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Geochemistry and origin of elements of Upper Triassic Olang coal deposits in northeastern Iran

Nader Taghipour*, Zahra Solaymani Marshk
School of Earth Sciences, Damghan University, Damghan, Iran
**Corresponding author, e-mail: taghipour@du.ac.ir*
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Abstract

The Olang area is a part of Gheshlagh-Olang synclinal, which is a member of eastern Alborz coal basin and is situated at a distance of 70 km northeast of Shahroud city. Coal-bearing strata of this region are part of the Shemshak group (Upper Triassic to Lower Jurassic). Samples from the 9 coal seams of the Olang coal deposits were collected and ashed. The aim of this study is to determine the occurrence and distribution of major and trace elements in the coal ashes of Upper Triassic Olang coal deposits in northeastern Iran. The concentration of the elements in the coal ashes of the Olang region is higher than the Clarke value and the average of World coal ash. The coal ashes have been enriched in Zn, Mn, and P in comparison with the average of the World coal ash. The correlation coefficient analysis on the major and trace elements in the ash yielded in four groups including: A (Rb, K, Cs, Si), B (Al), C (Tl, Ca, Nb, Ta, V) and D (Cr, Hf, Sn, Zr, Th, Zn, Ti, Ba, W, Mg, Na, P, Sr, Co, Cu, Mo, Ni, U, Fe, Ca). The first two groups are strongly correlated with ash yield and mainly have an inorganic affinity. C and D groups are negatively or less strongly correlated with ash yield. The rare earth elements' abundances are negatively correlated with the ash yield and exhibit an organic affinity. Based on correlation, cluster analyses, and rare earth elements' distribution characteristics, two separate modes of occurrence can be considered for rare earth elements: 1) Accompanying phosphate minerals with organic origin (phosphorites) or phosphate organic materials, and 2) Accompanying the vitrinite maceral group.

Keywords: *Coal, Geochemistry, Iran, Olang.*

Introduction

Iranian coal resources are estimated about 7–10 Gt, mostly occurring in the northern (Alborz basin) and central parts of Iran. The Alborz coal basin is divided into three parts: western, central, and eastern (Yazdi and Esmaeilnia Shiravani, 2004). The study region is located in the eastern part of the Alborz basin (Fig. 1a, b).

Knowledge of the element composition of the coal ash is important in understanding the inorganic chemistry associated with coal formation. It is also important in understanding aspects of material handling, boiler erosion, ash formation, and slagging in coal processing or utilization (Ward, 1984; Gupta *et al*., 1999). The behavior of coal in industrial situations depends on the crystallographic form of the different constituents that make up the mineral matter. This requires an understanding of the actual mineral species present in the coal, as well as the coal's total inorganic geochemistry. However, properties and characteristics of coal depend on its combustible organic and inorganic constituents. Among the coal quality parameters, trace elements in coal can have important environmental, economic, technological, and human health impacts. The environmental impact of trace elements is generally associated with the concentration and the modes of occurrence of trace elements in coal (Finkelman *et al*., 1981; Swaine & Goodarzi, 1995).

The aims of the present study are: (a) to determine the element content of coal ashes of Upper Triassic Olang coal deposits; (b) to compare the trace element concentrations in the coal ash of the Olang coal deposits with crust's Clarke value and World coal ash aiming at determining the enrichment or depletion of the elements; and (c) to determine the mode of occurrence and origin of elements, especially rare earth elements in the coal ash of the Olang region.

Geological setting

The Olang region is situated at about a distance of 70 km northeast of Shahroud city, northeast of Iran (longitude 55° 10´; latitude 36° 50´, Fig.1b). This region is part of the Gheshlagh-Olang syncline with a NS–SW axis. The coal-bearing strata of this region are part of the Shemshak group (Upper Triassic to Lower Jurassic). Characteristic features of the Shemshak group are highly variable thicknesses reaching up to 4000 m, a nearly exclusively siliciclastic nature, widespread coal beds, and environments ranging from proximal alluvial fans to deep marine (Fürsich *et al.,* 2009).

Shemshak group rests with erosional unconformity on Lower and Middle Triassic limestone and dolomite of the Elika formation and is succeeded, apparently disconformably, by the marl and limestone of the Middle Jurassic Dalichai formation (Nabavi & Seyed-Emami, 1977) (Fig. 2). The Shemshak group consists mainly of sandstone, shale, siltstone, clay stone, with several interbedded coal seams. Some coal seams reach a workable thickness of between 40 cm and a few meters. Shemshak coal-bearing strata in the Alborz coalfield have continental characteristics and were deposited in fresh water, lacustrine and deltaic environments, upon carbonate bedrocks and, rarely, on Paleozoic and Precambrian rocks (Fürsich *et al.*, 2009; Yazdi & Esmaeilnia Shiravani, 2004). Based on a regional classification, the Shemshak group in Eastern Alborz consists of the Akrasar, Allah band, Kelariz, Alasht, Shirin Dasht, and Dancerit formations (Rad, 1986). The Kalariz and Alasht formations are the main host rocks for coal deposits in the Alborz range (Fig. 2). They are mainly composed of silty-clay sediments and fine-grained sandstone with numerous intercalations of coal and carbonaceous shale, representing fluvial, swamp and lake environments (Fürsich *et al.*, 2009; Yazdi, 2012).

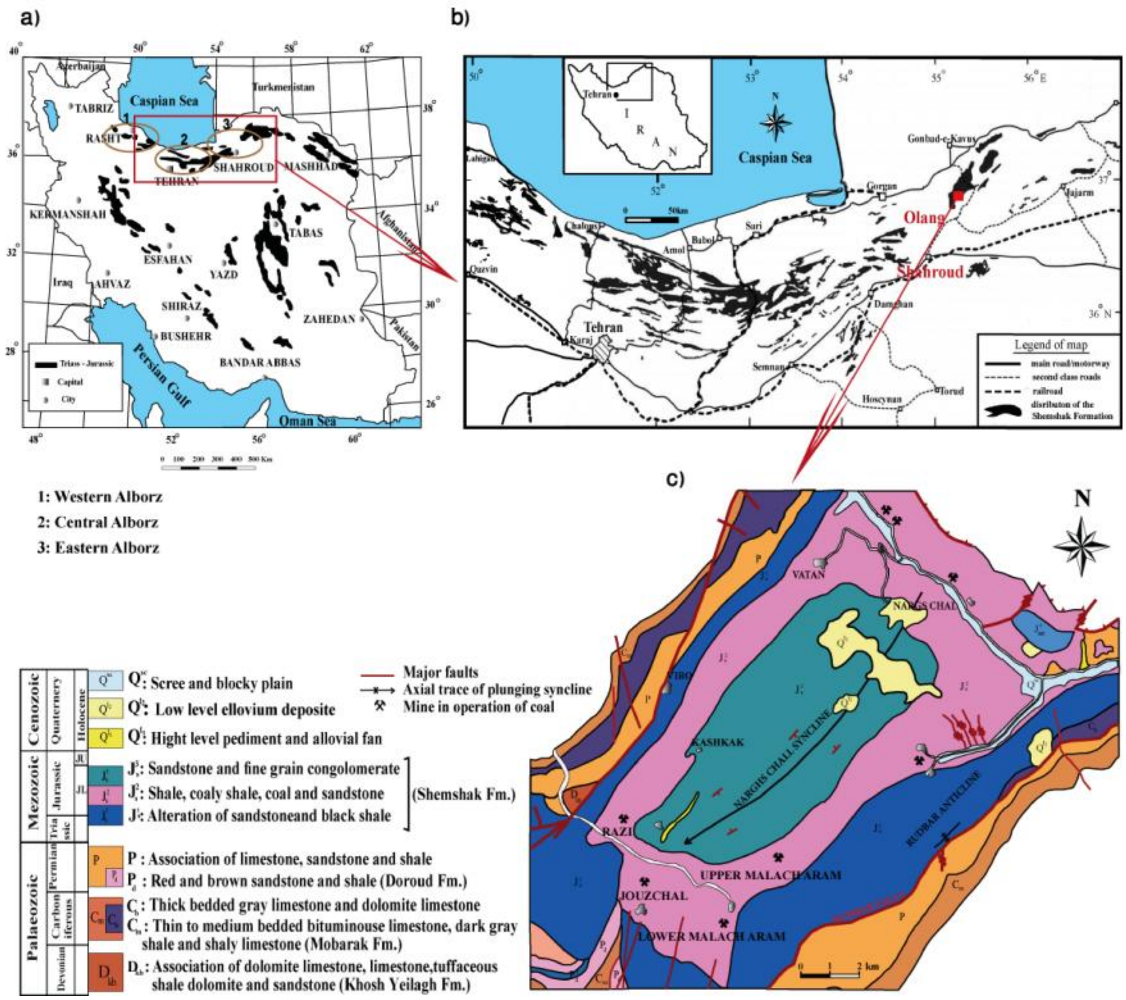

Figure 1. a) Coal-bearing strata of Iran (Modified after Yazdi & Esmaeilnia Shiravani, 2004). b) Locality map with outcrop distribution of the Shemshak Formation in the central and eastern Alborz Mountains, northern Iran. The Olang region is marked with an arrow (Modified after Seyed-Emami *et al.*, 2006). c) Geological map showing locations of the studied coal mines in the Olang area (Modified after Zahrab, 2004).

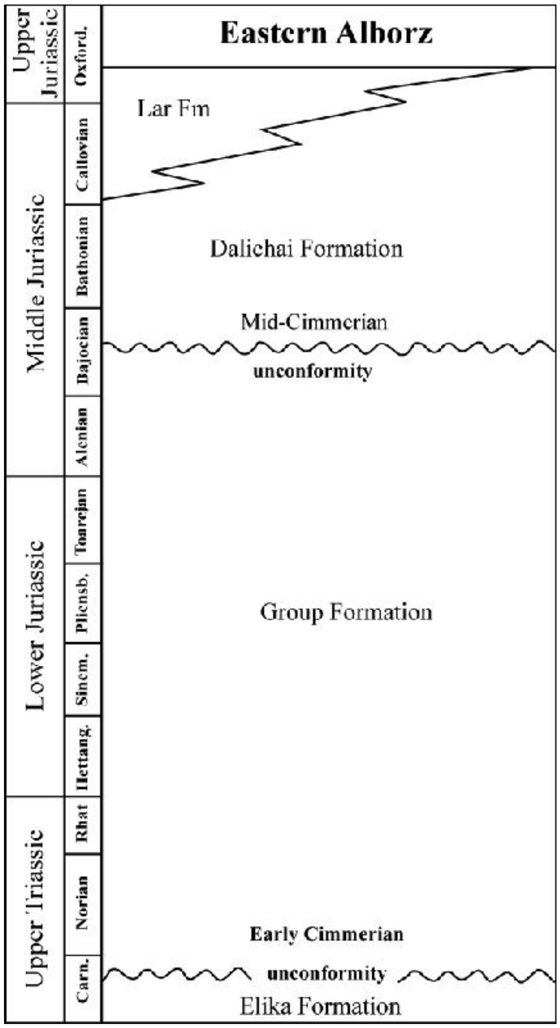

Figure 2. Upper Triassic to Upper Jurassic lithostratigraphic units in the eastern Alborz Mountains (Seyed-Emami *et al.*, 2001)

Olang coal-bearing strata occur in the Kalariz formation, which consists mainly of coal seams, siltstone, fine grained sandstone, and locally coarse grained sandstone (Fig. 3).

Analytical methods

In total, 90 blocks of coal samples were randomly collected from 9 freshly mined coal seams of 3 active coal mines (Alborzegan, Razi, and Melech Aram) for geochemistry study in the Olang coal deposits (Fig. 1c and 3). All samples were collected and stored in plastic bags to prevent contamination and weathering. Coal samples were subsequently air dried, crushed, and ground to pass 200 mesh sieves and then homogenized. The coal samples were dried in 120°C and ashed at 750˚C and 2 g coal ash of each coal seam was sent to the ALS Chemex laboratory of Canada for geochemical analysis.

Trace elements' concentrations were determined using a lithium borate ($LiBO_2$) fusion method, followed by inductively coupled plasma mass spectrometry (ICP-MS). The major oxides, including SiO_2, Al_2O_3, CaO, K_2O, Na_2O, Fe_2O_3, MnO, MgO, SrO, BaO, Cr_2O_3, TiO_2, and P_2O_5 were determined using a lithium borate fusion and acid dissolution, followed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The major element contents were determined by stoichiometric re-calculation from the content of their oxides in the coal ash. The ash yield in coal was determined according to ISO 1171 (1981) procedures.

The results were processed statistically and Pearson's correlation coefficient between the element concentration in the coal ash and ash yield was determined with cluster analysis. SPSS ver. 16 was used for statistical analysis**.**

Results and Discussion

Coal characteristics

The coals resources of Eastern Alborz region are estimated to be about 1 Gt occurring in two areas, Tazareh and Gheshlagh. The Olang region is located in the Gheshlagh area. In general, coals of the Gheshlagh area are high volatile bituminous (% Romax: 0.82–0.88) and have variable ash yield (9 to 40 wt %), volatile matter (26 to 28 wt %), and sulfur (0.6 to 1.02 wt %) contents (Razavi-Armagani and Moenoalsadat, 1994).

Coals of the Olang region are medium volatile bituminous (% Romax: 0.84 –0.93) and have variable ash (5.6 to 30.8 wt %, dry basis) (Table 2).

Coal petrography

Based on petrographic analyses, all maceral groups are present in coal seams of the Olang area. Vitrinite is the most important maceral group and it's volume percentage varies between 82.9 and 95.5 vol. % (average 82.3 vol. %) in different coal seams. The inertinite maceral group has a concentration of up to more than 15 vol. % with an average of 8.9 vol. %. The concentration of liptinite is very low and the average for all of the coal seams is 0.4 vol. %. Macerals of the vitrinite group include collotelinite, collodetrinite and corpogelinite with collotelinite and collodetrinite present in approximately equal content with a very small percentage of corpogelinite.

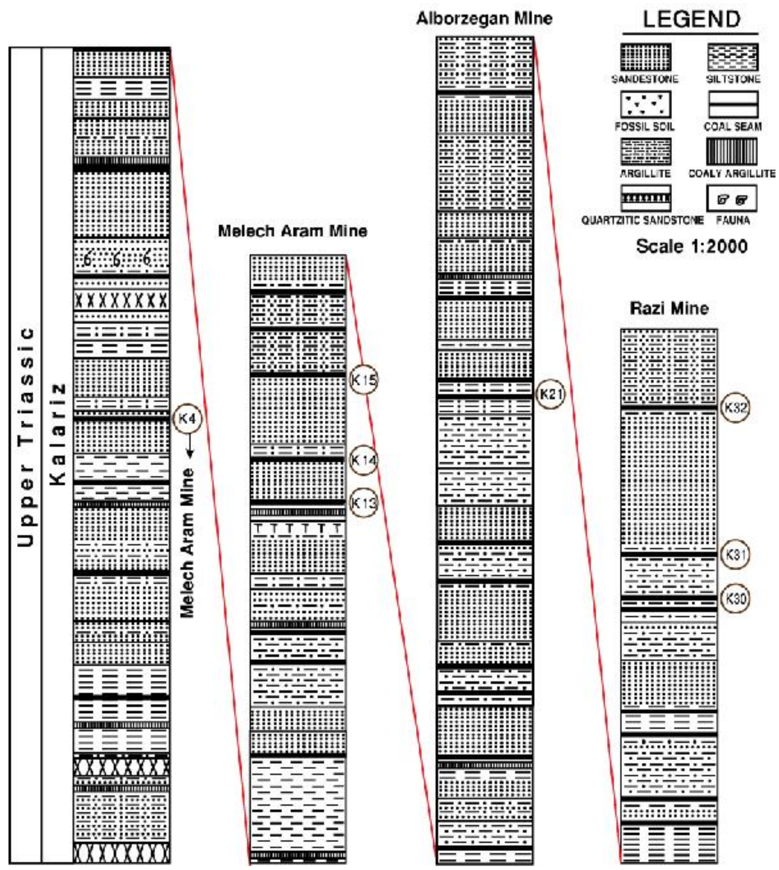

Figure 3. Lithostratigraphic column of the study coal seams in the Olang region, northeastern Iran. Coal seams studies (K4, K13, K14, K15, K18, K21, K30, K31, and K32) are indicated on it

The inertinite macerals consist of fusinite, semifusinite, secretinite, inertodetrinite, macrinite, micrinite, and funginite. Semifusinite and fusinite are the most abundant in this group. Sporinite, cutinite, and resinite macerals of the liptinite group are present in all coal seams (Solaymani & Taghipour, 2012).

Table 1 shows the results of the coal petrographic analyses. Volumetric concentrations of the vitrinite, inertinite, and liptinite maceral groups are given.

Concentration of elements in coal ash

The concentration of the major and trace elements in the coal ash of Alborzegan, Razi, and Melech Aram mines are presented in Table 2. The content of these elements in the coal ash of the Olang region are compared with the Clarke value of crust (Zhao, 2002) and World coal ash (Ketris and Yudovich, 2009) (Table 3). The content of most elements in the coal ash of the Olang coal seams are higher than the Clarke value that is reported by Zhao et al. (2002). The concentration of Al, Ba, Co, Cr, Cs, Cu, REE, Pb, Ga, Mo, Ni, Hf, Sn, Sr, V, Th, Tl, U, P, Fe, W, and Zr are 1.5 –13.04 times higher than the Clarke value. Ti, Nb, and Zn display concentrations slightly more than the Clarke values (Enrichment Factor from 1.2 to 1.4 times); but the contents of Ga, Rb, Sr, Th, and Zr are lower than unity compared to the Clarke value (Table 3).

The concentration of the elements in the coal ash of the Olang region is compared with the average World coal ash from Ketris and Yudovich (2009) (Table 3). It is established that Mn, P, and Zn concentrations are between 4 and 9.3 times higher than the average World coal ash (Table 3). The values of Cs, Ce, Ho, Tm, Hf, Sn, Sr, Tl, and U are lower than the World coal ash averages. The concentration of other elements is close to unity (Table 3). Sample K_{21}A (Alborzegan mine) is much enriched in Ca, P, Ba, Cu, Sr, and Th elements in comparison with other coal ash samples.

Table 1. Maceral composition analysis and mineral content of the coal seams of the Olang area (in vol. %)

Sample	CD	CT	Cg	V-G	Sp	Cu	Re	LD	L-G	Fu	Sf	Ma	In	Fg	Sc	I-G	Mm
Alborzegan mine																	
$K_{18}A$	60.1	14.6	1.3	76.0	0.5	0.4	0.0	0.2	1.1	1.6	5.8	0.5	0.7	0.1	0.1	8.8	14.1
$K_{19}A$	76.3	15.4	0.1	91.8	0.4	0.3	0.0	0.3	1.0	2.8	2.8	0.2	0.5	0.1	0.2	6.6	0.6
$K_{20}A$	67.5	15.2	0.2	82.9	2.5	1.0	0.0	0.3	3.8	4.2	2.5	1.0	0.1	0.0	0.0	7.8	5.5
$K_{21}A$	68.0	26.0	0.0	94.0	0.2	0.1	0.0	0.0	0.3	0.7	3.5	0.7	0.4	0.1	0.0	5.4	0.3
Razi Mine																	
$K_{30}R$	35.3	48.6	0.3	84.2	0.0	0.0	0.0	0.0	0.0	8.4	7.0	0.2	0.1	0.0	0.0	15.7	0.1
$K_{31}R$	59.3	13.4	0.4	73.1	0.0	0.1	0.1	0.1	0.3	10.2	10.3	0.0	0.2	0.0	0.2	20.9	5.7
$K_{32}R$	50.4	20.4	0.8	71.6	0.1	0.3	0.0	0.3	0.7	5.6	9.2	0.1	0.1	0.0	0.2	15.2	12.5
Melech Aram mine																	
$K_{4}M$	50.7	11.7	0.3	62.7	2.2	0.5	0.1	0.4	3.2	9.6	12	0.8	0.5	0.1	0.1	23.1	11.0
$K_{13}M$	72.8	4.9	0.0	77.7	1.2	0.3	0.1	1.1	2.7	3.5	1.1	0.6	0.1	0.1	0.2	5.6	14.0
$K_{14}M$	63.0	20.1	0.0	83.1	1.7	0.3	0.0	0.8	2.8	5.2	2.4	0.7	0.1	0.0	0.1	8.5	5.6
$K_{15}M$	69.0	14.4	0.1	83.5	0.4	0.4	0.0	0.0	0.8	4.6	2.7	0.9	0.2	0.3	0.2	8.9	6.8
Granite mine																	
$K_{6}G$	52.0	5.7	0.0	57.7	0.9	0.3	0.1	0.0	1.3	2.3	2.8	0.4	0.7	0.0	0.1	6.3	34.7

CD:collodetrinite; CT:collotelinite; Cg:corpogelinite; V-G:vitrinite group total; Sp: spornite; Re:resinite; LD: liptodetrinite; L-G: liptinite group total; Fu:fusinite; Sf : semifusinite; Ma: macrinite; In: inertinite; Fg:funginite; Sc:secretinite; I-G: Inertinite group total; Mm: mineral matter

Mode of occurrence of elements

The mode of occurrence and association of elements are important factors in influencing the fate of elements during combustion. In addition, if the association of trace elements with specific minerals and macerals is known, there is the possibility of reducing concentrations by selected mining and coal-cleaning. Information on the distribution of trace elements within the coal also enables predictions to be made for other coals. In addition to the applied aspects, more precise information on the location of elements within the coal leads to a better understanding of geochemical processes during deposition and diagenesis (Spears *et al.*, 2007).

Geochemical association of elements

The elemental associations were studied by cluster analysis. Four groups of elemental association were identified (Fig. 4) referred to as groups A, B, C, and D.

Group A: This group includes Rb, K, and Cs and ash yield (Fig. 4). These elements are strongly correlated with ash yield (Table 4). There are correlation coefficients among Rb, K, Cs elements and the composition of Al and Si (r_{Al-Si}> 0.7) that indicate these elements are associated with aluminosilicate minerals.

Group A: This group includes Rb, K, and Cs and ash yield (Fig. 4). These elements are strongly correlated with ash yield (Table 4). There are correlation coefficients among Rb, K, Cs elements and the composition of Al and Si (r_{Al-Si}> 0.7) that indicate these elements are associated with aluminosilicate minerals.

Group B: This group includes Nb, Si, Ga, Al, Cr, V, Sn, Th, Hf, Zr, Ta, and Ti (Fig. 4). Ga, Al, and Ta in this group exhibit relatively positive correlation coefficients with ash yield, ranging from 0.30 to 0.7 (Table 4). The correlation coefficients among the composition of Al, Si, Cr, Hf, Sn, V, Zr, Ga, Nb, and Ta are higher than 0.50. The other elements display lower than 0.50 positive correlation coefficients with ash yield.

Group C: This group includes Ba, Sr, Ca, P, U, Cu, and Pb (Fig. 4). All these elements are negatively correlated with ash yield (-0.74 to -0.26) and positively correlated with Ca and P (r> 0.5).

Group D: This group includes Fe, Mn, Zn, Tl, Co, Mo, Ni, Na, REE, and Mg (Fig. 4). With the exception of Tl, the other elements are negatively correlated with ash yield and the composition of Al and Si. Mn, Fe, and Mg display high positively correlation coefficients all together (r> 0.7).

Negative correlation coefficients of these elements with Ca show the absence of carbonate minerals such as calcite, dolomite, and ankerite in these coal seams.

Table 2. Concentration of major and trace elements in the coal ash from nine different coal seams of the Olang region

Element	**Alborzegan mine**		**Razi mine**			**Melech Aram mine**			
	$K_{18}A$	$K_{21}A$	$K_{30}R$	$K_{31}R$	$K_{32}R$	K_4M	$K_{13}M$	$K_{14}M$	$K_{15}M$
Si%	25.43	18.09	22.63	18.70	20.06	27.30	9.96	22.91	10.52
Al %	12.97	14.72	12.76	12.02	13.45	13.76	8.63	14.08	9.45
Fe %	5.66	4.35	9.44	13.85	10.49	1.81	32.52	6.22	26.85
Ca %	0.86	6.98	0.71	2.07	1.31	1.07	1.83	1.02	2.72
Mg %	0.76	0.43	1.06	1.22	1.00	0.77	1.13	1.05	1.76
Na %	0.36	0.50	0.97	0.42	0.42	0.23	0.22	0.34	0.25
K %	2.12	1.17	2.06	1.62	2.23	2.27	0.37	2.24	0.50
Ti %	0.86	1.13	0.62	0.60	0.55	0.82	0.50	0.63	0.31
Mn %	0.05	0.05	0.09	0.19	0.09	0.02	0.42	0.06	0.50
P %	0.25	3.30	0.08	0.39	0.44	0.34	0.31	0.31	0.41
Trace Elements (ppm)									
Ba	671	2550	693	917	980	523	996	1230	932
Co	29.4	31.2	114.5	48.7	32.6	13.4	62.3	28.3	101.5
Cr	150	240	250	160	150	160	50	19	100
Cs	14.4	5.26	8.29	10.9	14.05	17.8	1.48	16.1	3.27
Cu	62.0	253	193	120	103	84	69	136	144
La	78.8	113	76.5	68.4	64.5	73.7	68.2	73.8	60.1
Ce	159.5	224	164	136.5	128.5	146.5	134.5	149.5	121.5
Pr	16.7	25.4	19.55	15.35	14.05	15.65	15.75	17.75	14.95
Nd	63.1	99.9	83	59.3	53.7	58.2	63.9	73.2	67
Sm	11.8	20.7	20	12.1	10.5	11	13.75	15.55	18.05
Eu	2.38	4.55	5.05	2.71	2.38	2.28	3.21	3.62	5.02
Gd	10.35	19.25	22.1	11.75	10.15	9.87	13.9	15.7	21.8
Tb	1.49	2.96	3.59	1.84	1.56	1.51	2.21	2.38	3.74
Dy	8.69	16.85	21.8	10.65	9.08	8.99	13.3	13.45	23.1
Ho	1.85	3.41	4.67	2.2	1.87	1.87	2.75	2.69	4.82
Er	5.64	10.05	13.05	6.28	5.35	5.57	7.82	7.5	13.15
Tm	0.84	1.42	1.81	0.88	0.78	0.82	1.1	1.03	1.72
Yb	5.71	9.76	11.2	5.92	5.23	5.39	7.16	6.73	10.8
Lu	0.89	1.49	1.73	0.89	0.81	0.84	1.07	1	1.61
Y	51.7	102.5	156	64.8	50.5	53.7	89.2	76.6	162
Mo	7	14	41	19	11	3	21	15	45
Nb	30.2	32.1	27.1	19.6	20.4	29.6	10.6	2	12.2
Ga	38.3	46.7	38.7	35.2	37.9	40.6	24.7	45.7	29
Ni	98	152	321	131	102	54	78	122	199
Pb	31	63	42	50	42	31	51	53	69
Rb	142	72.3	122.5	122	164.5	163	21.6	167.5	37.3
Hf	8.10	10.4	8.1	6.7	6.8	8.4	6.3	7.4	5
Sn	5	8	5	5	5	5	3	5	2
Sr	300	2080	142.5	437	548	619	673	601	422
Ta	2.3	2.9	1.5	1.5	1.5	2.2	0.9	1.7	0.6
Th	28.3	45.4	24.7	26	25.4	26.4	26.4	26.6	19.3
Tl	0.8	1.1	1.2	1	3	0.9	1	1.6	1.6
U	6.72	13.7	10.5	8.15	6.94	6.88	10.15	11	11
V	201	309	292	260	267	225	77	308	157
W	4	4	6	3	2	3	2	4	4
Zn	75	60	127	105	95	62	58	162	172
Zr	277	358	306	231	234	293	213	245	167
Ash %	21.1	6.1	8.3	12.9	24.8	30.8	8.0	22.8	5.6

Table 3.Mean value of major and trace elements in the coal ash from the Olang region compared to the average Clarke of crust and the World coal ash

Element	**Olang coal ash**		**Clarke of crust**		**World coal ash [c]**	
	Range	**MM**	**Clarke [a]**	**EF [b]**	**Average**	**EF**
Si%	18.09-27.3	19.53	28.1	0.69	nd	-
Al%	8.63-14.72	12.43	8.23	1.51	nd	-
Fe%	1.81-26.85	12.35	5.63	2.19	nd	-
Ca%	0.71-6.98	2.06	4.15	0.50	nd	-
Mg%	0.43-1.76	1.02	2.33	0.44	nd	-
Na%	0.22-0.97	0.41	2.36	0.17	nd	-
K%	0.37-2.27	1.62	2.09	0.78	nd	-
Ti%	0.31-1.13	0.67	0.57	1.18	0.53	1.3
Mn%	0.02-0.5	0.16	0.95	0.17	0.04	4.0
P%	0.08-3.30	0.65	0.10	6.19	0.15	4.3
Trace Elements (ppm)						
Ba	523-2550	1054.7	425	2.48	980	1.1
Co	13.4-114.5	51.32	25	2.05	37	1.4
Cr	19-250	161.1	100	1.61	120	1.3
Cs	1.48-17.8	10.17	3	3.39	110	0.1
Cu	62-253	129.3	55	2.35	110	1.2
La	60.1-113	75.2	30	2.51	76	1.0
Ce	121.5-224	151.6	60	2.53	140	1.1
Pr	4.05-25.4	17.24	8.2	2.10	26	0.7
Nd	53.7-99.9	69.03	28	2.47	75	0.9
Sm	11-20.7	14.83	6	2.47	14	1.1
Eu	2.28-5.05	3.47	1.2	2.89	2.6	1.3
Gd	9.87-21.8	14.99	5.4	2.78	16	0.9
Tb	1.49-3.74	2.36	0.9	2.62	2.1	1.1
Dy	8.69-23.1	13.99	3	4.66	15	0.9
Ho	1.85-4.82	2.90	1.2	2.42	4.8	0.6
Er	5.35-13.15	8.27	2.8	2.95	6.4	1.3
Tm	0.82-1.81	1.16	0.48	2.42	2.2	0.5
Yb	5.23-11.2	7.54	3	2.51	6.9	1.1
Lu	0.81-1.73	1.15	nd	Nd	1.3	0.9
Y	50.5-162	89.67	33	2.72	51	1.8
Nb	2-32.1	22.87	20	1.14	22	1.0
Ni	54-199	139.7	75	1.86	100	1.4
Pb	31-69	48	12.5	3.84	55	0.9
Ga	24.7-46.7	37.42	15	2.49	36	1.0
Mo	3-45	19.56	1.5	13.04	14	1.4
Rb	21.6-167.5	112.52	90	1.25	82	1.4
Hf	5-10.4	7.47	3	2.49	9	0.8
Sn	2-8	4.78	2	2.39	8	0.6
Sr	142.5-2080	646.9	375	1.73	730	0.9
Ta	0.6-2.9	1.68	2	0.84	20	0.1
Th	19.3-45.4	27.61	9.6	2.88	23	1.2
Tl	0.8-3	1.36	0.45	3.02	6.6	0.2
U	6.72-13.7	9.45	2.7	3.50	15	0.6
V	77-309	232.9	135	1.73	170	1.4
W	2-6	3.56	1.5	2.37	7.8	0.5
Zn	58-172	101.78	70	1.45	11	9.3
Zr	167-358	258.2	165	1.56	230	1.1

[a] Zhao *et al.*, 2002; [b]EF, Enrichment Factor [c]Ketris & Yudovich, 2009 MM: Mean values concentrations

Table 4. Element affinities deduced from the calculation of Pearson correlation coefficients between the content of each element in coal ash and ash yield or selected major elements.

Correlation with ash yield

Group A: r_{ash} = 0.5 – 1.0 → Cs (0.93) – Rb (0.84) – K (0.78) – Si (0.74) - Al (0.51)

Group B: r_{ash} = 0.22- 0.51 → Ga (0.39) – Nb (0.37) – Ta (0.31) – Tl (0.23) – V (0.22)

Group C: r_{ash} = 0.22 – (-0.22) → Cr (0.2) – Hf (0.12) – Sn (0.14) – Zr (0.08) – Th (-0.17) – Zn (-0.17) – Ti (0.16) - La (-0.22)

Group D: r_{ash} = -0.22 > → Ba (-0.5) – Sr (-0.26) – W (-0.33) - Mg (-0.31) - Na (-0.31) - P (-0.35) – Sr (-0.26) – Ba (-0.39)- Fe (-0.59) – Ca (-0.53) –Co (-0.71) – Cu (-0.55) – Mo (-0.74) – Ni (-0.59) – Pb (-0.72) – U (-0.71) – Y (-0.76) – REE (-0.5)

Aluminosilicate affinity

r_{Al-Si} = 0.7 - 1.0 → Cs – Ga – Nb – Rb – Ta – K

r_{Al-Si} = 0.5 - 0.7 → Cr – Hf – Sn – V – Zr – Ti

r_{Al-Si} = 0.22 - 0.5 → La – Ce –Th – W

Carbonate affinity

r_{Ca-Mg} = 0.7-1.0 → Ba - Cu - Pb - Sr - U

r_{Ca-Mg} =0.5 -0.7 → La - Ce - Pr - Sm -Th - Cu - Nd

r_{Ca-Mg} =0.22 - 0.5 → Ti - Mn - Gd -Tb - Dy - Eu - Hf - Ho - Er - Tm - Lu - Y - Sn - Ta - Yb – Zr

Phosphate affinity

r_{Ca+P} > 0.7 = Ba– Cu– Sn – Sr – Th – Ce – La – Nd – Pr – Sm

r_{Ca+P} =0.5 – 0.7 → Ti – Hf – Sn – Pb – Gd

Correlation coefficients between selected major elements

Si- Al = 0.81 ; Ca –Mg = -0.34 ; Ca – Fe = -0.03 ; Mg – Fe = 0.71; Ga – Al = 0.97

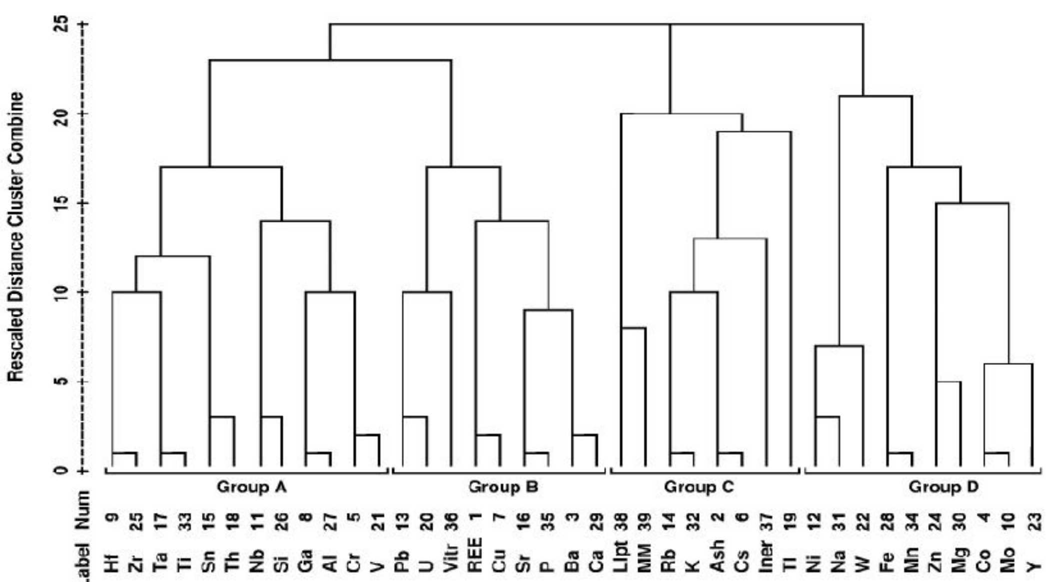

Figure 4. Dendrogram produced by the hierarchical cluster analysis of analytical results on 9 coal ash samples (cluster method, centroid clustering; interval, Pearson correlation; transform values, maximum magnitude of 1)

Affinity of the elements

The correlation of the element concentrations with ash yield may provide preliminary information for their organic or inorganic affinity (Kortenski and Sotirov, 2002). The ash yield of coal seams in the Olang region ranges from 5.6 to 30.8 wt% (Table 2). Four groups of elements are classified according to their correlation coefficients with ash yield (Table 4).

Group A: This group includes Al, Cs, Rb, K, and Si which are strongly correlated with ash yield (r_{ash}=0.5–1.0; Table 4) and illustrate high inorganic affinity. The value of these elements increases with the increase of ash content. These elements are characterized by aluminosilicate affinity (Table 4).

Group B: This group includes elements with prevailing inorganic affinity. They show positive correlation coefficients with ash yield, which vary from +0.22 to +0.51 (Ga, Nb, Ta, V, and Tl; Table 4). The concentration of these elements increases with the increase of ash content. These elements are also characterized by aluminosilicate affinity (Table 4).

Group C: This group includes Cr, Hf, Sn, Zr, Th, Zn, Ti, and La that display weak positive and negative correlation coefficients with ash yield varying from +0.22 to –0.22.

Group D: This group includes Ba, Sr, W, Mg, Na, P, Sr, Ba, Co, Cu, Mo, Ni, U, Fe, Ca, Co, Cu, Mo, Ni, Pb, U, Y, and REE (Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) which are negatively correlated with ash yield (<-0.22). These elements exhibit a relatively strong organic affinity and an appreciable portion of these elements may be associated with organic matter. Among these elements, Ba, Cu, Sn, Sr, Th, Ce, La, Nd, Pr, Sm, Ti, Hf, Sn, Pb, and Gd have a phosphate affinity, with correlation coefficients $r_{Ca}> +0.5$.

Rare earth elements (REEs)

The study of rare earth elements (REE) in coals is significant in three aspects. Rare earth elements are related to the origin of coals. Because the REE are a kind of tracer in geological studies, their geochemical characteristics may provide abundant reliable information about the source rocks and environments of coals, including the sedimentary environment of peat swamp and the geological setting of source area in the period of coal formation as well as other geological processes after coal formation.

The second aspect is related to their potential economic value. Seredin (1996) discovered some coal seams with high REE concentrations (300-1000 ppm) in the far east of Russia. Finkelman (1993) reported that the contents of most rare elements and REE in coals and coal ash from the United States would satisfy the annual demands of these elements by 50% in the country.

The third is related to their possible detrimental effects. An additional factor motivating this investigation is concern over the possible negative occupational health aspects of rare earth elements, particularly with regard to coal mine workers. While medical data suggest potential health problems related to worker exposures in high-REE environments, there is a lack of understanding regarding how REE exposures affect the human body, and few exposure data exist that indicate the concentration levels of REE in mining and related industrial environments (Sulotto *et al.*, 1986; McDonald et al., 1995; Pairon et al., 1995; Hirano and Suzuki, 1996). In underground mines, limitations in airflow can lead to relatively high concentrations of dust. The possibility exists for the mixed exposure of REE with other known hazardous particles to worsen mining dust-related illnesses (e.g., coal workers pneumoconiosis, silicosis).

There have been many studies on the distribution and geochemistry of REEs in coal and coal ash (Eskenazy, 1987a, 1987b; Birk & White, 1991; Kortenski & Bakardjiev, 1993; Huang *et al.*, 2000; Dai *et al.*, 2002, 2003, 2008, 2014; Liu *et al.*, 2006; Seredin, 1996; Seredin & Dai, 2012; Wang *et al.*, 2007). These studies indicate that ∑REE content in most coals varies from several ppm to several hundred ppm, and the REEs are distributed in minerals although some are associated with the organic material in coal. Rare earth elements in coal are generally related to minerals, primarily clay minerals, phosphates, and often positively correlated to ash yield (Finkelman, 1995; Chou, 1997). However, rare earth elements may also be partly associated with the organic matter in coal (Eskenazy, 1987b). Due to different coal-forming paleoenvironments and geologic settings, some coals are enriched in heavy REEs (HREEs) relative to light REEs (LREEs) (Eskenazy, 1987a, 1999), whereas some are enriched in LREEs (Goodarzi, 1987; Seredin, 1996; Dai *et al.*, 2008).

REE abundances

The concentration of rare earth elements in the coal ash from Alborzegan, Razi, and Melech Aram mines are presented in Table 5. The ∑REE in the coal ash of the Olang region ranges from 308.46 to 552.7 ppm, in which the sample $K_{21}A$ with 552.7 ppm displays the highest content of ∑REE. The concentration of these elements in the coal ash from the Olang region are compared with the Clarke value of crust from Zhao *et al.* (2002) and World coal ash from Ketris and Yudovich (2009) (Table 6). The average of ∑REE for the Olang coal ash is 383.7 ppm (Table 6) that is very close to World coal ash average (388.3 ppm; Ketris and

Yudovich, 2009). Olang coal ashes illustrate 100–200 times more enrichment than chondritic abundances reported by McDonough and Sun (1995). The value of rare earth elements is also 2.2 times richer than the average total rare earth elements (173.2 ppm) reported by Haskin *et al.* (1968) for North American shale (NASC). Rare earth elements' content of Olang coal ashes is 2 to 4 times higher than the Clarke values (Table 6).

REE distribution patterns

In this study, geochemical parameters relating to rare earth elements are calculated based on methods presented by Wang et al., (1989) (Table 5).

$(La/Sm)_n$
$(La/Yb)_n$
$(Gd/Yb)_n$
$\delta Eu = Eu_n/ (Sm_n \times Gd_n)^{½}$
$\delta Ce = Ce_n/ (La_n \times Pr_n)^{½}$
Eu_n, Sm_n, Gd_n, Ce_n, La_n, and Pr_n are chondrite-normalized element values.

The characteristics of rare earth elements' distribution patterns in coal ash are presented as follows:

1. The REE distribution patterns of coal ash are very similar. The LREE are apparently enriched while the HREE patterns are flat, and Eu is generally depleted (Fig. 5).

Table 5. Concentration and geochemical parameters of the rare earth elements in the coal ashes of the Olang region

Element	Alborzegan mine		Razi mine			Melech Aram mine			
	$K_{18}A$	$K_{21}A$	$K_{30}R$	$K_{31}R$	$K_{32}R$	K_4M	$K_{13}M$	$K_{14}M$	$K_{15}M$
La	78.8	113	76.5	68.4	64.5	73.7	68.2	73.8	60.1
Ce	159.5	224	164	136.5	128.5	146.5	134.5	149.5	121.5
Pr	16.7	25.4	19.55	15.35	14.05	15.65	15.75	17.75	14.95
Nd	63.1	99.9	83	59.3	53.7	58.2	63.9	73.2	67
Sm	11.8	20.7	20	12.1	10.5	11	13.75	15.55	18.05
Eu	2.38	4.55	5.05	2.71	2.38	2.28	3.21	3.62	5.02
Gd	10.35	19.25	22.1	11.75	10.15	9.87	13.9	15.7	21.8
Tb	1.49	2.96	21.8	10.65	9.08	1.51	2.21	2.38	3.74
Dy	8.69	16.85	21.8	10.65	9.08	8.99	13.3	13.45	23.1
Ho	1.85	3.41	4.67	2.2	1.87	1.87	2.75	2.69	4.82
Er	5.64	10.05	13.05	6.28	5.35	5.57	7.82	7.5	13.15
Tm	0.84	1.42	1.81	0.88	0.78	0.82	1.1	1.03	1.72
Yb	5.71	9.76	11.2	5.92	5.23	5.39	7.16	6.73	10.8
Lu	0.89	1.49	1.73	0.89	0.81	0.84	1.07	1	1.61
Ash%	5.6	22.8	8	30.8	24.8	12.9	8.3	6.1	21.1
∑LREE	332.28	487.55	368.1	294.36	273.63	307.33	299.31	333.42	286.62
∑HREE	35.46	65.19	79.95	40.41	34.83	34.86	49.31	50.48	80.74
∑LREE/∑HREE	9.37	7.48	4.6	7.28	7.86	8.82	6.07	6.6	3.55
∑REE	367.74	552.74	448.05	334.77	308.46	342.19	348.62	383.9	367.36
∑REE+Y	419.44	655.24	604.05	399.57	358.96	395.89	437.82	460.5	529.36
$(La/Yb)_n$	9.37	7.87	4.64	7.85	8.38	9.29	6.47	7.45	3.78
$(La/Sm)_n$	4.17	3.41	2.39	3.53	3.84	4.18	3.1	2.96	2.08
$(Gd/Yb)_n$	1.47	1.6	1.6	1.61	1.57	1.48	1.57	1.89	1.63
δEu	0.66	0.69	0.73	0.69	0.7	0.67	0.71	0.71	0.77
δCe	1.06	1.01	1.03	1.02	1.03	1.04	0.99	1	0.98

$\delta Eu = Eu_n/ (Sm_n\, Gd_n)^{½}$, $\delta Ce = Ce_n/ (La_n\, Pr_n)^{½}$. The subscript n stands for the chondrite-normalized value.

Table 6. Comparison of the average values of rare earth elements in the coal ash of the Olang region with the Clarke value of crust, the World coal ash, and Chondrite values.

Element	Olang coal ash	Clarke[a]	EF	Upper crust[b]	EF	World coal ash[c]	EF	Chondrite[d]	EF
La	75.2	30	2.5	31	2.22	76	1	0.24	313.3
Ce	151.6	60	2.5	63	2.20	140	1.1	0.61	248.5
Pr	17.24	8.2	2.1	7.1	2.22	26	0.7	0.04	431
Nd	69.03	28	2.47	27	2.33	75	0.9	0.46	150.1
Sm	14.83	6	2.47	4.7	2.87	14	1.1	0.15	98.9
Eu	3.47	1.2	2.89	1	3.15	2.6	1.3	0.06	57.8
Gd	14.99	5.4	2.78	4	3.41	16	0.9	0.2	75
Tb	2.36	0.9	2.62	0.7	3.07	2.1	0.1	0.04	59
Dy	13.99	3	4.66	3.9	3.26	15	0.9	0.25	56
Ho	2.9	1.2	2.42	0.83	3.48	4.8	0.6	0.05	58
Er	8.27	2.8	2.95	2.3	3.42	6.4	1.3	0.16	51.7
Tm	1.16	0.48	2.42	0.3	3.36	2.2	0.5	0.02	58
Yb	7.54	3	2.51	2	3.88	6.9	1.1	0.16	47.1
Lu	1.15	-	-	0.31	3.36	1.3	0.9	0.02	57.5
Y	89.67	33	2.72	21	3.88	51	1.8	1.57	57.1

[a] Zhao *et al.,* 2002; [b] Rudnick & Gao, 2004; [c] Ketris & Yudovich, 2009; [d] McDonough & Sun, 1995; EF: Enrichment Factor

2. The δCe values of the coal ash of the Olang area vary from 0.98 to 1.06; values of all coal seams are higher than unity, except the two samples of $K_{13}M$ and $K_{15}M$, whose values are very close to unity (0.98 and 0.99, respectively) (Table 5).
3. The δEu values of all of the samples are smaller than unity (0.66 to 0.77) that show negative Eu anomalies. An obvious "V" shape at Eu features the normalized distribution patterns (Fig.5), which is consistent with the results published in the literature (Seredin, 1996; Eskenazy, 1987a; Birk and White, 1991). The negative Eu anomaly of the coal ash may be inherited from the source regions with Eu depletion (Eskenazy, 1987a; Huang et al., 2000). However, another possibility is the Eu mobility of the coal during coal formation. Although Eu concentrations in the sediments are generally not affected by diagenesis, strongly reducing conditions at low temperatures can lead to REE mobility during coal formation (Eskenazy, 1987a, 1999; Ismael, 2002).
4. The LREE/HREE ratios of the Olang coal ashes vary from 3.55 to 9.37; $(La/Yb)_n$ values, 3.78 to 9.37; $(La/Sm)_n$ values, 2.08 to 4.18; $(Gd/Yb)_n$ values, 1.47 to 1.89. These values are greater than unity, reflecting that the enrichment degree of LREE is larger than that of HREE and a certain extent of fractionation occurred between the LREE and HREE.
5. The $(La/Sm)_n$ values vary from 2.08 to 4.18, which indicate that a certain extent of fractionation occurred among the LREEs (Table 5).

Mode of occurrence of REE

Correlation coefficients of ∑REE and ash yield, maceral groups, mineral matter, and the contents of other elements in coal ashes of the Olang region are exhibited in Table 7.

Some results are obtained as follows:
1. There is a negative correlation between ∑REE and ash yield (r=-0.5). The correlation coefficients of ∑REE and associated elements are illustrated in Table 7. The ∑REE content of coal ashes correlates weakly and negatively not only with major elements including Si, K, Fe, Mg, Mn, and Na, but also with trace elements, including Rb, Tl, Cs, and Zn, which are lithophile elements being likely associated with clay minerals and transported to the coal swamp during peat deposition (Chou, 1997). It is demonstrated that rare earth elements have organic origins.
2. ∑REE has positive correlation coefficients with Ca, P, Na, Al, Ti, Ba, Ga, Hf, Nb, Sn, Sr, Ta, Th, U, V, Y, Zr, Cr, Ni, Cu, and Pb elements (Table 7).
3. Cluster analysis of the ∑REE and other elements (Fig. 4) shows that REE and the elements P, Cu, Sr, Ba, and Ca can be classified as one group. All of the elements similar to REE have negative correlation coefficients with ash yield.

Table 7. Correlation coefficients among ∑REE and other elements in the coal ash of the Olang region.

Element	Correlation	Element	Correlation	Elemen	Correlation	Element	Correlation
Ba	0.77	Pb	0.39	Y	0.45	Ti	0.80
Co	0.14	Rb	-0.26	Zn	-0.1	Mn	-0.83
Cr	0.67	Sn	0.64	Zr	0.73	P	0.80
Cs	-0.24	Sr	0.71	Si	0.01	Vitrinite	0.5
Cu	0.88	Ta	0.55	Al	0.38	Inertinite	-0.5
Ga	0.51	Th	0.78	Fe	-0.30	Liptinite	-0.4
Hf	0.72	Tl	-0.31	Ca	0.74	Mineral matter	-0.8
Mo	0.18	U	0.79	Mg	-0.49	Ash yield	-0.5
Nb	0.52	V	0.44	Na	0.50		
Ni	0.47	W	0.60	K	-0.15		

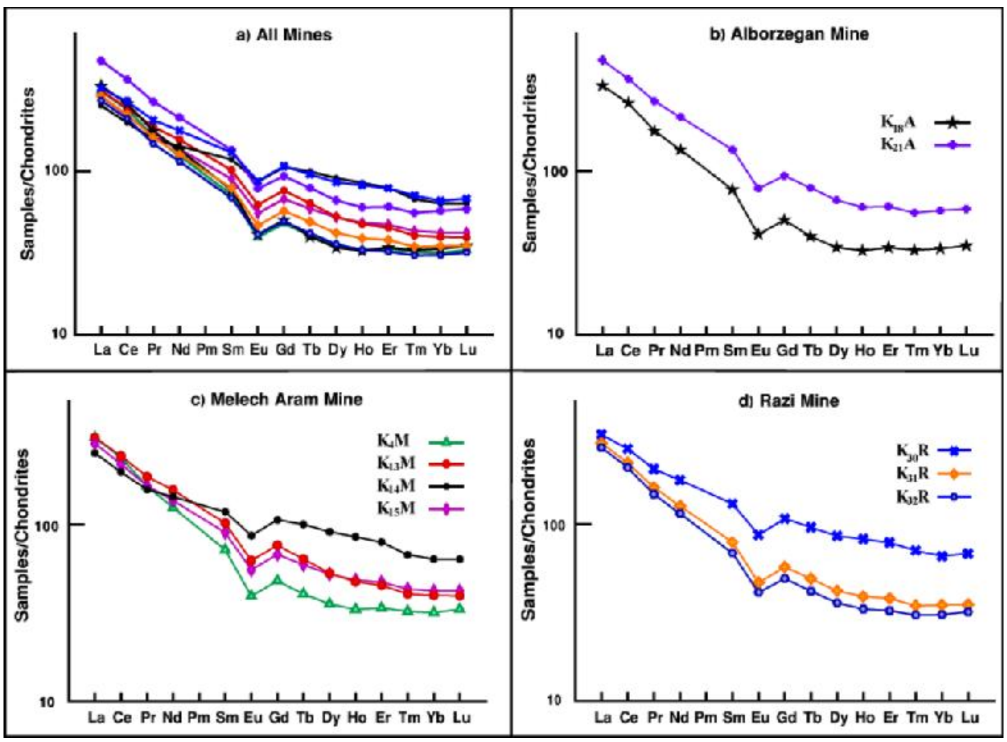

Figure 5 Chondrite-normalized rare earth element patterns of the coal ash of the Olang region

In sample K_{21}A, Ca, P, Ba, Cu, Sr, Th, and REE elements are much enriched in comparison with other samples; in addition, ∑REE in the sample is also enriched, which indicates the accompanying of these elements together.

4. Silicon and Al are likely present in kaolinite, the dominant mineral in coal (Wang et al., 2007), and P mainly in phosphate (Finkelman, 1994; Spears and Zheng, 1999). Ca, Fe, K, Na, Mg, and U are generally variable in coal and significantly affected by post depositional processes (Schatzel & Stewart, 2003). Negative or weak correlation of REEs with ash yield, mineral matter, Si, Mg, K, Cs, and Rb and strong positive correlation with P, Ca, and Ba (Table 7) suggest that REEs are mainly derived from organic sources and occur dominantly in phosphate with organic origins.

5. The REE is negatively correlated with the inertinite and liptinite maceral groups, but shows a positive correlation with the vitrinite maceral group (Fig. 6), which exhibits a certain affiliation between REEs and organic matter.

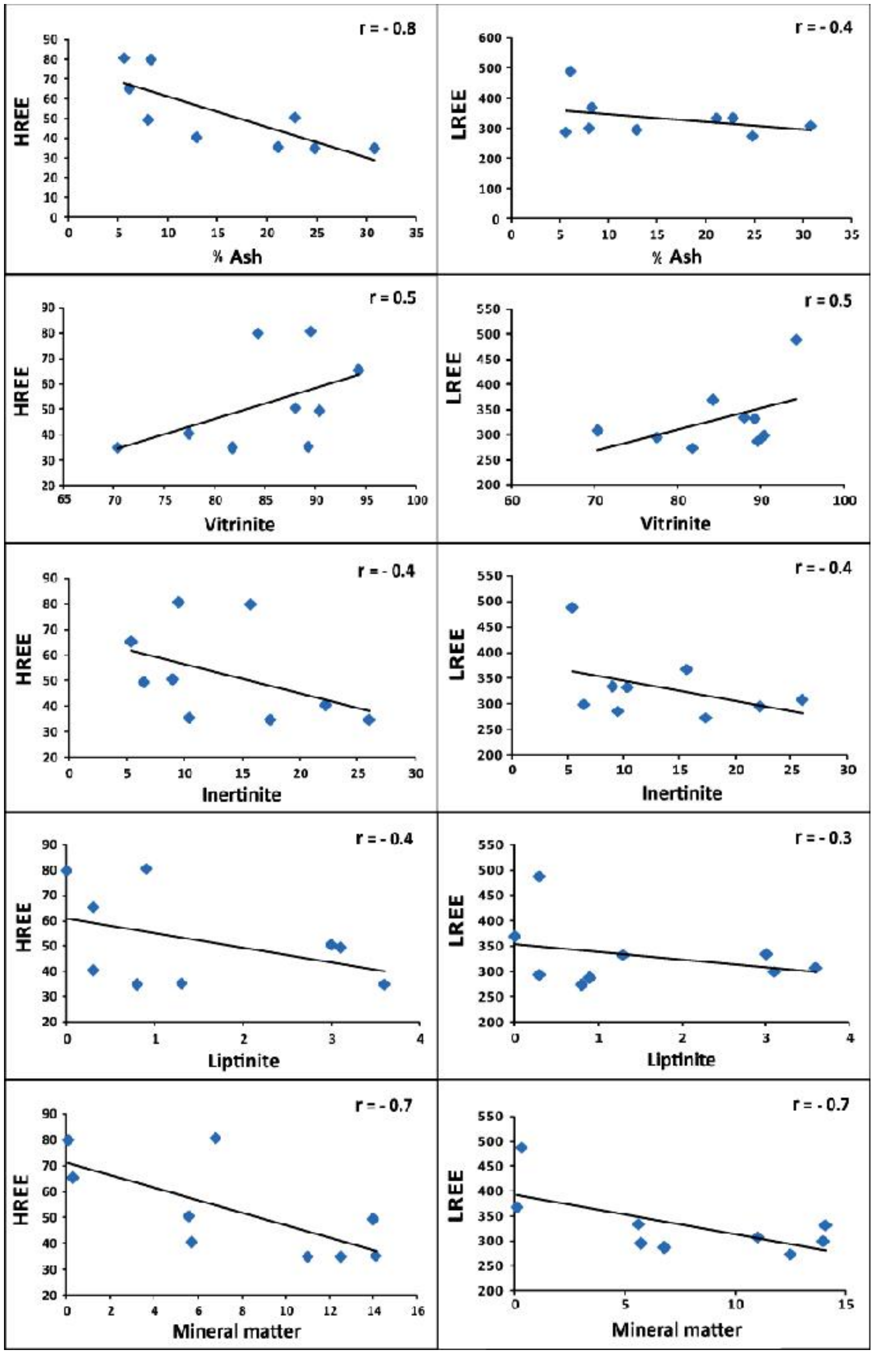

Figure 6. Relationship between HREE and LREE with ash yield, mineral matter and maceral groups (vitrinite, inertinite, and Liptinite)

It appears that REEs were transported to the coal swamp during peat accumulation possibly by adsorption on clay minerals or in colloidal form in solution. REEs in the solution were largely adsorbed by organic matter during diagenesis. Some studies reported that a portion of the REEs may be associated with the organic fraction of coal based on selective leaching and particle segregation experiments (Dai *et al*., 2002; Palmer *et al*., 1990; Willett *et al.*, 2000).

6. The light rare earth elements (LREEs, from La to Eu) and heavy REEs (HREEs, from Gd to Lu) are negatively correlated with the ash yield (Fig. 6); further, the heavy REEs (HREE) have clearly more negative correlation coefficients with ash yield (-0.8), indicating that the HREEs have a stronger

organic affinity than the LREEs. The data on REE published recently also show greater organic affinity for HREE than for LREE (Querol *et al.*, 1995). Palmer *et al.* (1990) found a distinct enrichment of the heavy REE in two out of five vitrinite concentrates.

Conclusions

The value of most of the elements in the coal ashes of the Olang region is higher than the Clarke value and higher than that of World coal ash averages in Zn, Mn, and P.

The elements in the Olang coal ashes are classified into four groups of association according to their mode of occurrence including A (Rb, K, Cs, Si, Al), B (Ga, Nb, Ta, Tl, V), C (Cr, Hf, Sn, Zr, Th, Zn, Ti, La) and D (Ba, W, Mg, Na, P, Sr, Co, Cu, Mo, Ni, U, Fe, Ca, REE (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y)). The first two groups are strongly correlated with ash yield and mainly have an inorganic affinity. Most of these elements are mainly associated with aluminosilicate minerals, especially clay minerals. The elements of C and D groups exhibit negative or weak correlation coefficients with ash yield and mainly have an organic affinity.

The ∑REE content in the Olang coal ashes ranges from 308.46 to 552.7 ppm. The average ∑REE in the coal ashes of the Olang region (383.7 ppm) is close to the average of World coal ash, while it is about 100 to 200 times more than chondritic abundances and also 2.2 times more than the average ∑REE (173.2 ppm) reported for North American shale (NASC).

The ∑REE content is correlated negatively with ash yield and weakly to negatively correlated with major elements, including Si, K, Fe, Mg, Mn, and Na, and also with trace elements, including Rb, Tl, Cs, and Zn, which are lithophile elements, indicating that REEs are distributed in organic matter. Positive correlation of ∑REE with vitrinite maceral group is also another reason for the approval of their organic origin. Based on cluster analysis, ∑REE, P, Cu, Sr, Ba, and Ca can be classified as one group, all of whose elements like REEs have negative correlation coefficients with ash yield and are also major components of phosphate minerals. Therefore, two separate modes of occurrence for rare earth elements can be considered: (1) Accompanying phosphate minerals with organic origin (phosphorites) or phosphate organic materials. (2) Accompanying vitrinite maceral group.

The coal ashes of the Olang region exhibit a clear negative Eu anomaly, which is inherited from the source regions. $(La/Yb)_n$, $(La/Sm)_n$, and $(Gd/Yb)_n$ values are higher than unity, reflecting that the enrichment degree of LREE is larger than that of HREE and a certain extent of fractionation occurred between the LREE and HREE. The $(La/Sm)_n$ values are also higher than unity, which indicates that a certain extent of fractionation occurred among the LREEs.

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