Comparative Chemical and Mineral Characterization of Paleocene Coal of Sonda Coalfield, Sindh, Pakistan

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RECEIVED ON 08.02.2012 ACCEPTED ON 31.12.2012

ABSTRACT

The Sonda coalfield is located in the 125 km east of Karachi covering an area of about 1400 sq. km. Sonda coal was deposited in the Bara Formation, this Formation contains two main coal-bearing horizons; one is in the upper part and the second is lower part, which is recognized as Jheruck coal zone. In the Bara Formation, coal at Sonda was deposited in three main horizons, named as Daduri, Sonda and Jherruck coal zone. The coal was deposited in in Paleocene age. Sonda coal is enriched with Zn, Ni and Pb. Present mineralogical study shows that Sonda coal contains calcite, dolomite, kaolinite and quartz. The comparison with US and Chinese coal values indicates that among all the analyzed elements, only Ni has high geometric values in Sonda than Chinese coal. GM (Geometric Mean) concentration for Al is higher in Sonda coal than US and Chinese coal values. Clarke values comparison shows that according to Zoller formula all elements in Sonda coal are depleting.

Key Words: **Sonda, Paleocene Coal, Bara Formation, Sindh.**

1. INTRODUCTION

Sonda coalfield was discovered in 1981 in a small village of Sonda, located in district Thatta, 150 km east of Karachi (Fig. 1). This coalfield lies in the east and northeast of Keenjhar Lake in District Thatta and falls in toposheet No. 40 D/1 and 40 C/4. It extends from Jherruck to Thatta in northwest direction and Jhimpir to Sujawal in North-South direction covering an area of 260 Sq. Km (Fig. 1) [1].

The total estimated reserves are over 295 million tones [2]. No detailed geochemical and mineralogical studies have been carried out so far to ascertain the origin of this coal. The present study is one of such attempts to determine the mineralogical and geochemical characteristics of this coalfield.

2. GENERAL GEOLOGY

The stratigraphic units in Sonda coalfield area range in age from the Paleocene to Recent. The oldest unit of the Cenozoic age is the upper part of the Bara Formation, Sonda coal was deposited in the Bara Formation, this Formation contains two main coal-bearing horizons; one is in the upper part and the second is lower part, which is recognized as Jheruck coal zone. In the Bara Formation, coal at Sonda was deposited in three main horizons, named as Daduri, Sonda and Jherruck coal zone [3]. Fig. 2 shows the generalized stratigraphic sequence exposed in the area.

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The Sonda coal-field comprises a nearly flat or lenticular, north-south trending anticline, occurring in thick lenses of siltstone and mudstone of the Bara Formation, Coal occurs relatively more persistently at the three main horizons [3] which have been named as Dadhuri, Sonda and Jherruck coal zones (Fig. 2). In between these coal zones four other (but minor and less persistent) zones, referred to as "Upper Strays", Inayatabad, "W" and "Lower Strays", have been identified [4]. These minor coal zones consist of one or more recognisable coal beds separated by relatively persistant parting of sandstone or shale or both. More than 29 coal seams of varying thickness and continuity have been encountered in various test holes. The Sonda coal ranks from lignite 'A' to sub-bituminous C [4].These minor coal zones consist of one or more recognizable coal beds separated by relatively persistent coal bed, though at places it splits into thinner seams and become discontinuous or changes to carbonaceous shale. Near Jherruck, the cumulative thickness of coal reaches 9m, and the Sonda coal seam attains a thickness of 6.2m. The floor rocks are under clays that are light bluish grey, compact, fissile at places and interbedded with brownish black, laminated carbonaceous claystone [5].

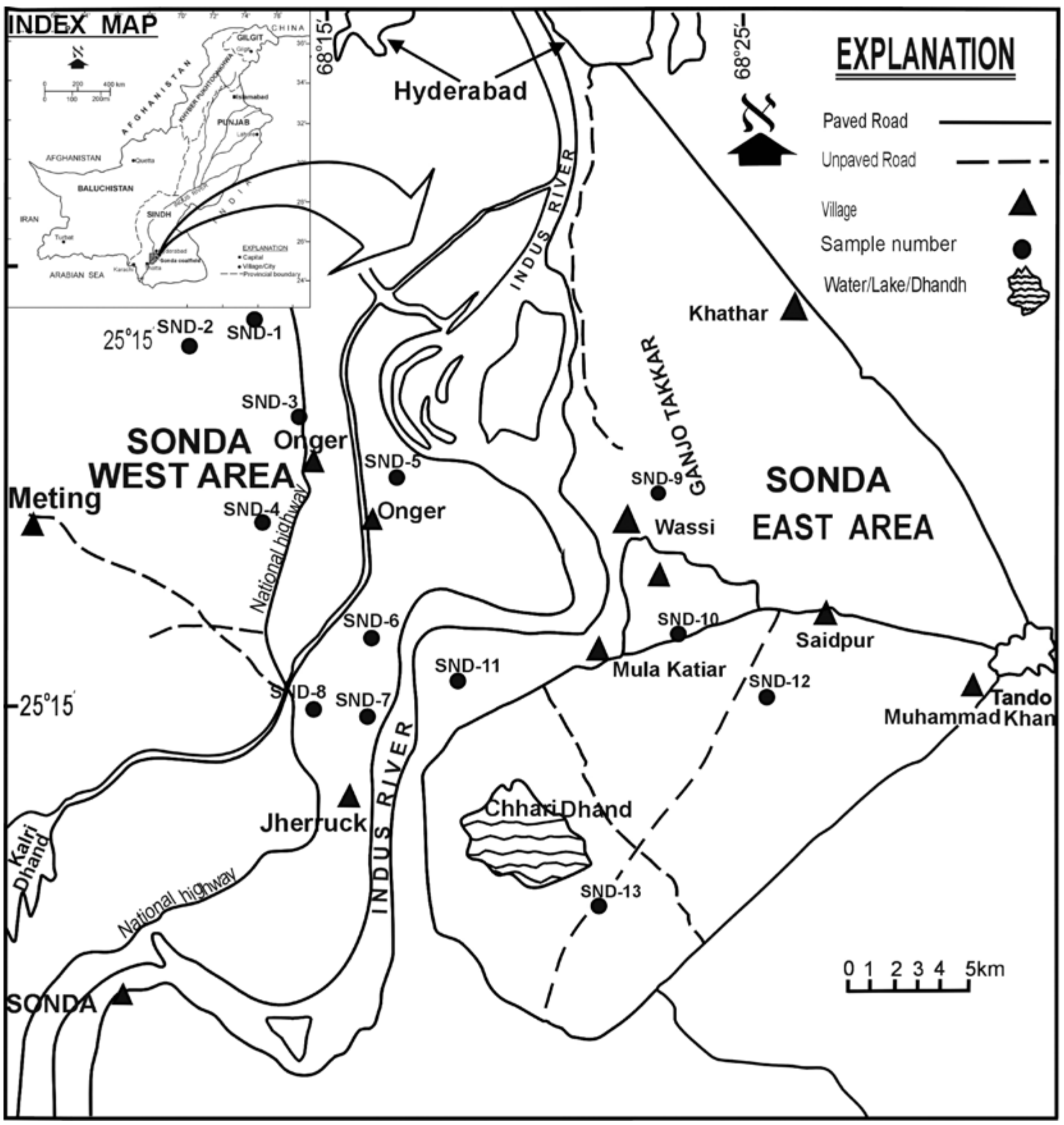

FIG. 1. MAP SHOWING LOCATION OF SONDA COAL FIELD AND THE SAMPLING LOCATION

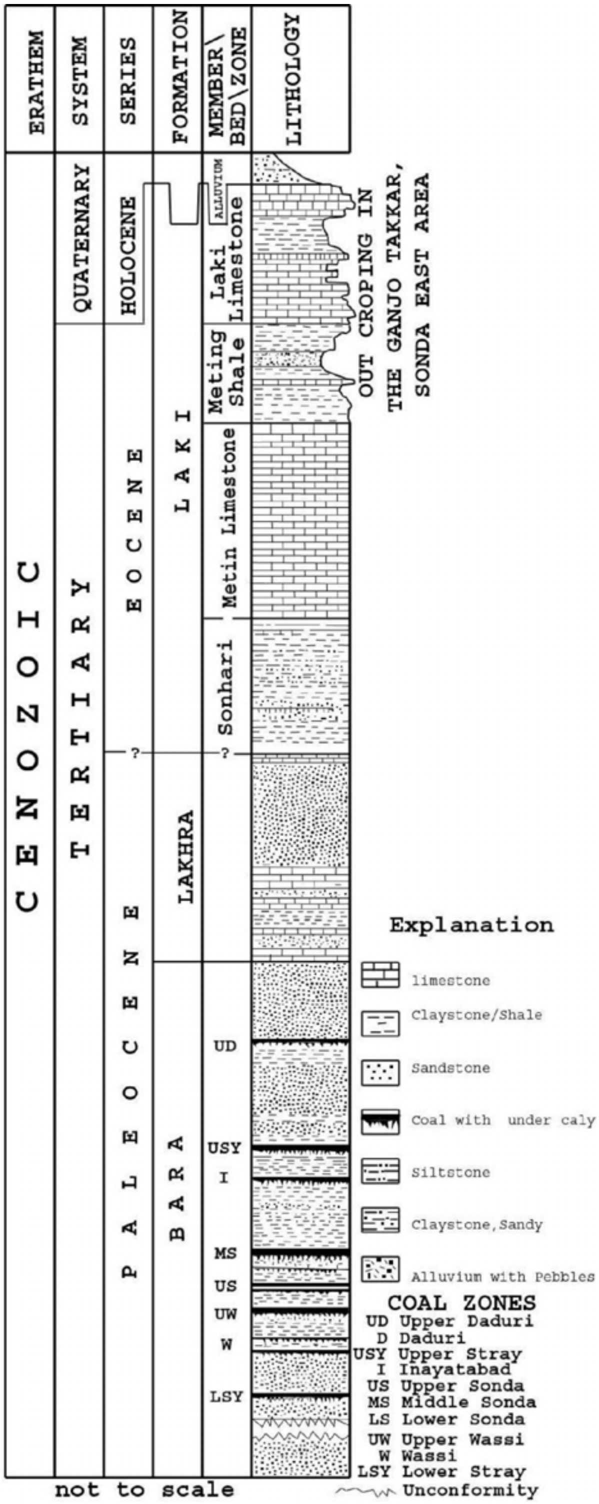

FIG. 2. STRATIGRAPHIC SECTION OF SONDA COALFIELD (MODIFIED AND REDRAWN FROM THOMAS AND KHAN [8]

Sonda coal was deposited on a lower deltaic plain. Filipo, et. al. [6] suggests marriginal marine conditions for Bara Formation. Kazmi, et. al. [7] have shown that the coal was deposited in near shore paleo-chnannels and swamps. Coal petrology data (high ulminite, textinite and well preserved homodetrinite) confirm Kazmi's view [7]. Based on subsurface data from bore holes the coal resources of Sonda have been estimated at about 7300 mt. Its heating value ranges from 3600-5700 KCl/kg [8].

Coal is generally brownish-black to black, brittle, pyritic, dull, laminated with uneven to conchoidal fractures. This zone consists of sandstone (Silica 85%), siltstone, sandy claystone and interbedded claystone. Generally roof rock is siltstone of dark grey to olive grey, hard, compact, sandy, with clayey laminations and pyritic.

3. MATERIALS AND METHOD

Thirteen core samples were collected from the field core library of Geological Survey of Pakistan, and pulverized to 75µ (200 mesh size). Coal samples were air dried as ASTM D-2013 methods, small and homogenized portion of individual sample of coal were air dried using an oven by setting temperature 10-15^{o}C above room temperature with a maximum oven temperature of 40^{o}C. This method removes most of the surface moisture in coal, while as per ASTM method; temperature of 107-110^{o}C is set for removing the inherent moisture for approximately one hour.

For the geochemical analysis, samples were prepared by acid digestion method in concentrated HF, HNO_3 and HCl as described by Jeffery and Hutchinson [9]. For the elemental analysis (i.e. Pb, Zn, Cu, Ni, Cr, Co, Cd, As, Fe, Mn) samples was run by Perkin Elmer-600 graphite furnace Atomic Absorption Spectrophotometer.

Moreover, S4-PIONEER X-Ray fluorescence was used for the determination of arsenic (As), antimony (Sb) and uranium (U) [10-11]. The method of Klug and Alexander [12] was followed for the determination of mineral constituents in the studied coal. For this purpose Rigaku x-ray diffractometer, with Ni filtered Cu K radiation and scintillation detector was used. The XRD patterns were recorded over 2 interval of 2-34^{o}, with a step size 0.5 and 0.1 respectively. For the interpretation of XRD patterns, Hanawalt method of quantitative analysis was referred [13].

4. RESULTS AND DISCUSSION

The range, AM (Arithmetic Mean) and GM values along with calculated EF (Enrichment Factor) of total seventeen analyzed trace elements including Al, As, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, U and Zn for Sonda coal are listed in Table 1. The ranges, arithmetic mean and geometric mean values for analyzed elements of the Sonda coalfield are compared with the US, China and World coal are also shown in Table 2.

Table 1 reveals that among the studied coal samples, the AM value of Zn is the highest i.e. 44 ppm and this may supports the presence of sphalerite in the study coal as is reported in Canadian coals [14]. Ni is the next and results in Table 1 shows that the Sonda coal is enriched with the mean value of 34 ppm (AM). In various coals, Ni is generally present in the inorganic and organic part of the mineral matter [15]. Pb value in studied coal samples vary from 8-28 ppm (AM=17ppm). Table 1 shows that in most of the studied samples Pb is more than 11 ppm. Lead in coal primarily occurs as associated sulphide mineral phase. Cu in coal is usually considered to be associated with chalcopyrite [16]. It is also associated with different sulphide phases [17].

The present results from Sonda coal (Table 1) reveal that Cu concentration ranges from 6-32 ppm (AM=14 ppm).

TABLE 1. RANGE, ARITHMETIC MEAN, GEOMETRIC MEAN, STANDARD DEVIATION AND ENRICHMENT FACTOR OF ELEMENTS IN SONDA COAL -SINDH-PAKISTAN, VALUES ARE IN PPM EXCEPT AS INDICATED (%)

Element	Sonda Pakistan Coal					
	Range	Arithmetic Mean (%)	Geometric Mean (%)	Standard Deviation (%)	ClarkeValue (%)	Enrichment Factor
Al	1-12	4.9	3.1	4.9	8.23	1.00
Ca	0.0085-0.0512	0.023	0.017668	0.0123	4.15	0.08
Mg	0.0028-0.0068	0.0043	0.004164	0.00137	2.33	0.28
K	0.0218-0.034	0.0289	0.028661	0.0041	2.09	0.23
Na	0.037-0.0438	0.0414	0.041329	0.0020	2.36	0.01
Fe	0.0891-0.8451	0.5867	0.5867	0.5216	5.63	0.18
(ppm)						
As	0.7-2.3	1.45	1.38	0.47	1.8	1.35
Cd	0.1-0.4	0.19	0.16	0.12	0.2	1.50
Co	2-4	3	2.38	0.70	25	0.20
Cr	7-18	11	10.25	3.87	100	0.81
Cu	6-32	14	12.18	9.12	55	0.43
Mn	0.14-0.42	0.27	0.25	0.09	950	0.00
Ni	14-46	34	32.64	8.75	75	0.76
Pb	8-28	17	16.2	6.55	12.5	2.20
Sb	0.8-2.1	1.37	1.29	0.47	0.2	11.50
U	2.8-4.1	3.36	3.32	0.53	2.7	2.55
Zn	9-75	44	34.84	25.64	70	1.06

The concentration of Cr in the studied samples varies from 7-18 ppm (AM =11 ppm). Chromium in coal occurs in various forms such as the illite (clay mineral) and as accessory mineral associated with the organic matter [18] (Fig. 2). Uranium content in the studied coal samples ranges from 2.8-4.1 ppm (AM =3.36 ppm). Various sources have been postulated for the presence of uranium in the coal, such as the syngentic, diagenetic and epigenetic [19]. In the studied coal, it is probable that the uranium may be syngenetic or diagenetic rather than epigenetic.

The mean (AM) value of Co in studied coal samples is 3 ppm (Table 1). It has been suggested that the presence of Co in coal is due to the sulphide minerals. The mean values (AM) of As and Sb in studied coal are 1.45 and 1.37 ppm. In coal arsenic is present as an accessory sulphide in solid solution. Due to the process of pyritization, the grains/crystals of stabinite (Sb_2S_3) are resulted [20]. The arithmetic mean values of Cd, and Mn in studied coal are found in lowest concentration (i.e. 0.19, and 0.27ppm). Sphalerite is considered to accommodate the Cd along with Zn in the solid solution as described by [21]. Manganese occurs with organic and inorganic matter, particularly in siderite and calcite minerals (Fig. 3). Fe content in studied coal ranges from 0.089-0.8451% (891-8451 ppm). The mean (AM) value of Fe in Sonda coal is 0.5867%. It is suggested that the higher concentration of Fe has been consumed by the pyrite, which is associated as a minor inorganic mineral phase in the studied coal samples.

TABLE 2. CONCENTRATION OF HEAVY AND TRACE ELEMENTS IN SONDA-SINDH-PAKISTAN COAL, USA , CHINESE AND WORLD COALS, VALUES ARE IN PPM EXCEPT AS INDICATED (%)

Element	Sonda Pakistan Coal				US Coal[a]			Chinese Coal[b]			World Coal[c]	
	Range	Arithmetic Mean	Geometric Mean	Standard Deviation	Range Maximum	Arithmetic Mean	Geometric Mean	Range	Arithmetic Mean	Geometric Mean	Range	Arithmetic Mean
(%)												
Al	1-12	4.9	3.1	4.9	10.6	1.5	1.1	0.10-7.11	1.941	1.377	-	1.0
Ca	0.0085-0.0512	0.023	0.017668	0.0123	72	0.46	0.23	0.17-4.82	1.306	0.851	-	1.0
Mg	0.0028-0.0068	0.0043	0.004164	0.00137	1.5	0.11	0.07	0.05-3.97	0.421	0.261	-	0.02
K	0.0218-0.034	0.0289	0.028661	0.0041	2.0	0.18	0.10	0.01-2.89	0.330	0.214	-	0.01
Na	0.037-0.0438	0.0414	0.041329	0.0020	1.4	0.08	0.04	0.002-0.46	0.081	0.047	-	0.02
Fe	0.0891-0.8451	0.5867	0.5867	0.5216	24	1.3	0.75	0.01-2.89	1.211	0.916	-	1.0
(ppm)												
As	0.7-2.3	1.45	1.38	0.47	2200	24	6.5	0.21-3.2%	276.61	4.26	0.5-80	5
Cd	0.1-0.4	0.19	0.16	0.12	170	0.47	0.02	0.04-1.2	0.46	0.32	0.1-3	0.3
Co	2-4	3	2.38	0.70	500	6.1	3.7	0.03-39.6	6.72	4.75	0.5-30	5
Cr	7-18	11	10.25	3.87	250	15	10	0.46-942.7	34.87	17.97	0.5-60	10
Cu	6-32	14	12.18	9.12	280	16	12	4.28-133.7	28.22	20.50	0.5-50	15
Mn	0.14-0.42	0.27	0.25	0.09	2500	43	19	6.02-8540	271.22	49.45	5-300	50
Ni	14-46	34	32.64	8.75	340	14	9.0	1.10 - 255	22.62	15.22	0.5-50	15
Pb	8-28	17	16.2	6.55	1900	11	5.0	5.28-69.7	24.77	19.69	2-80	25
Sb	0.8-2.1	1.37	1.29	0.47	35	1.2	0.61	0.05-120.0	2.56	0.58	0.05-10	3
U	2.8-4.1	3.36	3.32	0.53	13	2.1	1.1	0.16-199.3	7.52	2.71	0.5-10	3
Zn	9-75	44	34.84	25.64	19000	53	13	0.56-193	43.24	28.90	5-300	50
a=26, b=27, c=2												

Among the light elements such as the Al, Ca, Mg, Na, and K; the Al concentration varies from 1-12% (AM=4.9%). The higher percentage of aluminum in various coals is generally associated due to presence of different clay minerals as is reported by [22] and same is found within the studied coals. The occurrence of sodium in various coals is attributed to the carbonate and silicate mineral constituents [23]. The Na content in studied coal ranges from 0.037-0.0438% and the mean (AM) value is 0.414%. Along with Aluminum, the Potassium and Magnesium in different coals are also attributed to the presence of clay and carbonate minerals e. g. dolomite (Fig. 3) as reported by [24] Calcium content in Sonda coal ranges from 0.0085-0.0512%. Ca in coal is present as carboxyl-bound calcium or it is distributed among calcite, gypsum and illite [25]. It has been suggested [24,26] K and Mg concentration in studied coal varies from 0.028-0.034%, 0.0028 -0.0068% respectively as the XRD peaks/patterns of the studied coal (Fig. 3).

Comparing minerals in Sonda coal with USA, Chinese and World coals, it is found that in American coal (Upper

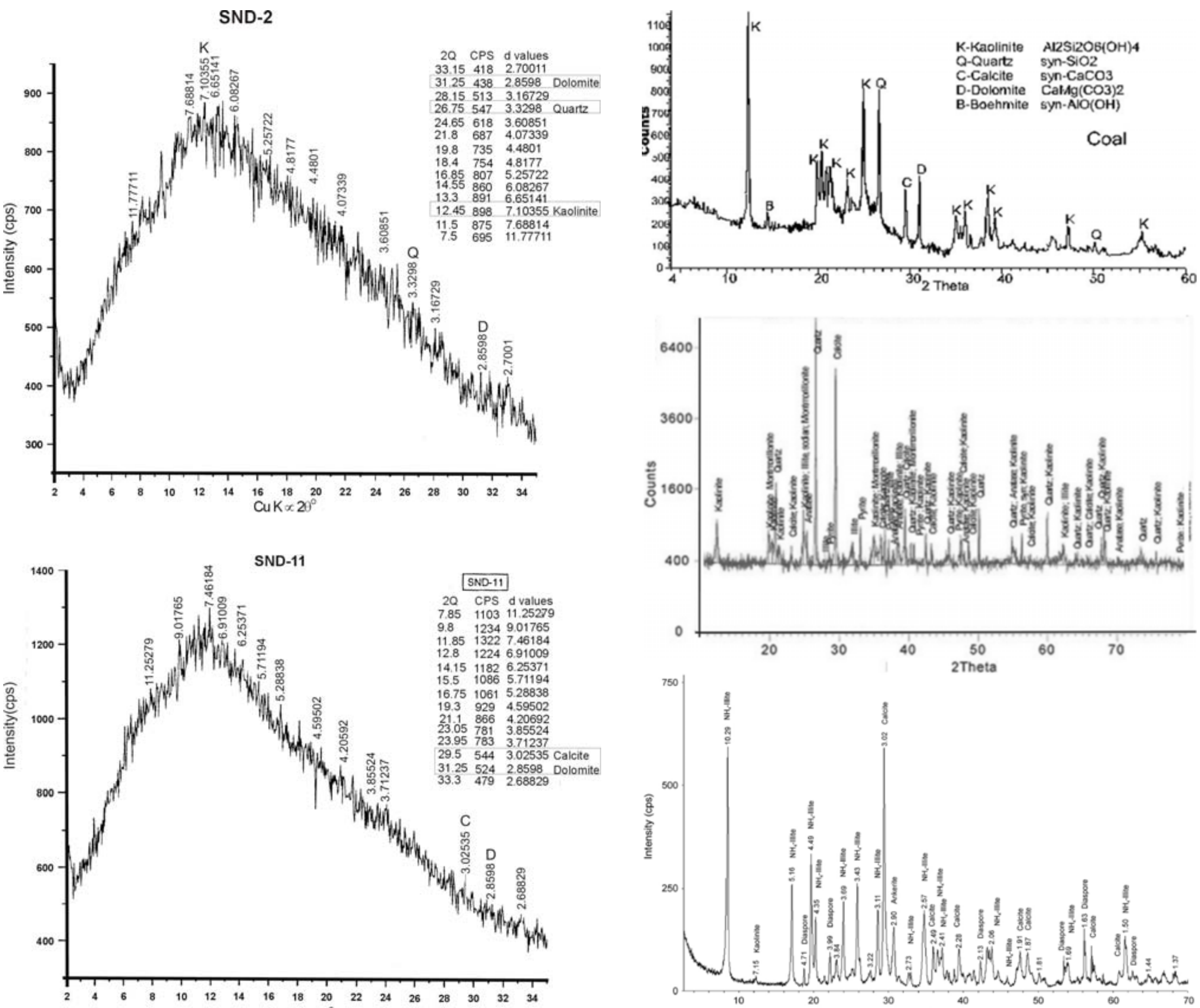

FIG. 3. XRD PATTERNS OF SONDA COAL [24-25]

Fort, Wyodk, Illinois, Pitsburg, Pocahonates, Blind Canyon, Lewiston-Stockton, Beulah-Zap, Lower Wilcox, Dietz and Buck Mountains), Quartz, Calcite, Kaolinite/ illite are found as major minerals. Pyrite, Kaolinite, calcite, Kaolite, bassanite and calcite are found as minor minerals while Illite, Calcite, Kaolinite and Albite are found as trace minerals. In coal from Chinese coalfields Quartz, calcite and Kaolinite are found as major minerals, while calcite, Kaolinite and Bo are found in trace. In World coals Quartz, Kaolinite and Illite is found as major minerals and Pyrite, Calcite and Dolomite is found as minor minerals.

The AM concentrations for Sonda coals are compared with US coal values and it shows that except Ni, Pb, Sb, and U concentrations; the elements like As, Cd, Co, Cr, Cu, Mn, and Zn in Sonda coals are less than US coals (Table 2). In addition, the arithmetic mean concentrations for Sonda coals are also compared with Chinese coals. Table 2 shows that the arithmetic mean concentrations of Ni and Zn are higher than Chinese coal values, while the (AM) concentrations for Sonda coals shows that except Ni and U, all analyzed elements i.e. As, Cd, Co, Cr, Cu, Mn, Pb, Sb and Zn in world coals have higher arithmetic mean values.

The AM concentrations of Al, Fe and trace elements (Ca, Mg, Na and K) are also compared with US, Chinese and world coals. The comparison shows that except Al in Sonda coals, rest of the coal trace elements have lowest concentrations in Sonda as compared to the US, Chinese and world arithmetic mean for coals.

The comparison of geometric mean concentrations for Sonda coal with US coals shows that geometric mean values of Cr, Cu, Ni, Pb, Sb, U, and Zn for Sonda coal are higher than US geometric mean concentrations [15,27]. The comparison of GM values of studied coal with Chinese coal shows that among all the analyzed elements i.e. As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, U and Zn; the GM concentration of Ni only in Sonda coals are higher against Chinese geometric values [16]. For Sonda coals the geometric concentrations of Fe, Al and trace elements i.e. Ca, Mg, K, an d Na; are also compared with US and Chinese coals and the Table 2 shows that geometric mean concentrations for Al in Sonda coal is higher than these countries. While among the trace elements like Ca, Mg, Na and K GM concentrations for Ca, Mg, Na and K in Sonda coals are less than the US and Chinese coal concentrations.

5. ENRICHMENT AND DEPLETION

The AM values are calculated for the Al, As, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb and Zn and the resulting mean values are divided by the Clarke values to get the EF (the term 'Clarke' is defined as the average of an element in the earth's crust; described by [28]. This EF is the ratio of element content in coal to the Clarke value. For calculating this ratio, the Gordon and Zoller formula [29] was applied. Aluminum is usually chosen normalization element, as source is primarily earth's crust and the concentrations do not vary greatly around the world. A comparison of the concentration of an element in coal with the Clarke value for that element provides an approximation as to the amount by which the element is enriched or depleted by the total coal forming processes. A mean value is calculated for elements under study and resulting mean were divided by their Clarke Value [30].

The resulting number is called Enrichment Factor, this was calculated as:

$$EFx = \frac{\left(\frac{C_x}{C_{al}}\right)A_{icoal}}{\left(\frac{C_x}{C_{Al}}\right)crust} \tag{1}$$

The elements in coal are considered as enriched if its content is six times its clarke value and depleted if it is 1/6 (or less) of the Clarke. Based on this criteria no element is enriched or we can say Al, Ca, Mg, K, Na, Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, U and Zn are depleted in the studied coal samples of Sonda (Table 1).

6. CONCLUSION

The present study shows that the AM value of Zn, Ni and Pb are in higher concentration in the studied coal samples. The comparison of GM values of studied coal with US and Chinese coal values shows that among all the analyzed elements, only Ni in Sonda coals is high against Chinese geometric values. Geometric mean concentrations for Al in Sonda coal is higher than US and Chinese coal values. On the basis of Clarke value, elements such as the Al, Ca, Mg, K, Na, Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, U and Zn are depleted in the studied coal samples of Sonda and no enrichment is found. The XRD investigation shows that Sonda coal contains Calcite, Dolomite, Kaolinite and Quartz minerals

ACKNOWLEDGEMENTS

The authors are highly thankful to the kind administration of National Centre of Excellence in Geology, University of Peshawar, Peshawar, Pakistan, to avail the laboratory facilities of the centre. Authors are also highly acknowledged to Prof. Dr. Muhammad Tahir Shah, for personally reviewing this paper before submission. Moreover, Dr. Islam, Institute of Nuclear Science & Technology, Atomic Energy Research Establishment, Dhaka, Bangladesh, is also acknowledged for guiding to calculate the enrichment and depletion factor.

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