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Selected Major, Minor and Trace Elements in Lignite Deposits of Saurashtra Basin, Gujarat: Their Association, Distribution and Environmental Implications

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Abstract: **In the present paper, distribution and association of selected major/minor/trace elements have been studied on the basis of petrology and geochemistry. The selected elements like Ca, Na, Mg, K, Fe, Cr, Ni, Mn, Co, Cu, Zn, Pb, Cd, As, C, H, N, O and S are analyzed in lignite seams of Bhavnagar, Saurashtra Basin. The samples were subjected to geochemical (proximate, ultimate and rock eval pyrolysis) and petrological (maceral, mineral matter and microlithotype) analyses through advanced technique. In Bhavnagar lignite seams Cu is anomalously high especially in the lower seam, while the concentration of Na and Mg is several folds high. Ni, Co and Cr are high in few samples as compared to the Clarke values for brown coal. The elements are associated with organic and inorganic components of coal in different forms.**

Index Terms: **Lignite, Elements, Saurashtra Basin, Mineral Matter, Microlithotype.**

I. INTRODUCTION

Saurashtra Peninsula is bordered by alluvial plains in the northeast while other sides are bordered by sea (Merh, 1995). In Saurashtra Basin, lignite seams are of Eocene and occur in Khadsaliya clays Formation. Coal is an organo-clastic sedimentary rock and consists of organic constituents along with varied proportions of inorganic minerals. The major, minor and trace elements occur in different amounts which are reported through direct as well as indirect analysis in form of ash, mineral carbon, mineral matter and carbominerite.

Coal is also a significant source of environmental pollution and affects air, water and landmass which make up our ecosystem. Pollution is caused at every stage, from coal mining to utilization. It generates dust during coal mining processes which gets deposited around the mining area and also contaminates the ground water. Significant contributions have been made by Prakash (2007), Sarkar et al. (2007), DeKok (1986) and Krajick (2005).

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This paper entails the result of a study on the distribution and geochemical characterization of selected environmentally sensitive elements in Bhavnagar lignite of Saurashtra Basin, Gujarat.

II. GEOLOGICAL SETTING

In Bhavnagar lignite field, the lignite bearing sequence is Khadsaliya Clay Formation (Biswas, 1982). The overburden strata consist of top soil, bentonitic clay and compact greenish hard strata. Strata overlying the lignite are soft in nature and can be easily removed by hydraulic excavators (Biswas, 1987). The lignite seams are associated with carbonaceous and grey shales (Merh, 1995; GMDC, 2013).

The marine Tertiary rocks occur along the fringe portion of the Saurashtra peninsula. Regular break in sedimentation has been observed in the area which is marked by unconformities. Khadsaliya clay is lignite bearing which is greenish-grey clay formation of Eocene age. There is no exposure of lignite and it occurs as two sub-surface horizons, top/upper lignite horizon and bottom/lower lignite horizon. The lignite seams unconformably lie over the weathered Trappean sediments on the lithomargic clay. It is encountered deeper towards the eastern and north-eastern part of the basin and diminishes towards the sea. On the basis of drilling data the local stratigraphic succession has been established by GMDC (2013).

III. MATERIALS AND METHODS

Lignite samples have been collected from the working faces of upper and lower seams of Bhavnagar lignite mines following Pillar sampling method (Schopf, 1960). The samples have been crushed to -70 and -18 mesh size. The -70 mesh samples have been subjected to various geochemical analyses that include proximate analysis, ultimate analysis, rock-eval pyrolysis and elemental determination. Details of the methods have been discussed by Singh et al., 2016a,b, 2017. Fe, Ca, Mg, Mn, K, Na, Cu, Co, Ni, Cr, Zn, Pb and As have been determined on ‘whole-lignite samples’ using atomic absorption spectrometer (AAS).

The maceral analysis was performed using a Leitz Orthoplan-Pol Microscope equipped with Wild Photoautomat MPS-45 following Taylor et al. (1998). Huminite macerals were termed and described as per ICCP-1994 (Sykorova et al. 2005), while the description provided by the ICCP (2001) was followed for inertinite macerals. Liptinites have been described as per Pickel et al. (2017).

IV. RESULTS AND DISCUSSION

A. GEOCHEMICAL COMPONENTS

The content of ash yield varies from 5.9-14.6% ($\bar{x}$ = 9.3%) on weight percentage while the volatile matter varies from 48.9-74.3% ($\bar{x}$ = 61.8%) and fixed carbon content varies from 25.7-51.1% ($\bar{x}$ = 38.2%) on daf basis. The carbon content varies from 62.4-83.0% ($\bar{x}$ = 71.9%), hydrogen content ranges from 3.4-6.1% ($\bar{x}$ = 5.0%), nitrogen content varies from 0.8-1.1% ($\bar{x}$ = 1.0%), and oxygen content ranges from 8.8-29.5% ($\bar{x}$ = 19.9%). The sulfur content is moderately high and varies from 1.8-2.7% ($\bar{x}$ = 2.2%). Mineral carbon (MINC %) component is analysed through rock eval pyrolysis and it varies from 1.3-2.6% ($\bar{x}$ = 1.7%). Variation in the proximate components (ash yield, volatile matter and fixed carbon), ultimate constituents (carbon, hydrogen, nitrogen, oxygen and sulphur) and Mineral carbon % (MINC%) is shown in Tables 1A and 1B.

B. DISTRIBUTION OF MAJOR, MINOR AND TRACE ELEMENTS

The result of major/minor element analysis shows that Ca varies from 272-6774 ppm ($\bar{x}$ = 4040.3 ppm), Na varies from 1074.0-10414.0 ppm ($\bar{x}$ = 6008.3 ppm), Mg varies from 46.6-4560.0 ppm ($\bar{x}$ = 1968.3 ppm), K varies from 29.2-117.8 ppm ($\bar{x}$ = 69.2 ppm), Fe varies from 270.0-5015.0 ppm ($\bar{x}$ = 380 ppm), and Mn varies from 15.6-34.4 ppm ($\bar{x}$ = 30.3 ppm). The trace element analysis indicates that Cr varies from 1.8-59.2 ppm ($\bar{x}$ = 20.9 ppm), Ni from 1.2-44.0 ppm ($\bar{x}$ = 16.6 ppm), Co varies from 0.5-13.6 ppm ($\bar{x}$ = 6.6 ppm), Cu varies from 6.5-4480.0 ppm ($\bar{x}$ = 589.2 ppm), Zn varies from 0.6-12.2 ppm ($\bar{x}$ = 5.8 ppm), Pb varies from 0.5-5.1 ppm ($\bar{x}$ = 3.0 ppm), Cd varies from 0.2- 3.0 ppm ($\bar{x}$ = 1.0 ppm) and As varies from 0.0-0.54 ppm ($\bar{x}$ = 0.1 ppm). Detailed result of elements in the lignites of Saurashtra basin is furnished in Table 2.

C. PETROGRAPHIC COMPONENTS

Micropetrographic analysis reveals that these lignites are predominantly rich in huminite which varies from 48.4-77.0% ($\bar{x}$ = 65.1%). Liptinite varies from 4.6-14.8% ($\bar{x}$ = 9.2%), inertinite varies from 2.4-21.2% ($\bar{x}$ = 6.0%) and total mineral matter varies from 10.0-28.2% ($\bar{x}$ = 19.7%). Among the mineral matter, sulphide varies from 1.4-10.6% ($\bar{x}$ = 6.5%), carbonate varies from 0.0-6.0% ($\bar{x}$ = 1.1%) and argillaceous mineral matter varies from 7.6-25.2% ($\bar{x}$ = 12.0%) (Fig. 1). Petrographic analysis reveals that microlithotype (maceral association) varies from 72.6-89.9% ($\bar{x}$ = 82.9%) and the total carbominerite (maceral-mineral association) varies from 10.1-27.4% ($\bar{x}$ = 17.1%). Among the carbominerites, carboankerite varies from 7.8-25.6% ($\bar{x}$ = 12.4%), carbopyrite varies from 0.0-7.4% ($\bar{x}$ = 2.6%) and carbankerite varies from 0.0-6.6% ($\bar{x}$ = 2.1%) (Fig. 2). Petrography based mineral matter components are shown in Table 2.

Ash yield ($\bar{x}$ = 9.3 in weight %) and fixed carbon ($\bar{x}$ = 38.2 on dry ash free basis) content show decreasing trend while volatile matter ($\bar{x}$ = 61.8% on daf basis) shows an increasing trend from top to bottom of the seam profile. Based on ash yield ($\bar{x}$ = 9.3 in weight %), these lignites may be classified as 'low ash coal' (GB/T 15224.1-94) (Table 1A and 1B).

In ultimate components nitrogen and sulfur are considered as potential pollutants. Trend of variation of carbon, hydrogen and nitrogen are increasing from top to bottom of the seam while oxygen and sulfur show a decreasing trend from top to bottom of the seam. Carbon content ($\bar{x}$ = 71.9% on daf basis), in these lignites, is moderately high while sulfur content ($\bar{x}$ = 2.2% on daf basis) is moderately high as per Chinese standard classification (GB/T15224.2-2004). Sulphur content in this lignite indicates marine influence during coal forming processes (Chau, 2012). Presence of sulphur also affects the present day environment, from lignite mining activity till its utilization process; very often it leads to acid rain, sulfur rich water near coal mine and disturbs the ecosystem (Patra, 2010). Petrologically, Fe-disulfide occurs as pyrite in these lignites. Sulphide and carbopyrite are distributed in the different pyrite forms like, discrete grains, disseminated grains, massive pyrite, fissure-crack fillings and framboidal pyrite. This indicates of marine influence and pyrite also formed as a result of bacterial reduction of SO_4^{2-} in pore waters during or after deposition of coal (Chou, 1990). The determination of mineral carbon percentage (MINC%) has been done through rock-eval pyrolysis and the mean value mineral carbon is $\bar{x}$ = 1.7% which is in accordance with the mineral percentage calculated in this lignite from the ash yield, mineral matter and carbominerite (Table 1A and 1B).

Elements affect the environment all the way through their mobility, concentration, and toxicity (Tang et al., 2009). The ash generated by coal combustion in the Thermal Power Plants contain large number of elements including Cd, Cr, Pb, Zn in varying concentrations. Further, these metals get up to ten fold enriched during combustion of coal (Turiel et al., 1994) as compared to their concentrations in the whole-coal samples. There is a direct environmental relevance of trace elements such as As, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Sr, U, V, and Zn (Pickhardt, 1989). Toxic airborne sulphur, PAH and legacy of trace elements in coal have been discussed by Medunić et al., (2018). Lithophilic elements like Ca, Na, Mg and K; siderophilic elements like Fe, Cr, Ni, Mn, and Co; and Chalcophilic elements like Cu, Zn, Pb, Cd and As, have been analysed from the whole-coal/lignite samples. These elements may enter into atmosphere during mining activity, transportation process and also during their utilization in the thermal power plants, and cause serious environmental implications (Kumar et al., 2020; Prachiti et al., 2011; Rajak et al., 2018, 2020; Singh et al., 2015a & b, 2016a & b; Spears and Tewalt, 2009. Vassileva and Vassileva (1997) determined and suggested the modes of element occurrence in coal. Occurrence and distribution of lithophilic, siderophilic and chalcophilic elements in the coal deposits of Russia, U.S. A. (Kentucky), China, India and Indonesia have been discussed by Yudovich (1978), Pareek and Bardhan (1985), Liu et al. (2001), Hower et al. (2003), Seredin (2005), Prachiti et al. (2011), Singh et al. (2015a, b; 2016a, b) and Rajak et al. (2018, 2020). Mean concentration of Ca lies within the world average (WCBC) value in coal (Table 2). Petrological analysis indicates the presence of carbonate ($\bar{x}$ = 1.1%) and carbankerite ($\bar{x}$ = 2.1%) in the investigated lignite; calcium is seen to be associated with clay minerals and anhydrite. There is positive correlation of Ca with Mg, Cr, Ni, Co, Zn, Pb and Cd (r = 0.886, r = 0.748, r = 0.858, r = 0.894, r = 0.810, r = 0.808 and r = 0.731 respectively) while negative correlation with K and Cu (r = -0.717 and r = -0.657 respectively). Further Ca maintains a negative correlation with liptinite (r = -0.607) also at 0.01 significance level. The correlation of Ca with Fe and As (r = 0.491 and r = 0.514 respectively) are observed at 0.05 significance level (Table 3). Na has 53 times higher than the WCBC value (Table 2). Na is associated with clay minerals and organic halite which is reflected by its presence in argillaceous (12.0%) minerals and carbargilite (12.4%) in the petrological studies. At 0.05 significance level Na has shown positive correlation with inertinite (r = 0.467) and negative correlation with huminite (r = -484) and element Mg (r = -0.463) respectively. Na correlates strongly with Fe is (r = -0.618) at 0.01 significance level (Table 3). In the lower lignite seam Mg is less than WCBC value while in upper lignite seam it is 23 times higher than the WCBC value (Table 2). Mg is associated with clay minerals, dolomite, siderite and organic matter. Mg maintains a positive correlation with Fe, Cr, Ni, Co, Zn, Pb and Cd (r = 0.662, r = 0.661, r = 0.826, r = 0.905, r = 0.780, r = 0.756 and r = 0.717 respectively) at 0.01 significance level. With As and huminite maceral, it correlates positively (r = 0.520 and r = 0.533 respectively) at 0.05 significance level. Negative correlation of Mg with K and liptinite (r = -0.670 and r = -0.621 respectively) is observed at 0.01 significance level while with Cu (r = -0.566) at 0.05 significance level (Table 3). K is observed above the WCBC value especially in the samples BHL-1, BHL-2 and BHL-9 (Table 2). K is associated with clay minerals, jarosite, siderite, and organic matter. Positive correlation of K exists with Cu and liptinite (r = 0.582 and r = 0.658) at 0.01 significance level while negative correlation with Ni, Cu, Pb and Cd (r = -0.609, r = -0.693, r = -0.618 and r = -0.691 respectively) at 0.01 significance level. K maintains a negative correlation at 0.05 significance level with Cr and Zn (r = -0.478 and r = -0.555 respectively) (Table 3). Concentrations of Ca, Mg and Na are higher in sea water than in fresh water. Presence of Ca and Mg in high concentration in the investigated lignites indicates periodic marine influence during its formation and the same has also been substantiated in the earlier studies (Singh et al., 2017; Reimann and de Caritat, 1998). Mg concentration may also harm the environment when enters through various process of coal mining and utilization (Gauch et al. 1979). Fe occurs in low concentration in these lignites than the WCBC value (Table 2). A relatively higher concentration is observed in the upper lignite seam than in the lower lignite seam of Saurashtra basin. Fe is associated with the minerals pyrite, calcite, gypsum, clay minerals, ankerite, and hematite. Cr occurs in concentration higher than the WCBC value in coal, especially in lower portion of upper seam (from BH-1 to BH-7 samples) (Table 2). Cr is associated with clay minerals, pyrite, magnetite, chromite, and organic matter. Positive correlation of Cr exists with Ni, Co, Zn, Pb and Cd (r = 0.942, r = 0.859, r = 0.887, r = 0.768 and r = 0.746 respectively) at 0.01 significance level while with liptinite it maintains a negative correlation (r = -0.519) at 0.05 significance level (Table 3). Ni occurs in high concentration and in the upper lignite seam it is upto five fold higher than WCBC value in coal (Table 2). Ni is associated with clay minerals, marcasite, pyrite, siderite, gypsum, and organic matter. Positive correlation of Ni exists with Co, Zn, Pb and Cd (r = 0.937, r = 0.892, r = 0.803 and r = 0.799 respectively) while with liptinite it is negatively correlated (r = -0.634) at 0.01 significance level. Ni has a negative correlation with Cu (r = -0.524) at 0.05 significance level (Table 3). Mn occurs in low concentration in both the lignite seams than the world average value (WCBC) in coal except in one sample of the lower lignite sample (BL 3) (Table 2). Mn has an association with pyrite, clay minerals, marcasite, gypsum, and organic matter. Mn has a negative correlation with Pb (r = -0.577) at 0.01 significance level (Table 3).

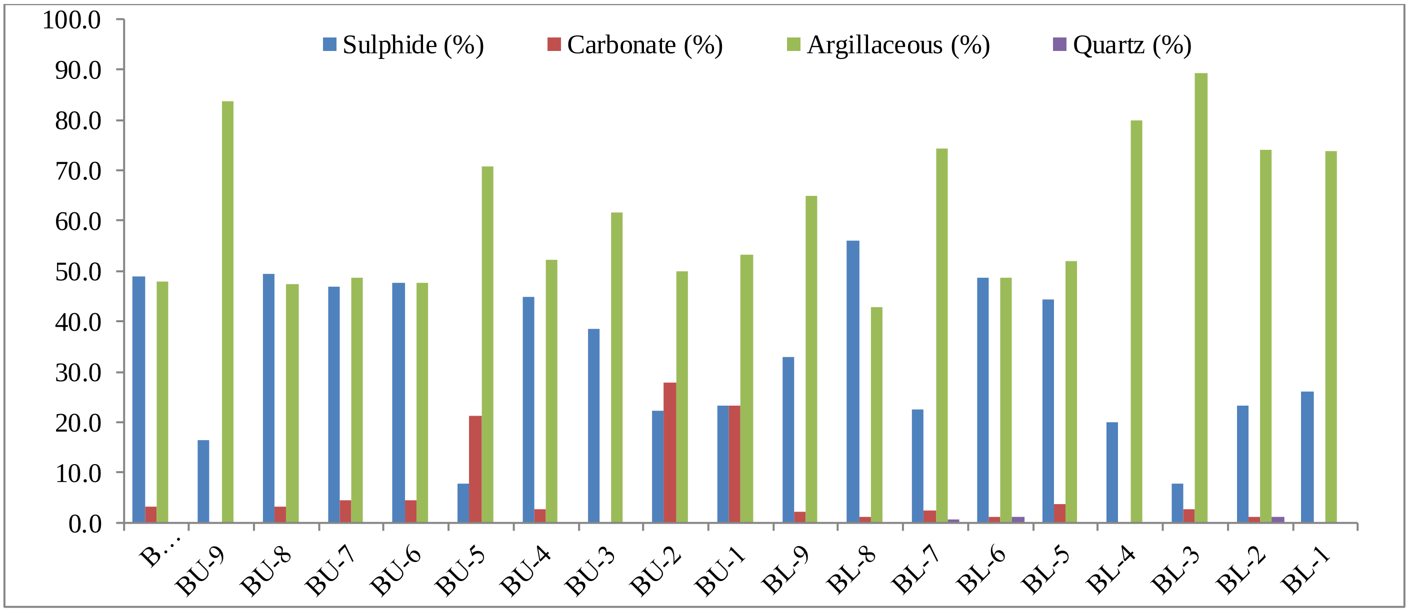

Figure 1. Mineral matter composition in Bhavnagar lignite identified through petrographic analysis

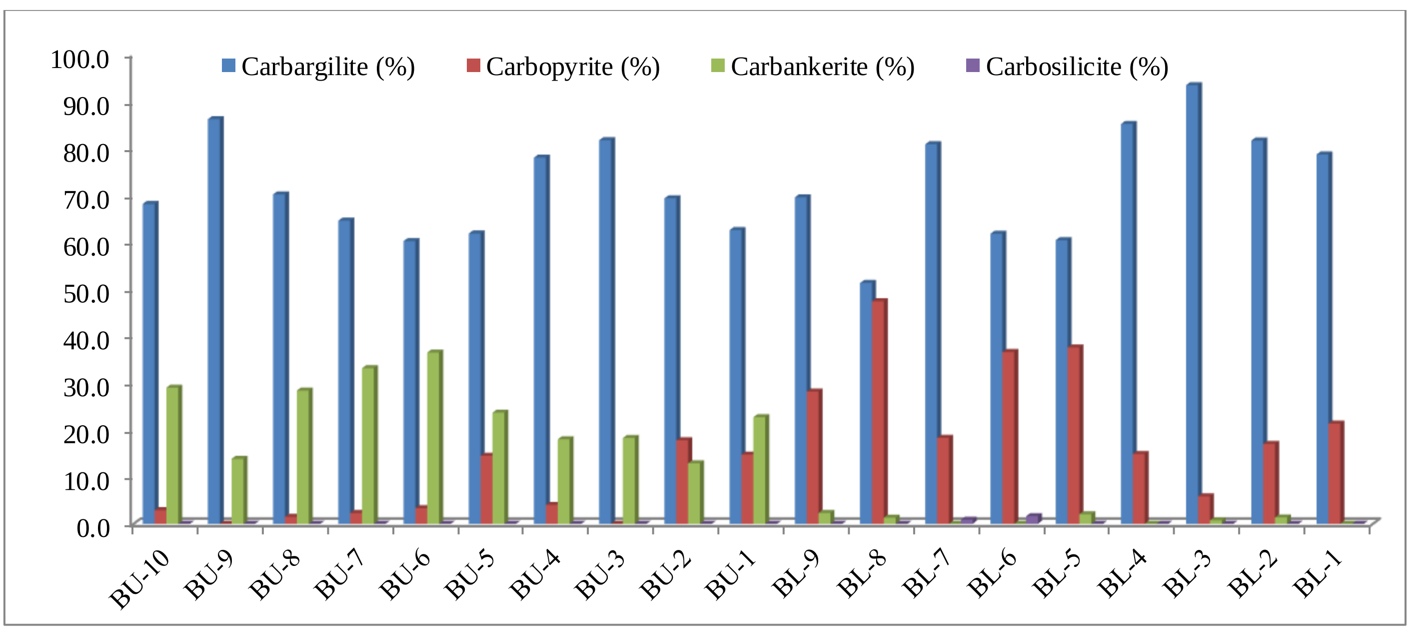

Figure 2. Carbominerite composition in Bhavnagar lignite

Table 1A. Assemblage of mineral matter components identified through geochemical and petrological analyses in upper lignite seam of Bhavnagar.

S. No.	MINERAL MATTER												
	Ash yield %	MINC %	MINERALS (in volume %)					Micro	CARBOMINERITE (in volume %)				
			T	S	C	A	Q		T	Car	Cpy	Can	Csi
BU-10	10.1	1.6	18.8	9.2	0.6	9.0	0.0	86.3	13.8	9.4	0.4	4.0	0.0
BU-9	10.3	1.5	12.2	2.0	0.0	10.2	0.0	87.7	12.3	10.6	0.0	1.7	0.0
BU-8	10.2	1.4	18.6	9.2	0.6	8.8	0.0	86.6	13.4	9.4	0.2	3.8	0.0
BU-7	10.6	2.0	22.6	10.6	1.0	11.0	0.0	82.5	17.5	11.3	0.4	5.8	0.0
BU-6	9.8	ND	22.2	10.6	1.0	10.6	0.0	81.9	18.1	10.9	0.6	6.6	0.0
BU-5	9.5	1.3	17.8	1.4	3.8	12.6	0.0	79.3	20.7	12.8	3.0	4.9	0.0
BU-4	8.4	1.6	21.8	9.8	0.6	11.4	0.0	85.1	15.0	11.7	0.6	2.7	0.0
BU-3	10.1	1.4	22.9	8.8	0.0	14.1	0.0	82.4	17.5	14.3	0.0	3.2	0.0
BU-2	10.1	ND	21.6	4.8	6.0	10.8	0.0	83.8	16.3	11.3	2.9	2.1	0.0
BU-1	14.6	1.4	18.8	4.4	4.4	10.0	0.0	83.7	16.3	10.2	2.4	3.7	0.0

T = Total; S = Sulphide; C = Carbonate; A = Argillaceous; Q=Quartz; Micro = Microlithotype; Car = Carbargilite; Cpy = Carbopyrite; CAn = Carbankerite; CSi = Carbosilicite; ND-not detected

Table 1B. Assemblage of mineral matter components identified through geochemical and petrological analyses in lower lignite seam of Bhavnagar.

S. No.	MINERAL MATTER												
	Ash yield %	MINC %	MINERALS (in volume %)					Micro	CARBOMINERITE (in volume %)				
			T	S	C	A	Q		T	Car	Cpy	Can	Csi
BL-9	10.3	2.4	18.2	6.0	0.4	11.8	0.0	82.6	17.4	12.1	4.9	0.4	0.0
BL-8	6.6	ND	18.2	10.2	0.2	7.8	0.0	84.6	15.4	7.9	7.3	0.2	0.0
BL-7	7.9	ND	25.0	5.6	0.6	18.6	0.2	76.5	23.5	19.0	4.3	0.0	0.2
BL-6	8.5	ND	15.2	7.4	0.2	7.4	0.2	87.7	12.3	7.6	4.5	0.0	0.2
BL-5	7.8	2.6	21.6	9.6	0.8	11.2	0.0	80.2	19.7	11.9	7.4	0.4	0.0
BL-4	8.4	ND	10.0	2.0	0.0	8.0	0.0	89.9	10.1	8.6	1.5	0.0	0.0
BL-3	5.9	ND	28.2	2.2	0.8	25.2	0.0	72.6	27.4	25.6	1.6	0.2	0.0
BL-2	10.4	ND	15.4	3.6	0.2	11.4	0.2	85.3	14.7	12.0	2.5	0.2	0.0
BL-1	8.0	2.1	25.2	6.6	0.0	18.6	0.0	76.2	23.9	18.8	5.1	0.0	0.0

T = Total; S = Sulphide; C = Carbonate; A = Argillaceous; Q=Quartz; Micro = Microlithotype; Car = Carbargilite; Cpy = Carbopyrite; CAn = Carbankerite; CSi = Carbosilicite; ND-not detected

Table 2. Distribution of major, minor and trace elements in Bhavnagar lignite, Saurashtra Basin (all values in ppm)

Elements & Sample No	Lithophile elements				Siderophile elements					Chalcophile elements				
	Ca	Na	Mg	K	Fe	Cr	Ni	Mn	Co	Cu	Zn	Pb	Cd	As
WCBC*	10000	200	200	100	10000	15±1	9.0	100±6	4.2±0.2	15±1	18±2	6.6±0.7	0.2±0.24	7.6
BU-10	6226.0	2442.0	4000.0	63.8	5015.0	16.5	18.4	19.6	10.6	10.7	6.6	3.6	1.3	0.09
BU-9	5306.0	1074.0	4520.0	59.0	3940.0	12.0	19.7	20.0	7.7	6.5	6.9	3.1	1.1	0.00
BU-8	5956.0	2976.0	4560.0	45.4	2860.0	10.0	21.8	23.2	8.4	8.2	5.8	3.7	1.3	0.18
BU-7	4272.0	3012.0	2644.0	40.8	1438.0	28.7	18.0	15.6	9.0	56.0	8.6	3.6	1.3	0.00
BU-6	5906.0	1528.0	3432.0	52.0	1060.0	24.2	17.7	19.2	10.4	16.2	6.9	3.6	0.9	0.54
BU-5	5152.0	3820.0	2528.0	29.2	798.0	27.7	22.4	18.0	10.4	34.0	8.2	5.1	3.0	0.00
BU-4	6582.0	6746.0	3596.0	48.0	704.0	50.8	42.8	19.2	13.6	17.0	9.2	3.8	1.7	0.29
BU-3	6478.0	5164.0	3200.0	40.6	940.0	55.2	44.0	18.0	13.2	14.6	10.6	4.7	1.8	0.02
BU-2	6758.0	8658.0	4520.0	64.4	928.0	59.2	40.1	23.2	12.0	27.0	12.2	4.5	1.8	0.22
BU-1	6774.0	10414.0	3976.0	68.0	1002.0	52.8	38.3	18.0	12.3	18.6	10.2	4.8	1.9	0.05
BL-9	2660.0	3602.0	47.0	111.6	454.0	12.9	7.3	29.2	2.3	408.0	7.0	1.2	0.6	ND
BL-8	494.0	7656.0	47.0	97.6	270.0	2.5	3.8	31.0	0.8	890.0	2.4	2.0	0.5	ND
BL-7	2240.0	10300.0	47.0	77.4	488.0	13.0	4.4	29.0	2.0	1162.0	4.9	2.8	0.8	ND
BL-6	3160.0	10260.0	47.2	86.6	462.0	7.7	4.0	34.4	1.4	722.0	3.9	3.2	0.4	ND
BL-5	4120.0	6100.0	46.8	52.2	416.0	2.7	3.3	30.4	0.9	1264.0	0.7	1.6	0.2	ND
BL-4	272.0	8410.0	46.8	75.8	278.0	1.8	1.2	23.8	0.5	1096.0	0.6	1.0	0.2	ND
BL-3	1252.0	6902.0	46.6	81.6	300.0	3.3	1.8	139.0	1.3	828.0	3.2	0.5	0.4	ND
BL-2	418.0	8182.0	46.8	117.8	444.0	7.0	1.9	32.8	2.7	4480.0	0.8	2.3	0.3	ND
BL-1	2740.0	6912.0	46.8	102.2	316.0	9.2	4.0	31.4	1.1	136.0	1.2	2.6	0.3	ND
Mean	4040.3	6008.3	1968.3	69.2	380.9	20.9	16.6	30.3	6.3	589.2	5.8	3.0	1.0	0.1

* World Clarke Brown Coal (WCBC) of Ca, Fe, Mn, Na, K and Mg in coal are after Valkovic (1983) and Clarke values of rest of the elements in coal are after Ketris and Yudovich (2009); ND-not detected

Table 3. Correlation matrix among elements and organic components in the Bhavnagar lignite seams

	Ca	Na	Mg	K	Fe	Cr	Ni	Mn	Co	Cu	Zn	Pb	Cd	As	Hu	Li	In	MM	OM
Ca	1	-0.37	.886[a]	-.717[a]	.491[b]	.748[a]	.858[a]	-0.434	.894[a]	-.657[a]	.810[a]	.808[a]	.731[a]	.514[b]	0.297	-.607[a]	-0.243	0.152	-0.152
Na	-0.37	1	-.463[b]	0.431	-.618[a]	0.065	-0.127	0.179	-0.341	0.378	-0.217	-0.126	-0.227	-0.294	-.484[b]	0.413	.467[b]	0.051	-0.051
Mg	.886[a]	-.463[b]	1	-.670[a]	.662[a]	.661[a]	.826[a]	-0.406	.905[a]	-.566[b]	.780[a]	.756[a]	.717[a]	.520[b]	.533[b]	-.621[a]	-0.404	-0.052	0.052
K	-.717[a]	0.431	-.670[a]	1	-0.336	-.478[b]	-.609[a]	0.289	-.693[a]	.582[a]	-.555[b]	-.618[a]	-.691[a]	-0.335	-0.346	.658[a]	0.259	-0.119	0.119
Fe	.491[b]	-.618[a]	.662[a]	-0.336	1	0.013	0.245	-0.251	0.42	-0.332	0.271	0.305	0.26	0.117	0.395	-0.3	-0.181	-0.248	0.248
Cr	.748[a]	0.065	.661[a]	-.478[b]	0.013	1	.942[a]	-0.35	.859[a]	-0.427	.887[a]	.768[a]	.746[a]	0.375	0.28	-.519[b]	-0.365	0.234	-0.234
Ni	.858[a]	-0.127	.826[a]	-.609[a]	0.245	.942[a]	1	-0.388	.937[a]	-.524[b]	.892[a]	.803[a]	.799[a]	0.416	0.42	-.634[a]	-0.399	0.123	-0.123
Mn	-0.434	0.179	-0.406	0.289	-0.251	-0.35	-0.388	1	-0.421	0.184	-0.328	-.577[a]	-0.363	-0.2	-0.433	0.265	0.071	0.428	-0.428
Co	.894[a]	-0.341	.905[a]	-.693[a]	0.42	.859[a]	.937[a]	-0.421	1	-.516[b]	.882[a]	.851[a]	.844[a]	.523[b]	.479[b]	-.655[a]	-.457[b]	0.099	-0.099
Cu	-.657[a]	0.378	-.566[b]	.582[a]	-0.332	-0.427	-.524[b]	0.184	-.516[b]	1	-.607[a]	-0.44	-.506[b]	-0.296	-0.143	0.281	0.279	-0.218	0.218
Zn	.810[a]	-0.217	.780[a]	-.555[b]	0.271	.887[a]	.892[a]	-0.328	.882[a]	-.607[a]	1	.768[a]	.820[a]	0.367	0.286	-0.439	-0.358	0.17	-0.17
Pb	.808[a]	-0.126	.756[a]	-.618[a]	0.305	.768[a]	.803[a]	-.577[a]	.851[a]	-0.44	.768[a]	1	.856[a]	0.332	0.212	-0.404	-0.116	0.038	-0.038
Cd	.731[a]	-0.227	.717[a]	-.691[a]	0.26	.746[a]	.799[a]	-0.363	.844[a]	-.506[b]	.820[a]	.856[a]	1	0.211	0.363	-.482[b]	-0.337	0.057	-0.057
As	.514[b]	-0.294	.520[b]	-0.335	0.117	0.375	0.416	-0.2	.523[b]	-0.296	0.367	0.332	0.211	1	0.229	-0.426	-0.287	0.183	-0.183
Hu	0.297	-.484[b]	.533[b]	-0.346	0.395	0.28	0.42	-0.433	.479[b]	-0.143	0.286	0.212	0.363	0.229	1	-.701[a]	-.678[a]	-.469[b]	.469b
Li	-.607[a]	0.413	-.621[a]	.658a	-0.3	-.519[b]	-.634[a]	0.265	-.655[a]	0.281	-0.439	-0.404	-.482[b]	-0.426	-.701[a]	1	.582[a]	-0.085	0.085
In	-0.243	.467[b]	-0.404	0.259	-0.181	-0.365	-0.399	0.071	-.457[b]	0.279	-0.358	-0.116	-0.337	-0.287	-.678[a]	.582[a]	1	-0.247	0.247
MM	0.152	0.051	-0.052	-0.119	-0.248	0.234	0.123	0.428	0.099	-0.218	0.17	0.038	0.057	0.183	-.469[b]	-0.085	-0.247	1	-1.000[a]
OM	-0.152	-0.051	0.052	0.119	0.248	-0.234	-0.123	-0.428	-0.099	0.218	-0.17	-0.038	-0.057	-0.183	.469[b]	0.085	0.247	-1.000[a]	1

Hu = Huminite, Li = Liptinite, In = Inertinite, MM = Mineral Matters, OM = Organic Matter

[a] Correlation is significant at the 0.01 level (2-tailed).

[b] Correlation is significant at the 0.05 level (2-tailed).

Co has high concentration especially in upper lignite seam wherein it is upto 3 fold higher than the average world value in coal (Table 2). Co is associated with clay minerals, carbonates, gypsum, and organic matter. Cobalt maintains a positive correlation with Zn, Pb and Cd (r = 0.882, r = 0.851 and r = 0.844 respectively) while with liptinite has a negative correlation (r = -0.655) at 0.01 significance level. At 0.05 significance level Co correlates positively with As and huminite (r = 0.523 and r = 0.479 respectively) and negatively with Cu and inertinite (r = -0.516 and r = -0.457 respectively) (Table 3).

Cu has a very high concentration especially in the lower lignite seam wherein it is upto 280 fold higher than the world average value (WCBC) in coal (Table 2). Cu is associated with pyrite, marcasite, chalcopyrite, calcite, and organic components. Cu correlates negatively with Zn (r = -0.607) at 0.01 significance level and with Cd (r = -0.506) at 0.05 significance level (Table 3). Zn occurs in low concentration and it is associated with magnetite, clay minerals, pyrite, calcite, and organic-components. Zn is positively correlated with Pb and Cd (r = 0.768 and r = 0.820 respectively) at 0.01 significance level (Table 3). Pb has been observed in low concentration in these lignites and it is associated with Galena, Pb-Sb sulphosalts, Fe sulphides, magnetite, calcite, aragonite, monazite and organic-components. Such association has also been reported by Finkelman (1994). Positive correlation of Pb exists with Cd (r = 0.856) at 0.01 significance level (Table 3). Cd occurs in high concentration in these lignites and it is seen associated with sphalerite, oxy-hydroxides, Fe sulphides, galena and organic-components. Negative correlation of Cd exists with liptinite maceral (r = -0.482) at 0.05 significance level (Table 3). Sometimes Cd and Ni are associated and organically bound with sulphide (pyrite) and Fe-disulfide structures (Kolker, 2012). Arsenic (As) occurs in low concentration in these lignites which could be due to its easy escape into the atmosphere along with other volatiles. It is associated with arsenopyrite, orpiment, realgar, clay minerals, Fe-sulphides, magnetite, jarosite, sphalerite, galena, calcite, gypsum, and organic-components. Higher concentration of environmentally sensitive elements like

Cu, Pb, Cd, Mg, Fe, etc. affects the ecological system and damage the living system (Alper et al. 2008; Gauch et al., 1979). Concentration of Cu in coal also causes chronic disease and may be sometimes fatal. Lead (Pb) and cadmium (Cd) affects the nervous organ and results in the form of disorder in human being (Alper et al. 2008). Cadmium is commonly associated with sphalerite in coal and responsible for the undesirable changes in the arteries of human kidneys (Alper et al. 2008).

In upper lignite seam, Na, Co, Ni, Cr, and Zn have shown an increasing trend from top of the seam towards bottom part of the seam, while Fe has a reverse trend. Other elements have not shown a definite pattern of variation. Similarly, in case of lower lignite seam, there is no definite pattern of variation of the elements from top to bottom portion, but certain bands have shown a sudden fluctuation in the values (Table 2).

CONCLUSIONS

The mean value of weight percentage of ash is 9.3 and the sulphur on dried basis is 2.2 which indicate that these lignites contain low inorganic matter and medium to high sulfur content. Petrographically the total mineral matter is 19.7% and its comprises of argillaceous minerals (12.0%), sulphide (6.5%), carbonate (1.1%) and quartz (0.1%) while total carbominerite is 17.1% and its components include carbargilite (12.4%), carbopyrite (2.6%), carbankerite (2.1%) and carbosilicite (0.01%). The average value of Ca, K, Fe, Mn, Zn, Pb and As are within the range of the World Clarke Brown Coal while Na, Mg, Cr, Ni, Co, Ca, Cu and Cd are observed above the range of the World Clarke Brown Coal value (WCBC). The association of toxic metal like Pb, Mg, Cd, Fe and Cu in these lignite seams may cause serious environmental implications especially around the mining and industrial area.

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