are clustered in the third association (Fig. 3) and are mainly present in organic matter.

Group D includes Cd, Zn, Sr and Ca. With an exception of the high correlation coefficients of Cd-Zn (R^2 = 0.958), the correlation coefficients of the other pairs of elements in this association are lower than 0.622. Elements of this group have positive coefficients of correlation with Ca content, indicating the prevailing Ca-bearing affinity.

To explain the relations between trace element contents and major element and TOC contents, and determine the modes of occurrence of trace elements, analysis of selected minerals was carried out. Tables 2 and 4 present trace element contents in 21 mineral separates and 2 fossil remains. The concentrations of As, B, Ba, Be, Bi, Co, Cr, Cs, Cu, Ga, Hf, Li, Mo, Nb, Ni, Pb, Rb, Sc, Sn, Ta, Th, U, V, W, Zr and REEs are higher in clay minerals and organic matter than in calcite, dolomite and fossil remains, suggesting that these elements are controlled mainly by organic matter and/or clay minerals. However, the average contents of some elements, such as Bi, Co, Cu and Ni, in isolated clay minerals and organic matter are lower than those in raw oil shale samples. These elements are correlated closely with Fe, and also form a group with Fe (Fig. 3), indicating that they are mainly present in pyrite.

Trace elements showing enrichment in calcite include Cd and Sr, while trace elements Cd and Zn are abundant mainly in fossil remains. Compared with other carbonate minerals, dolomite has a higher Ba concentration, indicating that Ba is controlled partly by dolomite besides clay minerals as discussed above.

By indirect and direct methods, the following main affinities are established: 1) clay mineral affinity – B, Ba, Be, Cr, Cs, Ga, Hf, Li, Nb, Rb, Sc, Sn, Ta, Th, V, W, Zr, REEs; 2) organic affinity – As, Mo, Se; 3) Fe-bearing mineral affinity – Bi, Co, Cu, Ni, Pb, U; 4) calcite affinity – Cd, Sr; and 5) fossil affinity – Cd, Zn.

4.4. Volatility of trace elements during oil shale combustion

The concentrations of trace elements in Changche Mountain oil shale combustion residues are presented in Tables 2 and 5. In order to understand the volatilization of trace elements during the combustion process, the volatility can be calculated by the following formula: $V\% = [1 - (C_i/C_0) \times Y] \times 100$,

Table 5. Concentrations of trace elements in Changshe Mountain oil shale combustion residues, µg/g

Sample no/Element	30-3-1	30-4-1	30-5-1	30-6-1	30-7-1	30-8-1	30-11-1	30-12-1	30-13-1	30-16-1	30-17-1	30-18-1	30-19-1	30-20-1	30-22-1	30-23-1	30-24-1	30-25-1	30-26-1	RE	Av volatility
As	10.1	17.0	14.6	12.8	11.2	9.58	11.2	11.5	16.9	13.7	13.4	13.3	10.8	13.5	7.92	8.95	8.62	8.53	6.38	1.09	23.8
B	63.9	79.2	13.4	11.0	20.0	45.4	78.3	61.2	39.3	237	176	143	126	173	185	150	137	105	52	1.27	19.4
Ba	107	228	68.1	79.8	80.4	142	246	226	117	420	356	306	281	374	323	352	334	270	138	1.04	26.7
Be	0.78	1.27	0.31	0.28	0.31	0.70	1.13	1.02	0.78	2.99	2.58	2.14	1.84	2.70	2.32	2.15	1.98	1.48	0.84	1.13	20.5
Bi	0.11	0.31	0.18	0.15	0.20	0.22	0.40	0.38	0.37	0.42	0.42	0.39	0.36	0.47	0.34	0.31	0.29	0.23	0.15	1.18	18.6
Cd	0.22	1.12	12.7	5.29	2.37	0.75	0.25	0.24	0.37	0.11	0.25	0.54	0.28	0.23	0.17	0.17	0.15	0.14	0.13	1.62	7.4
Ce	19.6	26.4	7.60	7.03	8.34	15.9	27.4	23.8	18.9	49.1	54.7	50.6	40.5	53.5	48.1	47.0	45.7	33.7	21.3	1.11	19.5
Co	6.63	16.6	13.2	15.0	12.2	9.72	16.2	17.0	19.4	17.1	17.8	28.1	17.5	21.3	16.1	17.0	17.0	13.7	10.1	1.03	29.6
Cr	40.4	53.7	15.3	12.1	15.3	33.6	49.5	39.5	30.2	160	138	121	103	149	118	108	105	78.5	41.7	1.18	20.5
Cs	4.25	6.15	1.26	1.02	1.56	3.98	6.34	4.9	3.13	18.1	15.8	10.4	9.29	12.8	12.2	10.8	10.4	7.47	3.84	1.11	17.5
Cu	14.1	78.9	81.7	73.4	73.6	49.0	105	108	109	97.1	95.9	113	64.9	111	77.8	79.7	78.4	63.5	44.2	1.19	19.1
Dy	1.20	2.00	0.88	0.86	0.85	1.10	1.94	1.82	2.00	2.33	3.15	4.37	2.84	4.02	2.95	3.16	3.26	2.71	2.06	1.29	9.4
Er	0.81	1.25	0.53	0.50	0.48	0.70	1.18	1.07	1.13	1.86	2.00	2.39	1.75	2.37	1.86	1.97	1.96	1.59	1.19	1.29	8.6
Eu	0.28	0.48	0.17	0.18	0.20	0.28	0.43	0.41	0.44	0.51	0.75	1.01	0.65	0.96	0.69	0.73	0.78	0.67	0.48	1.27	10.9
Ga	6.91	10.9	2.66	2.71	2.73	6.54	10.8	9.16	6.23	28.6	24.8	20.6	17.3	25.2	21.9	19.7	18.9	13.5	7.2	1.21	13.8
Gd	1.25	2.23	0.88	0.83	0.85	1.23	2.02	1.98	1.94	2.41	3.28	4.64	2.94	4.54	3.00	3.28	3.63	2.91	2.09	1.25	11.6
Hf	1.54	1.85	0.38	0.45	0.4	1.30	1.87	1.43	0.99	4.85	4.41	3.47	3.23	4.18	3.81	3.25	3.04	2.22	1.14	1.33	1.9
Hg	0.009	0.005	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	0.001	<0.001	0.004	<0.001	<0.001	0.003	0.002	0.002	<0.001	<0.001	0.04	93.0
Ho	0.25	0.42	0.17	0.17	0.17	0.23	0.40	0.35	0.38	0.52	0.63	0.81	0.57	0.76	0.61	0.61	0.65	0.54	0.38	1.25	11.8
La	10.7	14.3	4.59	4.15	4.63	8.52	14.6	12.3	10.1	30.7	28.0	24.0	21.0	26.8	25.2	23.9	23.1	17.6	11.8	1.21	14.0
Li	17.7	32.7	8.73	8.85	8.28	18.3	30.7	26.6	20.2	59.5	55.2	49.2	38.4	57.3	46.4	42.7	38.8	29.8	18.4	1.13	18.3
Lu	0.13	0.18	0.06	0.07	0.06	0.10	0.18	0.14	0.14	0.34	0.32	0.32	0.26	0.33	0.30	0.28	0.28	0.21	0.14	1.33	5.9
Mo	4.93	26.8	97.2	91.1	53.5	15.9	24.3	32.7	71.5	10.5	17.4	27.0	12.3	20.1	9.11	11.0	11.3	11.2	9.18	1.28	14.0
Nb	4.93	5.92	1.27	1.22	1.27	3.63	5.64	4.63	2.92	18.4	15.3	12.7	11.8	15.6	13.5	12.8	11.7	8.25	4.32	1.00	25.1

Table 5. (Continuation)

Sample no/Element	30-3-1	30-4-1	30-5-1	30-6-1	30-7-1	30-8-1	30-11-1	30-12-1	30-13-1	30-16-1	30-17-1	30-18-1	30-19-1	30-20-1	30-22-1	30-23-1	30-24-1	30-25-1	30-26-1	RE	Av volatility
Nd	8.17	12.1	3.62	3.52	3.83	7.02	11.7	10.4	9.41	22.4	22.7	23.7	17.4	23.9	20.7	21.2	20.2	15.3	10.1	1.23	11.7
Ni	35.1	84.9	89.5	85.5	81.0	74.1	99.9	101	100	86.2	92.8	152	95.9	111	90.2	97.9	96.8	78.9	49.8	1.19	18.3
Pb	6.82	17.5	7.24	6.46	7.62	8.77	19.7	18.1	19.2	22.6	23.5	22.8	15.0	24.7	16.4	15.3	14.5	11.6	8.84	1.17	19.1
Pr	2.40	3.17	0.99	0.92	1.05	1.94	3.29	2.84	2.44	6.61	6.45	6.33	4.86	6.39	5.76	5.71	5.52	4.15	2.64	1.26	9.3
Rb	66.7	100	16.1	13.0	19.3	59.7	92.1	77.1	44.8	253	221	189	171	235	210	183	173	126	64.1	1.25	12.8
Sc	6.36	8.67	2.35	2.68	2.25	5.20	7.99	6.91	5.13	20.7	19.8	18.7	15.1	20.8	16.3	15.5	15.3	11.2	6.34	1.12	24.2
Se	1.81	2.47	2.39	1.89	2.75	2.09	2.52	2.94	4.36	1.53	2.34	2.75	1.31	2.08	1.31	1.38	1.45	1.42	1.39	1.49	-3.2
Sm	1.56	2.37	0.76	0.76	0.9	1.41	2.22	2.11	2.04	3.29	4.22	5.25	3.38	5.16	3.75	4.09	3.97	3.20	2.06	1.28	9.7
Sn	1.95	1.94	0.68	0.70	0.78	1.40	2.17	1.84	1.28	4.8	4.07	3.4	2.98	3.98	3.36	3.2	3.2	2.19	1.31	1.23	17.0
Sr	420	325	779	631	411	402	278	286	344	428	388	354	336	378	223	315	356	456	652	1.33	3.2
Ta	0.51	0.58	0.15	0.15	0.14	0.37	0.53	0.44	0.29	1.72	1.44	1.17	1.09	1.42	1.27	1.13	1.07	0.77	0.42	1.31	7.0
Tb	0.20	0.31	0.14	0.14	0.13	0.19	0.31	0.28	0.30	0.34	0.50	0.69	0.47	0.66	0.45	0.51	0.53	0.44	0.33	1.24	11.5
Th	4.73	6.67	1.38	1.19	1.40	3.85	6.67	5.44	3.62	16.7	15.3	12.6	11.2	15.4	12.9	11.6	11.1	8.04	4.15	1.31	4.8
Tm	0.12	0.16	0.06	0.06	0.07	0.11	0.16	0.14	0.14	0.28	0.30	0.33	0.27	0.34	0.27	0.27	0.26	0.21	0.15	1.29	8.4
U	2.06	4.65	4.53	4.04	3.99	3.89	6.07	6.24	5.96	4.05	6.22	7.97	4.55	7.31	2.79	2.39	2.32	1.84	1.43	1.22	16.0
V	56.8	78.3	63.8	58.9	40.3	58.0	105	97.1	72.4	177	168	157	120	176	121	112	112	85.0	47.9	1.20	18.0
W	0.60	0.90	0.50	0.51	0.45	0.61	0.99	0.95	0.73	1.92	1.72	1.52	1.31	1.79	1.54	1.41	1.32	1.00	0.61	1.25	13.7
Y	6.67	10.4	5.53	5.16	5.23	6.41	10.2	9.77	10.8	12.5	14.8	20.2	14.2	18.5	14.2	15.9	16.0	13.5	10.5	1.22	14.0
Yb	0.79	1.17	0.45	0.41	0.40	0.63	1.14	1.00	0.92	2.11	2.08	2.27	1.81	2.27	1.98	1.86	1.92	1.43	0.96	1.28	8.9
Zn	27.0	96.7	865	357	234	48.4	25.1	23.4	27.1	33.8	33.7	39.9	26.4	32.9	27.7	25.0	24.0	18.5	34.0	1.59	14.7
Zr	50.8	57.7	14.3	14.7	14.4	42.3	60.3	49.5	32.3	164	137	115	106	137	115	105	101	69.5	37.3	1.06	23.0

RE – ratio of the concentration of an element in ash to its average concentration in oil shale;
Av volatility – average percent content of volatility.

where C_i is the content of trace elements in combustion residues (in μg/g); C_0 represents the content of trace elements in raw oil shale samples (in μg/g), and *Y* is the yield of ash [20].

The calculations show that some trace elements show susceptibility to release into the atmosphere. For example, about 93% Hg, 20–30% As, Ba, Be, Co, Cr, Nb, Sc and Zr, 10–20% B, Bi, Cs, Cu, Ga, Li, Mo, Ni, Pb, Rb, Sn, U, V, W and Zn, limited proportions (< 10%) of Cd, Hf, Se, Sr, Ta and Th, and as well as most REEs initially present in raw oil shale samples were emitted into the atmosphere during oil shale combustion.

The mode of occurrence of trace elements in raw oil shale may determine their volatilization behaviour during combustion. Volatile trace elements show a tendency to accumulate in the easily decomposing organic matter and/or authigenic minerals containing S, Cl, C, P, H anions and anionic groups in oil shale. This property favours their mobility during combustion by volatilization together with water vapours, sulphur, carbon, nitrogen, chlorine and other gases [21]. In the present study, Hg is shown to have the highest volatility during combustion, which can be explained by its bearing phase probably developing high vapour pressure during the phase decomposition, favouring the element mobility together with volatile sulphur, carbon and water vapour generated in oil shale. Trace elements with moderate volatility, such as As and Co, occur predominantly in organic matter and/or Fe-bearing minerals (Fig. 3). Ba, Be, Cr, Nb, Sc and Zr are mainly present in clay minerals (Fig. 6a–f), with possibly slight chemical shifts during a diagenetic reduction of Fe (Fig. 6g–l). Figures 6a–f show that Ba, Be, Cr, Nb, Sc and Zr have a strong positive relationship with Al_2O_3 content and Figures 6g–l reveal these elements to have a slight positive relationship with Cu content in low TOC (< 5.5%) oil shale samples. Other non-volatile or slightly volatile trace elements (e.g., B, Be, Cr, Cs, Ga, Hf, Li, Rb, Sn, Ta, Th, V, W, Zn, and REEs) may occur mainly in original and relatively refractory minerals contained in oil shale, such as clay minerals, feldspars and other inert minerals that may undergo weak changes during the combustion process. Additionally, the above-mentioned observations reveal that a number of highly mobile elements such as Cd, Sr and Zn, which are predominantly present in Ca-bearing minerals in Changshe Mountain oil shale, do not exhibit high volatility during combustion. This may be explained by an active role of Ca- and Mg-bearing oxyhydroxides in the partial capture and retention of some trace elements [22].

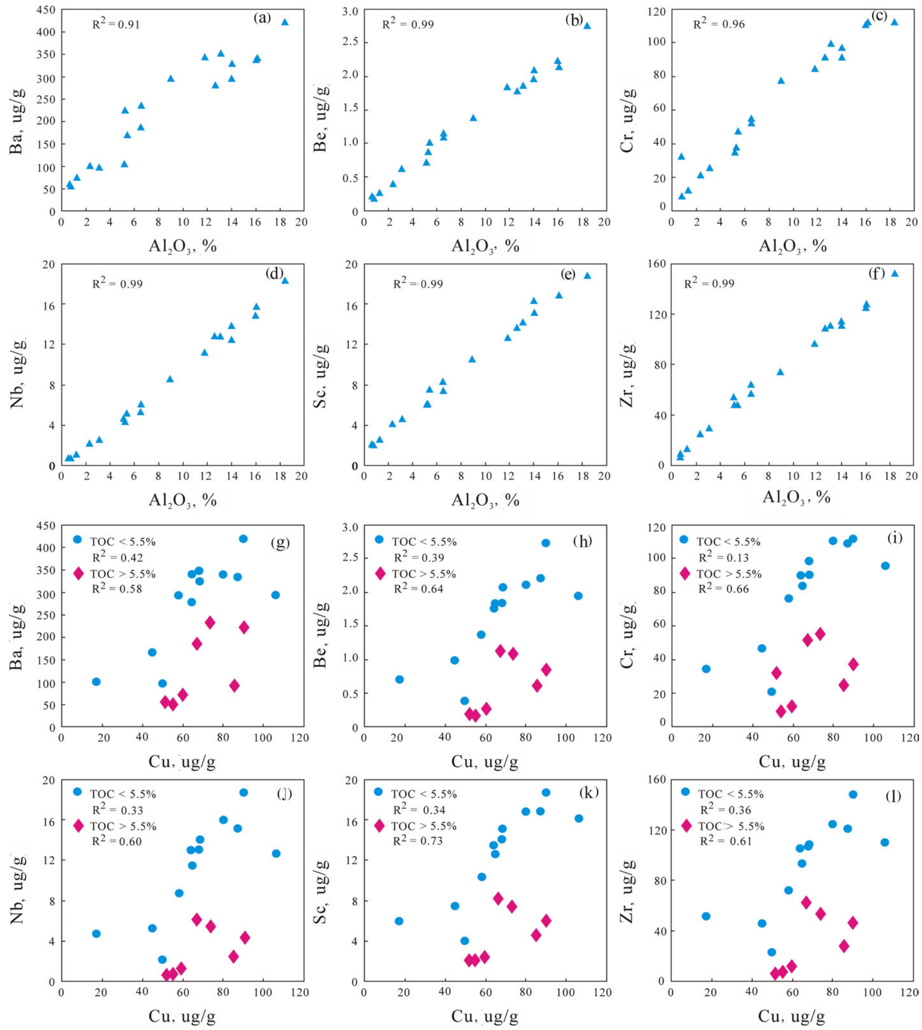


Fig. 6. Relationship of Ba, Be, Cr, Nb, Sc, and Zr contents with Al_2O_3 and Cu contents in low TOC (< 5.5%) Changshe Mountain oil shale samples.

5. Conclusions

1. The Changshe Mountain oil shale samples are characterized by high ash yield (54.69–86.75%) and TOC content (2.20–13.44%).
2. Marine oil shale is enriched in trace elements Se, Mo, Cd, and As. The enrichment of an element in oil shale seams may be a function of the association of an element concentration in oil shale with its UCC value and the origin of various oil shale fractions.
3. The following main modes of occurrence of trace elements in marine oil shale are distinguished: 1) clay mineral affined – B, Ba, Be, Cr, Cs, Ga, Hf, Li, Nb, Rb, Sc, Sn, Ta, Th, V, W, Zr, REEs; 2) organic affined – As,

Mo, Se; 3) Fe-bearing mineral affined – Bi, Co, Cu, Ni, Pb, U; 4) calcite affined – Cd, Sr and 5) fossil affined – Cd, Zn.

4. Some trace elements in Changshe Mountain oil shale show susceptibility to release into the atmosphere, including about 93% Hg and 20–30% As, Ba, Be, Co, Cr, Nb and Sc. The behaviour and migration of trace elements during oil shale combustion strongly depend on their mode of occurrence in the rock.

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