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Environmental Geochemistry of Selected Elements in Lignite from Barsingsar and Gurha Mines of Rajasthan, Western India

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Abstract: The present paper contains the result of investigation carried out on selected trace elements in the less studied lignite deposits of Rajasthan, Western India. The study has been made on two new lignite deposits – Barsingsar and Gurha. The former has elevated ash content (mean 20.8%) than the latter one (mean 5.1%) and both of them have high volatile matter (mean 43.7% and 49.9% respectively).

The lignite samples have been studied for selected elements like Fe, Ca, Mg, Mn, K, Na, Cu, Co, Ni, Cr, Zn, Pb, Cd and As. The elements like Cd, Co, Ni, Pb and Cu occur in high concentration when compared to the Clarke values for brown coal. Ca and Mg relate positively with organic matter in Barsingsar lignite indicating their organic source while K, Cu, Co, Pb and Cd indicate their inorganic origin. Ca might have come in contact with the organic matter during humification and would have become a part of humate. The elements like Cu, Co, Ni, Cr, Cd and Pb showing strong affinity with inertinite could have got associated with the mineral matter present in the fusinite and funginite macerals. In Gurha lignites Pb and Co have shown their affinity with inorganic matter which could have been drawn from sulphides and clay minerals.

Keywords: Elements, Lignites, Geochemistry, Rajasthan.

INTRODUCTION

There has been growing interest in the study of concentration and distribution of trace elements in coal in last few decades. The information is vital from economic as well as environmental point of view. In coal the metals get accumulated at various stages. There are three stages of ore processes in coal: syngenetic, diagenetic and epigenetic (Danchev and Strelyanov, 1979; Kler et al., 1988). The syngenetic process goes hand-in-hand during the pre-accumulation while the diagenetic processes become operative after burial and during the humification. The epigenetic process, however, works after the compaction of coal (Seredin and Finkelman, 2008). Seredin (2004) has further sub-divided the epigenetic into early, middle and late phases corresponding respectively to soft lignite, hard lignite to sub-bituminous, and bituminous to anthracite. The capacity of organic matter to bind the ions from solutions decreases progressively with maturity of coal. The trace elements get incorporated into coal as solid particles and also as dissolved species (Seredin and Finkelman, 2008).

Though the trace elements are ubiquitous but they are unevenly distributed in the earth's crust. Some elements like iron may occur in percentage concentration but a large range of elements like Cu, Co, Ni and Zn etc occur at part per million (ppm) concentration. Some of the elements like Hg, Ag and Au occur at part per billion (ppb) or even at lower concentrations.

The environmental significance of certain trace elements like As, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Sr, U, V, and Zn has been demonstrated by Pickhardt (1989), Turiel (1994), Singh et al. (1912), Sabbioni and Goetz (1983). Transport of trace elements into the atmosphere during power generation has become a matter of concern mainly because of its environmental implications. The environmental deterioration due to coal combustion and also the impact of hazardous trace elements on human health has caused much concern in the recent years (Gayer et al., 1999; Sahoo, 1991; Ren et al., 2004; Spears and Tewalt, 2009; Singh et al., 2011, 2012, 2014; Singh and Singh, 2011).

The lignite deposits of Rajasthan are located in Bikaner, Barmer and Nagaur districts and the important deposits include Barsingsar, Gurha, Giral and Kapurdi lignite deposits. In the present study the lignite deposits from Barsingsar and Gurha have been studied to know the concentration and distribution of selected trace elements.

GEOLOGY OF THE AREA

The lignite deposits of India have a wide sub-surface occurrence and vary in vertical and lateral extent. Their structural disposition, quality, multiplicity of seams and the overburden associated with them are highly variable. The lignites occur in the sedimentary sequence of lower Tertiary in the western and north-western parts. They include lignite deposits of Eocene (Jammu & Kashmir, Gujarat and Rajasthan), Miocene (Neyveli, Tamil Nadu) and Plio-Pleistocene (Nichahom, Jammu & Kashmir) ages. The western plate margin of India is believed to have suffered multiple transgressions nearly 55 my ago (Joshi, 2007) and the coal and lignite deposits of Rajasthan, Gujarat, Jammu & Kashmir and Pakistan occur along this plate margin. The lower Tertiary coal measures are believed to have been formed on the Indian Plate margin due to withdrawl of the Neotethys in Pakistan, western India (Rajasthan and Gujarat), Northern India (Jammu, Shimla and Solan) and northeastern India (Meghalaya) (Sahni et al., 2006).

The entire western and north-western part of the Indian sub-continent has a complex geological setting and the Rajasthan basin is a part of it. The western part of the Indian shield is mainly formed of rocks of Precambrian age of Aravalli and Delhi folding and they trend in NE-SW to NNE-SSW direction (Eremenko and Negi, 1968). The Aravalli range has acted as barrier preventing the Thar desert to expand towards the east. The part of Rajasthan located in the west of Aravalli has formed an extensive basin where thick pile of sedimentaries occur with a total extent of nearly 20,000 sq km. The area geologically forms the western flank of Indus shelf and may be sub-divided into four basins which are: (i) Bikaner-Nagaur basin, (ii) Jaisalmer basin, (iii) Barmer basin and (iv) Sanchor basin. Various structural trends and their reactivation have controlled the architecture of shelf. Consequently, marine transgression and regression occurred affecting the fluviatile and deltaic conditions in the shelf area. The lignite deposits of Rajasthan occur as arcuate and linear tracts and are distributed in these lower Tertiary basins. The accumulation of vegetal matter, which was ultimately converted into lignite deposits in Rajasthan, was not uniform in the channels but was controlled by meanders, sand bars and the alluvial fans. The occurrence of lignite in Rajasthan was first reported way back in 1896 when a well was dug in Palana (Bikaner) which subsequently led to opening an underground lignite mine in 1898. However, the mining activity could not sustain for long period and it had to be suspended because of low demand for lignite. After a long gap and with an increase in the demand of power in Rajasthan, Neyveli Lignite Corporation Ltd. has now developed an open cast lignite mine at Barsingsar area of Bikaner district with an estimated capacity of 2.1 MTPA. This is expected to meet the lignite requirements for the 250 MW capacity thermal power station located at the pit head. The stratigraphic succession of the area given by the Geological Survey of India (GSI) is furnished in Table 1 and the geological map is shown in Fig.1.

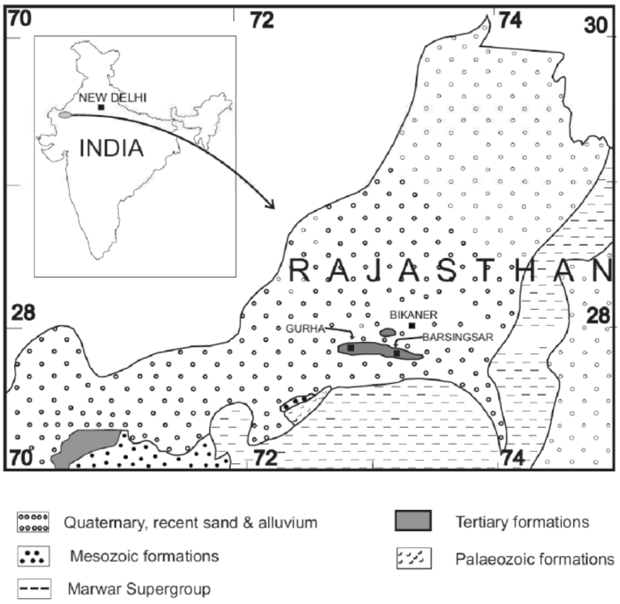

Fig.1. Geological map around Barsingsar and Gurha liggnite fields, Rajasthan.

MATERIALS AND METHODS

Coal Samples

In the present investigation brown coal (lignite) samples from Barsingsar lignite and Gurha lignite deposits have been collected following Pillar Coal Sampling Method (Schopf, 1960) from the working faces of the respective open cast mines so that the entire thickness of the seam is represented at the sampling point and the same may be reconstructed in the laboratory. The maceral analysis has been carried out in Coal and Organic Petrology Lab, Banaras Hindu University by Leitz Orthoplan Pol Microscope under white incident light. The samples have been subjected to trace element analysis. The samples have been crushed to -70 mesh size. The samples have been subjected to proximate analysis to

Table 1. General stratigraphic succession of Bikaner–Nagaur basin

Age	Formation	Lithology
Recent & sub Recent	—	Blown sand
Eocene to Paleocene	iii. Jogira	Fossiliferous Marl, Fullers earth. Forameniferal Lst. Impure Ash with ostrea, clayey Marl.
	ii. Marh	Ferruginous Sst., gritty Sst. and Siltstone
	i. Palana	Black shale, Carbonaceous pyrite shale, lignite, Fullers earth & fire clays.
	– – – – – – – – – – Unconformity – – – – – – – – – –	
Early Permian	Badhaura	Medium to coarse grained brownish, yellowish ferruginous Sst, clays, shales & siltstones containing Permina flora and fauna.
	– – – – – – – – – – Unconformity – – – – – – – – – –	
Early Carboniferous	Bap	Assorted pebbles and cobbles with occasional boulders of Malani igneous suite of rocks, phyllite, slates, quartzite and gneiss of Delhi Supergroup, limestones, dolomitic limestone of Bilara Group and Jodhpur sandstone.
	– – – – – – – – – – Unconformity – – – – – – – – – –	
Cambrian	Nagaur	Brick–red to red claystone, siltstone and sandstone with bands of clay and blocks of greenish clay.
Precambrian	Malani Igneous suite	Malani Rhyolites, Tuffs, Granites, Porphyry, Quartz, veins & dykes

determine the constituents like moisture, ash, volatile matter and fixed carbon. The elements Fe, Ca, Mg, Mn, K, Na, Cu, Co, Ni, Cr, Zn, Pb and As were determined on 'whole coal samples'.

Digestion of Coal Samples

Half gram (dry weight) of lignite sample is taken in a digestion vessel and 10 ml of digestion mixture (10 part conc. HNO_3 and 1 part $HClO_4$) is added. The mixture is refluxed for further 30 min. This step is repeated over and again until no brown fumes comes from the sample. It is filtered through Whatman No. 41 filter paper. The digested samples are rinsed with 1% Conc. HNO_3 and transferred into a separate test tube and the volume is made up to 20 ml.

The digested samples have been analyzed by Atomic Absorption Spectrophotometer (AAS, Model Perkin Elmer Analyst 800) to obtain the concentrations of various elements.

RESULT AND DISCUSSION

The Rajasthan lignite megascopically appears stratified, matrix rich, black to brown and inhomogeneous in nature. Indications of sulphur are a common feature and resin patches are also seen.

Petro-chemical Attributes

The petrographic study of these lignites reveals that they are highly rich in huminite group of macerals with subordinate amount of inertinite group while the liptinite macerals occur in low amount. The lignites of Barsingsar are composed of 74.95 to 83.04 % (mean 79.01 %) huminite, 2.37 to 5.86 % (mean 4.03 %) liptinite and 4.28 to 12.62 % (mean 8.53 %) inertinite while the mineral matter varies from 4.69 to 10.65 % (mean 8.43 %) (Table 2). On the other hand the lignites of Gurha mine are composed of 59.06 to 86.67 % (mean 73.10 %) huminite, 4.38 to 12.99 % (mean 8.28 %) liptinite and 3.53 to 24.02 % (mean 13.30 %) inertinite while the mineral matter varies from 3.94 to 7.43 % (mean 5.33 %). The proximate analysis reveals that the Barsingsar and Gurha lignite contain 20.8 % and 5.1 % ash; 43.7% and 49.9 % volatile matter and 31.4% and 40.9 % fixed carbon respectively. The details of the petrographic and chemical constituents are furnished in Table 2.

Trace Elements Distribution

The trace elements analysed for the lignite samples of the present study have been compared with the Clarke values. The brown coal (lignite) Clarke values represent the average content of elements/trace elements in the world of brown coal and are calculated based on a very large amount of information gathered through thousands of analyses of brown coal for elements/ trace elements. In Barsingsar lignite the concentration of Co, Ni, and Pb is 2-5 times higher and Cd is 10-20 times higher than the Clarke values for the brown coal/ lignite. The concentration of Co varies from 8.04 to 12.12 ppm, Ni from 17.5 to 24.0 ppm and Pb from 8.32 to 22.8 ppm while Cd varies from 2.2 to 5.32 ppm in Barsingsar lignite samples (Table 3). However, the elements like Cu, Cr, Zn, As are within the range. Similarly in Gurha lignite there is 2-4 times enrichment in Cu, Co and Ni while Cd is 5-10 times high as compared to the Clarke values. The concentration of Cu ranges from 21.12 to 57.6 ppm, Co from 5.96 to 15.2 ppm and Ni from 14.68 to 28.44 ppm while Cd ranges from 1.08 to 2.04 ppm in Gurha lignite samples (Table 3). The elements like Cr, Zn, Pb, and As are found to be within normal range. The vertical variation of ash and the elements along the lignite seam profile is shown in the Fig 2. In Barsingsar lignite seam Ca, Na, and Mg, in general, show decreasing trend from bottom to top while the remaining ones do not show a pattern. Similarly in case of Gurha lignite seam Mn, Ca, K and Na show an almost decreasing trend from bottom to top with some exception

Table.2. Data of Petrography (in vol %) and proximate (in wt %) analyses of Barsingasar and Gurha Lignite Seams, Rajasthan.

S. No.		Sample No.	Megascopic Characteristics	Petrographic Components				Proximate Components				
				Humi	Lipt	Inert	MM	Volatile Matter	Ash	Fixed Carbon	VM (daf)	FC (daf)
	BARSINGASAR LIGNITE SEAM	B 10 (CORE)	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	82.81	5.86	6.64	4.69	46. 7	4.2	39.1	54.4	45.6
1		B 9	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur and resin patches	78.06	3.16	9.88	8.89	42.1	24.2	29.9	58.4	41.6
2		B 8	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	75.53	4.85	12.62	6.99	40.9	26.5	29.2	58.3	41.7
3		B 7	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	76.41	3.31	12.28	7.99	39.1	27.9	28.9	57.5	42.5
4		B 6	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	78.63	4.20	6.68	10.05	40. 7	26.2	29.3	58.2	41.8
5		B 5	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	83.04	4.34	4.73	7.89	47.4	12.3	36.0	56.8	43.2
6		B 4	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	79.89	3.45	8.24	8.43	45.0	20.8	30.6	59.5	40.5
7		B 3	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	81.91	5.25	4.28	8.56	49.5	12.9	33.0	60.0	40.0
8		B 2	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	78.88	3.49	7.95	9.69	48.4	11.9	35.3	57.8	42.2
9		B 1	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	74.95	2.37	12.03	10.65	40.3	24.7	30.4	56.9	43.0
		Mean		**79.01**	**4.03**	**8.53**	**8.43**	**44.01**	**19.15**	**32.19**	**57.75**	**42.21**
11	GURHA LIGNITE SEAM	GU 10	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	67.77	10.10	17.09	5.05	49.1	4.5	41. 8	54.0	45.9
12		GU 9	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	67.44	9.88	17.64	5.04	54.9	4.7	37.5	59.4	40.6
13		GU 8	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	59.06	12.99	24.02	3.94	51.3	3.6	41.3	55.4	44.6
14		GU 7	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	71.98	7.98	13.23	6.81	50.6	6.7	39.2	56.3	43.7
15		GU 6	Stratified, matrix rich, brown inhomogeneous lignite with presence of sulphur	63.87	11.72	19.73	4.69	53.6	4.4	38.1	58.5	41.5
16		GU 5	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	86.67	4.90	3.53	4.90	50.7	4.6	40.9	55.3	44.7
17		GU 4	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	83.63	7.21	5.07	4.09	44.7	4.1	45.4	49.6	50.4
18		GU 3	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	83.05	4.38	5.33	7.43	49.6	7.4	40.2	55.3	44.8
19		GU 2	Unstratified, matrix rich, black inhomogeneous lignite with presence of sulphur	71.48	6.64	15.23	6.64	48.3	6.6	41.4	53.9	46.2
20		GU 1	Stratified, matrix rich, black inhomogeneous lignite with presence of sulphur	76.05	7.03	12.17	4.75	46.6	4.6	43.8	51.6	48.5
		Mean		**73.10**	**8.28**	**13.30**	**5.33**	**49.9**	**5.1**	**40.9**	**54.9**	**45.1**

Humi - huminite; lipt - liptinite; inert - inertinite; MM - mineral matter; VM - volatile matter; FC - fixed carbon

whereas others do not show a pattern. It is evident from the figure that there is no significant trend of variation of most of the elements from bottom to top of the Barsingsar and Gurha lignite seams. Similar studies have been attempted by several workers for different coal deposits of the world (Yudovich, 1978; Pareek and Bardhan, 1985; Seredin, 2005; Liu et al., 2001; Hower et al., 2008; Singh et al., 2011; Prachiti et al., 2011).

The mode of occurrence of the elements in the lignite deposits of Rajasthan has been discussed on the basis of their relationship with ash yield, the petrographic components and also the correlation coefficients among the

Table 3. Major, minor and trace element contents (in ppm) of Barsingsar and Gurha lignite seams, Rajasthan

		BARSINGSAR LIGNITE SEAM										GURHA LIGNITE SEAM									
Metals	WCBC*	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10	GU-1	GU-2	GU-3	GU-4	GU-5	GU-6	GU-7	GU-8	GU-9	GU-10
Fe	na	370	342	404	1758	238	306	192	476	156	1018	172	96	248	176	132	162	132	148	138	130
Cu	15	23.28	24.76	25.68	21.20	20.48	25.40	21.04	22.64	26.56	15.88	43.6	28.04	21.12	28.32	35.88	44.8	45.6	29.0	57.6	24.96
Co	4.2	10.32	10.16	11.52	10.08	9.28	8.64	9.68	10.96	12.12	8.04	12.18	8.96	8.80	5.96	11.72	12.88	15.2	7.76	11.48	10.64
Ni	9	20.2	20.1	23.2	19.4	18.9	17.8	20.7	23.1	24.0	17.5	19.04	14.68	15.88	19.72	21.88	20.64	28.44	15.28	25.72	22.80
Cr	15	12.88	11.76	15.92	7.08	10.52	8.44	5.64	14.5	9.56	9.44	7.56	7.72	7.18	9.84	6.76	11.4	7.48	8.16	10.8	8.12
Zn	18	13.08	14.84	19.20	17.32	18.08	15.00	18.36	11.80	15.92	13.08	12.24	8.96	10.28	10.44	9.84	12.92	11.04	10.08	12.20	11.36
Pb	6.6	18.21	18.28	21.6	22.76	15.96	20.6	14.44	16.64	22.8	8.32	3.36	3.44	3.0	5.28	3.08	8.88	3.56	9.16	6.24	4.16
Mg	na	752	744	784	696	884	832	908	1384	744	1144	1407	1056	1276	868	812	928	796‘	1188	716	1068
Cd	0.24	3.20	3.52	5.32	2.48	2.92	2.72	2.52	2.28	2.92	2.20	1.64	1.48	1.56	2.04	1.48	1.08	1.16	1.40	1.96	1.56
Na	na	784	896	960	760	830	812	990	1074	1242	1178	880	836	588	824	652	848	1040	954	998	1046
K	na	45.2	70.8	41.2	61.2	33.8	53.4	53.0	50.0	69.2	22.0	24.6	27.0	25.8	21.6	27.0	35.8	35.6	33.0	23.0	36.4
Ca	na	2434	1870	1874	1922	2354	2770	2404	2950	2274	3260	4464	4912	3722	3952	4242	6452	7716	8990	3852	7898
Mn**	100±6	33.2	31.2	32.4	34.0	41.6	51.2	36.8	42.4	41.2	28.2	41.2	56.0	48.4	30.8	40.0	38.0	64.4	38.6	51.6	51.6
As	7.6	NIL	NIL	NIL	0.215	NIL	0.375	0.147	0.410	0.492	0.595	0.664	NIL	NIL	NIL	NIL	0.508	NIL	0.241	NIL	0.229

*World Clarke for Brown coal by Yudovich and Ketris (2006); **by Ketris and Yudovich (2009); na- not available

elements. Arsenic is considered as the most abundant minor elements in iron-disulfide (pyrite) in coal (Kolker, 2012). In case of multiple generations of iron-disulfides, the earliest one is represented by framboidal pyrite. Subsequently, overgrowth of Fe disulfides occurs in the form of pyrite or marcasite. The last generation is represented by pyrite in cleats and veins which normally maintains a cross-cutting relationship. This pyrite may contain elevated arsenic content which is deposited from the hydrothermal fluids or metal rich basinal brines or compaction-driven fluids (Kolker, 2012). Sometimes there is preferential enrichment of Ni in framboidal pyrite. It is believed that arsenic along with Se and Sb may substitute for sulphur in the pyrite structure while Pb along with Hg substitutes for Fe. Cd relates positively with Zn in Barsingsar lignite samples which is in agreement with Finkelman (1994) who believes that Cd is associated with ZnS. However, this relation does not hold good in Gurha lignite samples as Cd may be present in many modes (Riley et al., 2012). The positive correlation of Cd with inorganic content/ash is in agreement with Querol et al. (1996) who showed that Cd has an association with iron sulphides and Kirsch et al. (1980) showed an affinity with clay and carbonate minerals. Cd has shown a poor correlation with Fe.

Co is normally associated with sulphides and also with clay minerals and organic matter (Finkelman, 1994) which appears to be the case in Rajasthan lignites as well; it is indicated by a positive correlation of Co with Cu, K and Na. Cr does not maintain any significant correlation with any of the analysed elements in the Rajasthan lignite samples except a medium correlation with Cu, Co and Ni. Further research work is needed to establish the mode of occurrence of Cr in coal (Finkelman, 1994). Cu occurs in coals in many modes. Swaine (1990) believes that it is present in coal as chalcopyrite or other sulphides and also as organically bound species. In Rajasthan lignite samples Cu correlates well with Co, Ni, Cr, Pb and Cd. Mn is usually associated with carbonates and clay minerals (Swaine, 1990). The data indicates that in all the lignite samples of Rajasthan the concentration of Mn is less than the Clarke values and maintains a low correlation with other elements. No direct evidence is available for the mode of occurrence of Ni in coal (Finkelman, 1994; Riley et al., 2012). It could be organically bound or it may get associated with sulphides. In the analysed samples Ni maintains a good correlation with Co, Cr, Pb, Na, K and Cu. Finkelman (1994) has demonstrated that lead occurs in coal as sulphides or associated with sulphide minerals while Hower and Robertson (2003) report lead selenide in coal and Dale et al. (1999) report lead in silicates (Riley et al. (2012). Positive

Table 4a. Correlation matrix between minor/trace elements in Barsingsar lignite

	Fe	Ca	Mg	Mn	K	Na	Cu	Co	Ni	Cr	Zn	Pb	Cd	As	Ash	OM	Humi	Lipti	Inert
Fe	**1**	-0.029	-0.015	-0.392	-0.094	-0.2	-0.48	-0.241	-0.342	-0.262	-0.041	0.004	-0.279	0.218	0.002	-0.002	0.13	0.165	-0.242
Ca	-0.029	**1**	.774**	0.23	-0.52	0.409	-0.534	-0.533	-0.333	-0.087	-.656*	-.689*	-0.629	.709*	-.821**	.821**	0.587	0.453	-0.428
Mg	-0.015	.774**	**1**	0.105	-0.371	0.466	-0.465	-0.204	0.047	0.231	-0.556	-0.624	-0.444	0.508	-.778**	.778**	0.433	0.606	-0.357
Mn	-0.392	0.23	0.105	**1**	0.243	-0.112	0.41	-0.01	0.027	-0.162	-0.016	0.339	-0.255	0.226	-0.026	0.026	0.089	-0.087	-0.175
K	-0.094	-0.52	-0.371	0.243	**1**	-0.048	.684*	0.552	0.441	-0.139	0.021	.675*	-0.002	-0.067	.637*	-.637*	-.717*	-0.616	0.448
Na	-0.2	0.409	0.466	-0.112	-0.048	**1**	-0.103	0.258	0.447	0.063	-0.232	-0.319	-0.149	.685*	-0.392	0.392	-0.098	0.372	0.17
Cu	-0.48	-0.534	-0.465	0.41	.684*	-0.103	**1**	.690*	0.586	0.334	0.165	.831**	0.546	-0.26	.797**	-.797**	-.810**	-0.406	.728*
Co	-0.241	-0.533	-0.204	-0.01	0.552	0.258	0.690*	**1**	0.952**	0.47	0.166	.657*	0.481	-0.173	0.603	-0.603	-.794**	-0.305	0.627
Ni	-0.342	-0.333	0.047	0.027	0.441	0.447	0.586	0.952**	**1**	0.483	0.114	0.463	0.408	-0.041	0.372	-0.372	-.656*	-0.13	0.517
Cr	-0.262	-0.087	0.231	-0.162	-0.139	0.063	0.334	0.47	0.483	**1**	-0.248	0.126	0.621	-0.276	0.223	-0.223	-0.424	0.298	0.589
Zn	-0.041	-.656*	-0.556	-0.016	0.021	-0.232	0.165	0.166	0.114	-0.248	**1**	0.346	0.478	-0.478	0.307	-0.307	0.032	-0.055	-0.129
Pb	0.004	-.689*	-0.624	0.339	.675*	-0.319	.831**	.657*	0.463	0.126	0.346	**1**	0.427	-0.261	.887**	-.887**	-.727*	-0.456	0.522
Cd	-0.279	-0.629	-0.444	-0.255	-0.002	-0.149	0.546	0.481	0.408	0.621	0.478	0.427	**1**	-0.594	0.617	-0.617	-0.521	0.092	.642*
As	0.218	.709*	0.508	0.226	-0.067	.685*	-0.26	-0.173	-0.041	-0.276	-0.478	-0.261	-0.594	**1**	-0.472	0.472	0.146	0.378	-0.123
Ash	0.002	-.821**	-.778**	-0.026	.637*	-0.392	.797**	0.603	0.372	0.223	0.307	.887**	0.617	-0.472	**1**	-1.000**	-.833**	-0.525	.711*
OM	-0.002	.821**	.778**	0.026	-.637*	0.392	-.797**	-0.603	-0.372	-0.223	-0.307	-.887**	-0.617	0.472	-1.000**	**1**	.833**	0.525	-.711*
Humi	0.13	0.587	0.433	0.089	-.717*	-0.098	-.810**	-.794**	-.656*	-0.424	0.032	-.727*	-0.521	0.146	-.833**	.833**	**1**	0.364	-.917**
Lipti	0.165	0.453	0.606	-0.087	-0.616	0.372	-0.406	-0.305	-0.13	0.298	-0.055	-0.456	0.092	0.378	-0.525	0.525	0.364	**1**	-0.134
Inert	-0.242	-0.428	-0.357	-0.175	0.448	0.17	.728*	0.627	0.517	0.589	-0.129	0.522	.642*	-0.123	.711*	-.711*	-.917**	-0.134	**1**

OM- organic matter, Humi-huminite, Lipti-liptinite, Inert-inertinite. ** - Correlation is significant at the 0.01 level (2-tailed). * - Correlation is significant at the 0.05 level (2-tailed)

Table 4b. Correlation matrix between minor/trace elements in Gurha lignite

	Fe	Ca	Mg	Mn	K	Na	Cu	Co	Ni	Cr	Zn	Pb	Cd	As	Ash	OM	Humi	Lipti	Inert
Fe	1	-0.348	0.445	-0.349	-0.279	-0.554	-0.270	-0.255	-0.274	-0.014	0.180	-0.047	0.161	0.112	-0.183	0.183	-0.340	0.303	0.331
Ca	-0.348	1	0.062	0.209	0.878	0.630	-0.104	0.196	0.115	-0.053	0.069	0.459	-0.600	0.228	0.172	-0.172	0.791	-0.233	-0.782
Fe	**1**	-0.348	0.445	-0.349	-0.279	-0.554	-0.270	-0.255	-0.274	-0.014	0.180	-0.047	0.161	0.112	-0.183	0.183	-0.340	0.363	0.331
Ca	-0.348	**1**	0.062	0.209	.878**	0.630	-0.104	0.196	0.115	-0.053	0.069	0.459	-0.600	0.228	0.172	-0.172	.791**	-.690*	-.782**
Mg	0.445	0.062	**1**	-0.164	-0.027	-0.222	-0.473	-0.256	-.682*	-0.423	-0.037	-0.125	-0.073	0.551	-0.220	0.220	-0.272	0.282	0.272
Mn	-0.349	0.209	-0.164	**1**	0.317	0.381	0.174	0.519	0.409	-0.310	-0.114	-0.429	-0.295	-0.353	-0.429	0.429	0.032	0.088	0.006
K	-0.279	.878**	-0.027	0.317	**1**	0.451	-0.049	0.460	0.235	-0.018	0.217	0.321	-.814**	0.258	-0.221	0.221	.730*	-0.527	-.701*
Na	-0.554	0.630	-0.222	0.381	0.451	**1**	0.410	0.308	0.512	0.301	0.377	0.318	-0.052	0.181	0.373	-0.373	.695*	-.755*	-.667*
Cu	-0.270	-0.104	-0.473	0.174	-0.049	0.410	**1**	.671*	.662*	0.483	.646*	0.225	-0.024	0.215	0.129	-0.129	0.322	-0.344	-0.309
Co	-0.255	0.196	-0.256	0.519	0.460	0.308	.671*	**1**	.700*	-0.028	0.533	-0.147	-0.569	0.267	-0.523	0.523	0.317	-0.087	-0.292
Ni	-0.274	0.115	-.682*	0.409	0.235	0.512	.662*	.700*	**1**	0.212	0.477	-0.107	-0.039	-0.149	-0.090	0.090	0.340	-0.251	-0.321
Cr	-0.014	-0.053	-0.423	-0.310	-0.018	0.301	0.483	-0.028	0.212	**1**	0.606	.698*	0.175	0.192	0.473	-0.473	0.479	-.644*	-0.454
Zn	0.180	0.069	-0.037	-0.114	0.217	0.377	.646*	0.533	0.477	0.606	**1**	0.355	-0.095	.664*	-0.039	0.039	0.428	-0.426	-0.391
Pb	-0.047	0.459	-0.125	-0.429	0.321	0.318	0.225	-0.147	-0.107	.698*	0.355	**1**	-0.184	0.322	.664*	-.664*	.713*	-.843**	-.710*
Cd	0.161	-0.600	-0.073	-0.295	-.814**	-0.052	-0.024	-0.569	-0.039	0.175	-0.095	-0.184	**1**	-0.285	0.471	-0.471	-0.514	0.211	0.508
As	0.112	0.228	0.551	-0.353	0.258	0.181	0.215	0.267	-0.149	0.192	.664*	0.322	-0.285	**1**	-0.088	0.088	0.319	-0.279	-0.307
Ash	-0.183	0.172	-0.220	-0.429	-0.221	0.373	0.129	-0.523	-0.090	0.473	-0.039	.664*	0.471	-0.088	**1**	-1.000**	0.327	-0.616	-0.349
OM	0.183	-0.172	0.220	0.429	0.221	-0.373	-0.129	0.523	0.090	-0.473	0.039	-.664*	-0.471	0.088	-1.000**	**1**	-0.327	0.616	0.349
Humi	-0.340	.791**	-0.272	0.032	.730*	.695*	0.322	0.317	0.340	0.479	0.428	.713*	-0.514	0.319	0.327	-0.327	**1**	-.918**	-.996**
Lipti	0.363	-.690*	0.282	0.088	-0.527	-.755*	-0.344	-0.087	-0.251	-.644*	-0.426	-.843**	0.211	-0.279	-0.616	0.616	-.918**	**1**	.905**
Inert	0.331	-.782**	0.272	0.006	-.701*	-.667*	-0.309	-0.292	-0.321	-0.454	-0.391	-.710*	0.508	-0.307	-0.349	0.349	-.996**	.905**	**1**

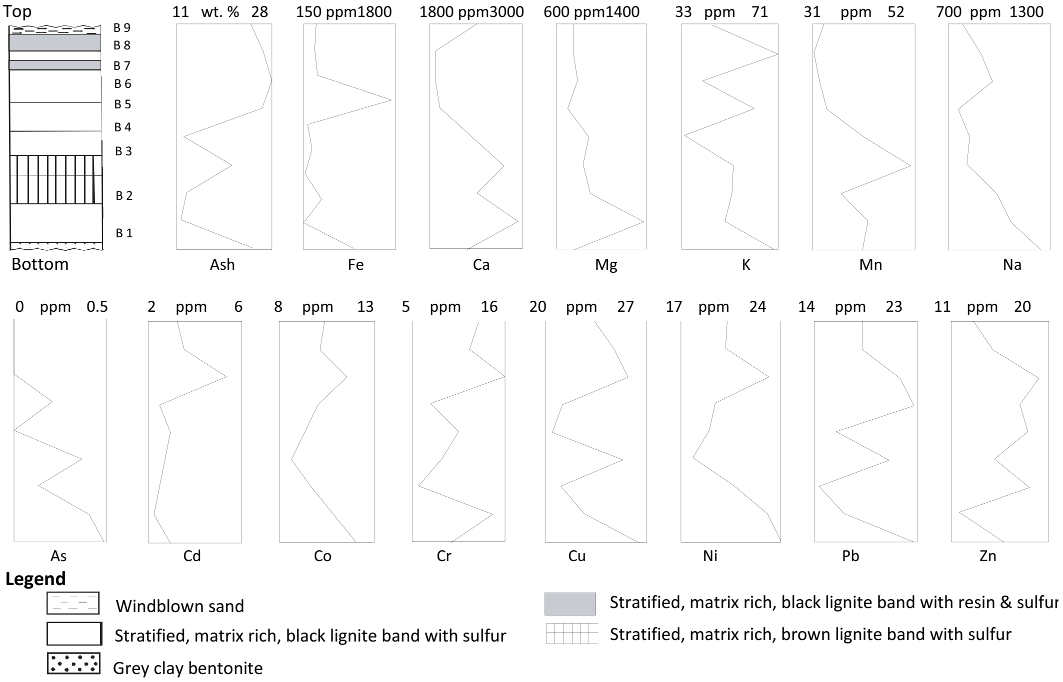

Fig.2a. Vertical variation of ash and some elements in Barsingsar lignite seam.

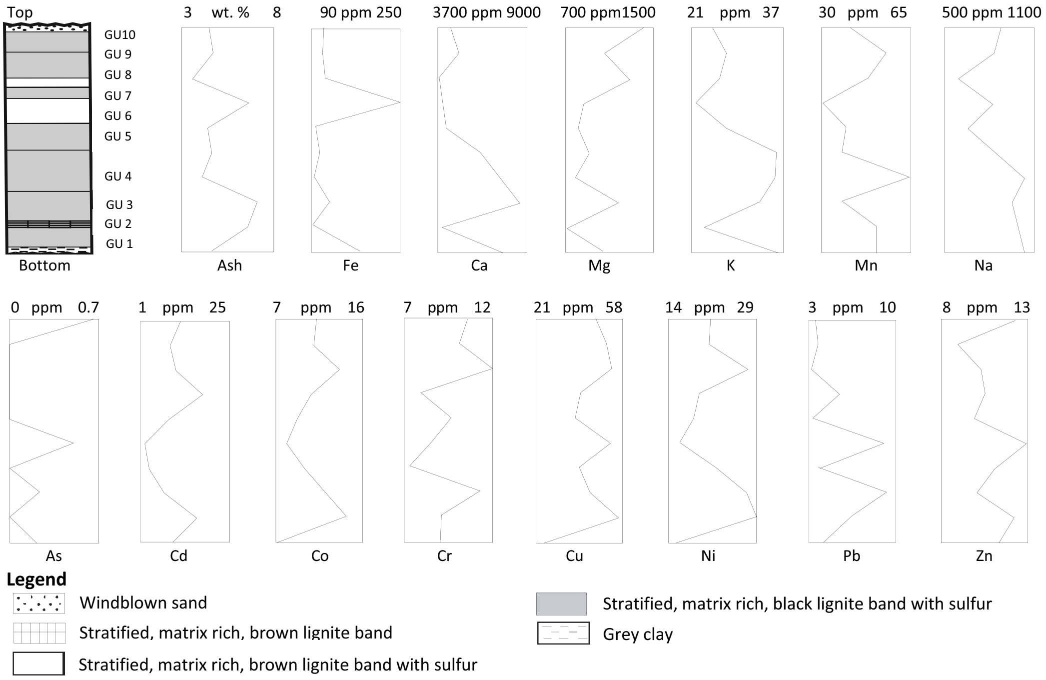

Fig.2b. Vertical variation of Ash and some elements in Gurha lignite seam

correlation of Pb with Cu, Co, Ni, Cr, K and Ca appears to be in agreement with these findings. Though Zn is considered as a notorious contaminant in analytical chemistry (Riley et al., 2012), it usually occurs as sphalerite in coal (Swaine, 1990). In the lignite samples of Rajasthan (especially Gurha lignite) there is prominent and positive correlation of Zn with Cu, Co, Ni and Cr. The unstratified band is seen to contain relatively low concentration of Fe, Zn and Pb.

The correlation coefficient (r) of the elements is calculated against organic matter to know also their organic or inorganic affinity. In Barsingsar lignite Ca and Mg have

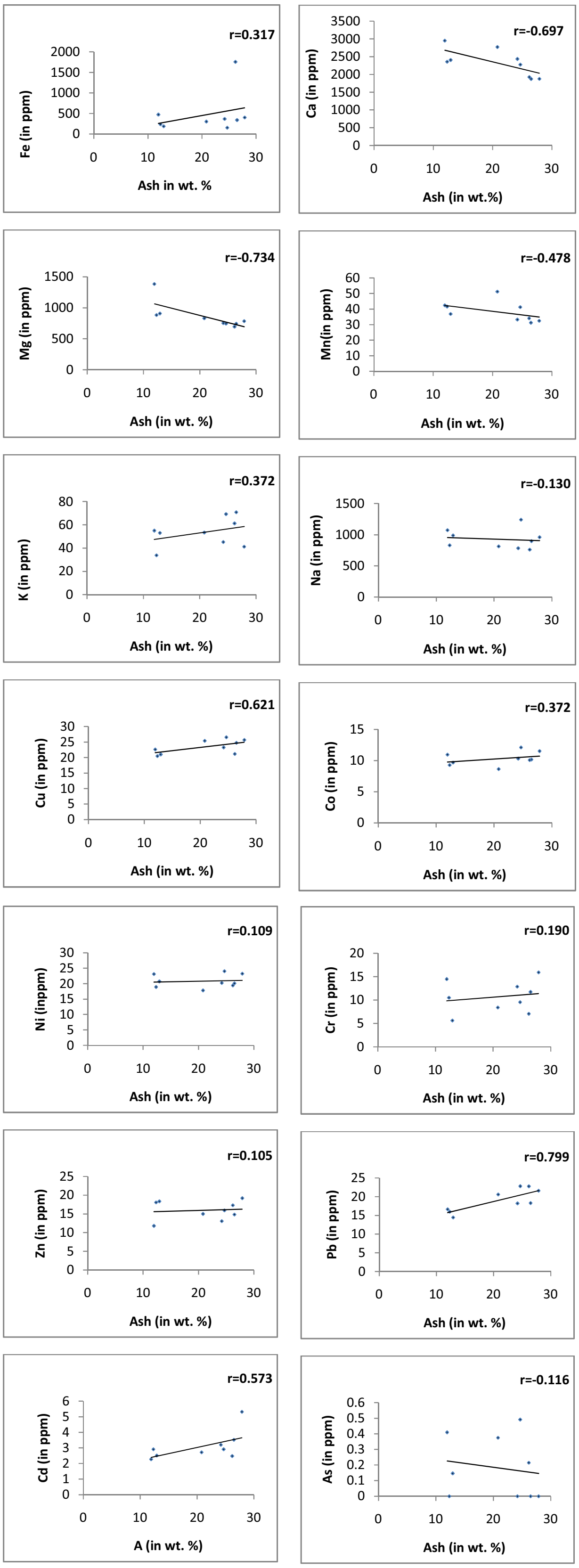

Fig.3. Relationship between ash content and minor/trace elements in Barsingasar lignite.

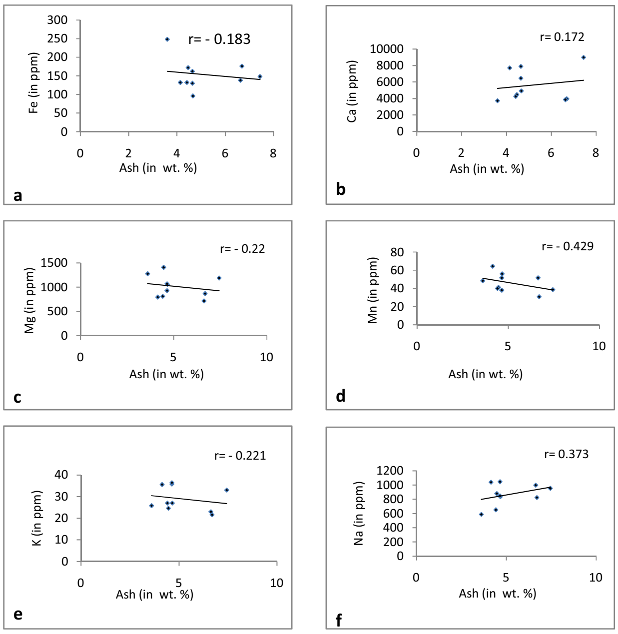

Fig.4a. Relationship between ash content and minor elements in Gurha lignite.

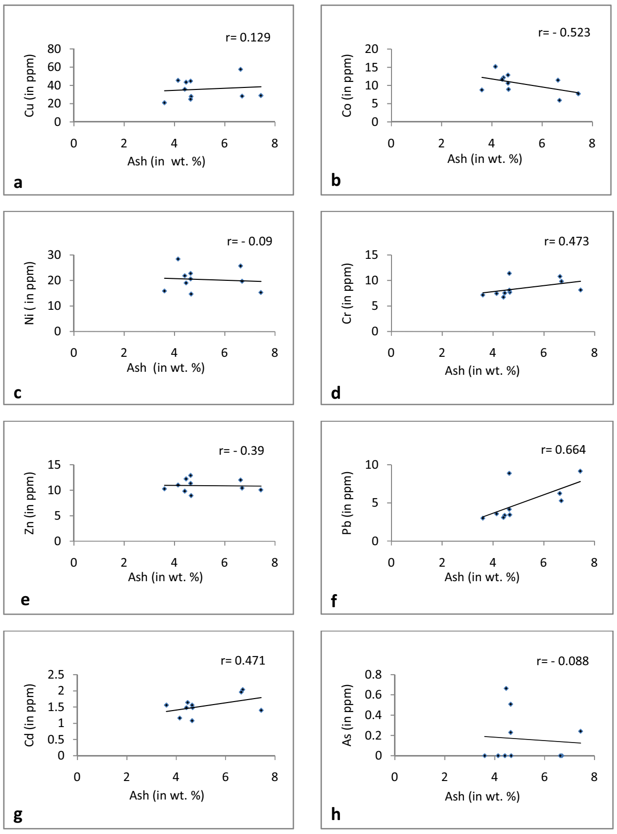

Fig.4b. Relationship between ash content and trace elements in Gurha lignite.

a strong affinity with organic matter showing their derivation from the organic source while K, Cu, Co, Pb, while Cd shows a strong affinity with inorganic matter (ash) which indicate their inorganic origin. Rest of the elements have a low correlation with organic matter or ash. The correlation of petrographic components with various elements reveals that in Barsingsar lignite Cu, Co, Ni, Cr, Cd and Pb have a strong positive relation with inertinite maceral group. This may be associated with the minerals which normally occupy the cell lumens of fusinite and the chambers of funginite macerals of the inertinite group. The huminite maceral group maintains a negative correlation with K, Cu, Co, Ni, and Pb but has shown a positive relation with Ca. A correlation matrix among the elements is provided in Table 4a. Similarly in Gurha lignite Pb and Co show a moderately strong affinity with inorganic matter which mean at least a part of them have been derived from the inorganic source while rest of the elements have low correlation with organic matter or ash content. The elements, however, show variation in organic or inorganic affinity. In these lignite samples the huminite maceral group has shown a strong positive correlation with Ca, K, Na and Pb; and a medium positive correlation with Cu, Co, Ni, Cr and Zn. The liptinite maceral group maintains a strong negative correlation with Cr and Pb. The inertinite maceral group also maintains a strong negative correlation with Ca, K and Na but has shown a positive relation with Cd. The correlation matrix among the various elements is shown in Table 4b. In general Ca and K are derived from inorganic source; however, in Barasingsar lignite it appears that Ca could have come in contact with the organic matter during the process of humification to become a part of humates.

A relative constancy in the concentration of trace elements in coal is an indication of sea water reservoir for their source (Spears and Tewalt, 2009; Spears and Zheng, 1999; Spears et al., 2007 and; Gayer et al., 1999). A nearly constant Cu and Ni in the lignite samples of Barsingsar and Gurha also favours the sea water influence and is in agreement with the studies.

CONCLUSIONS

The investigation indicates that the concentrations of Co, Ni and pb is two to five times higher while that of Cd is ten to twenty times higher than the Clarke values for lignite in Barsingsar. The elements like Cu, Cr, Zn and As occur in normal concentration. In the Gurha lignite deposit the enrichment of Cu, Co and Ni is two to four times while Cd is five to ten times higher than the Clarke values. However Cr, Zn, Pb and As have a normal range. The study further reveals that there is decrease in Ca and Na from bottom to top of the seams in both the deposits but there is no significant trend seen in most of the elements.

The concentration of elements like Cu and Ni in both the deposits is relatively uniform which is indicative of a marine influence during the peat formation. In Barsingsar lignite Ca and Mg have shown a strong affinity with organic matter. They could have come in contact with the organic matter during the humification process and could have become a part of humates. K, Cu, Co, Pb and Cd appear to have been derived from the inorganic source. The elements like Cu, Co, Ni, Cr, Cd and Pb have shown a strong positive correlation with inertinite group of macerals which could have got associated with the mineral matter occupying the cell lumens and the chambers of the fungal bodies. In Gurha lignite most of the elements have a moderate to low correlation except Pb which shows a strong affinity with inorganic matter.

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