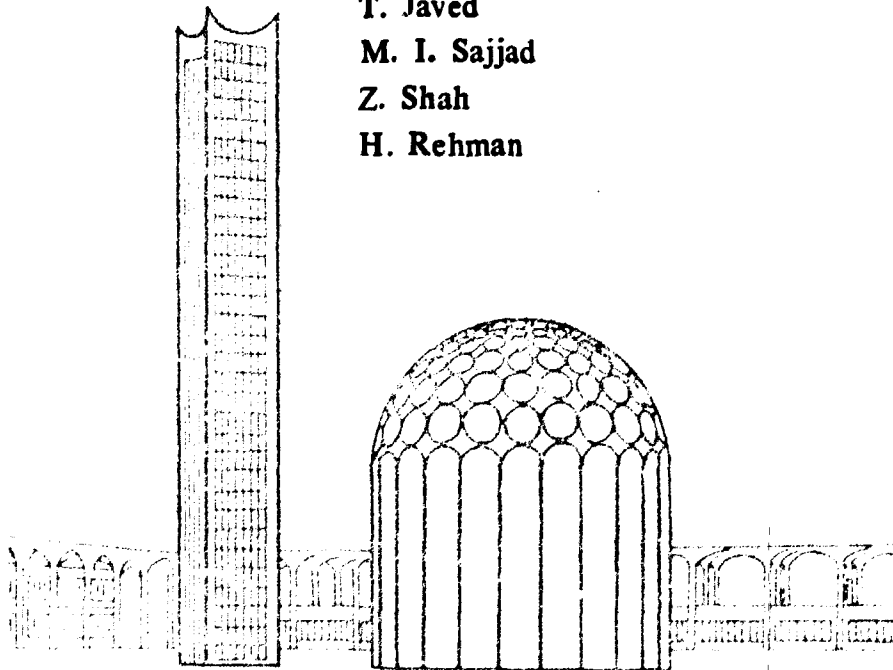


ISOTOPIC AND CHEMICAL CHARACTERIZATION OF COAL IN PAKISTAN

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ENVIRONMENTAL RESEARCH GROUP
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*Presented at the First South Asia Geological
Congress, Islamabad, Pakistan: February 23 - 27,
1992, Organized by the Ministry of Petroleum
and Natural Resources, Government of Pakistan.
GEOSAS-I Secretariat, Hydrocarbon Development
Institute of Pakistan, P.O. Box 1308, Islamabad,
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ABSTRACT

Stable carbon isotope ratios ($\delta^{13}\text{C}$ ‰ PDB) and toxic/trace element concentration levels are determined for Tertiary coal samples collected from seven coal fields in Pakistan. No systematic isotope effects are found in the process of coalification from peat to Tertiary lignites and sub-bituminous coal. Similarly, no age effects are observed during the Tertiary regime. The observed variations in the carbon isotopic composition of coal obtained from "Sharigh coalfield" and the "Sor-Range/Degari coalfield" in Baluchistan are attributed to the depositional environments. More sampling / stable carbon isotope analyses are required to validate these observations. Significant concentrations of toxic elements such as S, Cr, Cd and Pb in Makarwal coal may pose environmental and engineering/operational problems for thermal power plants.

* Published in the abstracts handout (page-32) of the First South Asia Geological Congress, Islamabad, Pakistan: February 23 - 27, 1992 (Eds. M. A. Khan, M. A. Sheikh, S. M. Raza), Organized by the Ministry of Petroleum and Natural Resources, Government of Pakistan. GEOSAS-I Secretariat, Hydrocarbon Development Institute of Pakistan, P.O. Box 1308, Islamabad, Pakistan.

1. INTRODUCTION:

The rapid growth in population (3.1 % per year) has led to a considerable rise in the demand of energy consumption for the development of industrial and commercial sectors in Pakistan. At present Pakistan is exploiting five sources of commercial energy namely: hydro, nuclear, oil, gas and coal. The former four sources do not have enough potential to cope with the country's increasing demand of energy. The only potential fossil fuel available in Pakistan which can practically meet this requirement is coal [Butt, 1980]. There has been a growing interest in the use of coal for energy production. The air pollution problems attending increased coal consumption have led much more stringent measures to control combustion process and the quality of the starting material. As far as coal is concerned, Pakistan has large reserves of coal out of which proven reserves are nearly 748 million metric tons [Talpur et.al., 1987]. The estimated reserves are about 1,178 million metric tons. Recently, some coal power plants are being installed along the coastal areas of Karachi.

The vast deposits of coal in Pakistan are classified as highly volatile to sub-bituminous with high ash and sulfur contents. The coal deposits of Pakistan differ from most of the major coalfields of the world in having been formed in an environment dominated by lacustrine - estuarine to marine conditions. They are relatively younger in age and fall into the poor grade - low rank category which has restricted their use for industrial purposes. Ahmed et. al. [1986] has emphasized the need

for obtaining more reliable data on the geology of coalfields in terms of petrographic studies as well as standardization of procedures for the collection, storage and versatile analysis of coal available in Pakistan in order to boost its utilization. In this paper, the carbon isotope technique is described as a fast method to study: a) relationship between isotope effects which may occur during the process of coalification and the maturity attained by Tertiary coals in Pakistan, and b) the possible existence of biotope and age effects during the Tertiary regime. Some toxic/trace elements of environmental concern are also determined and discussed for two coal samples collected from Makarwal coalfield.

2. PRESENT INVESTIGATIONS:

2.1. Coal Sampling and Preservation:

Fifty four coal samples ranging in age from Early Eocene to Lower Paleocene were obtained from seven coalfields namely: Makarwal, Katha-Pale, Cherat, Sharigh, Sor-range, Degari, and Lakhra through Pakistan Mineral Development Corporation and Geological Survey of Pakistan (Fig. -1). These were collected as "channel samples" or "run of mine" (ROM) samples from the top, middle and bottom of some coal seams. Coal samples were broken into small pieces using mortar and pestal and were crushed in a Wiley grinding mill. Powdered samples were sieved through 60 mesh size. The sieved samples were dried at 50°C and preserved in plastic bottles placed in a desiccator. Three SARM (South

COAL FIELDS

- ① LAKRA
- ② METING JHIMPIR
- ③ SONDA JHERUCK
- ④ MACH
- ⑤ SOR RANGE-DEGARI
- ⑥ KHOST SHARIGH HARNAI
- ⑦ DUKI CHAMALANG
- ⑧ MAKERWAL
- ⑨ SALT RANGE

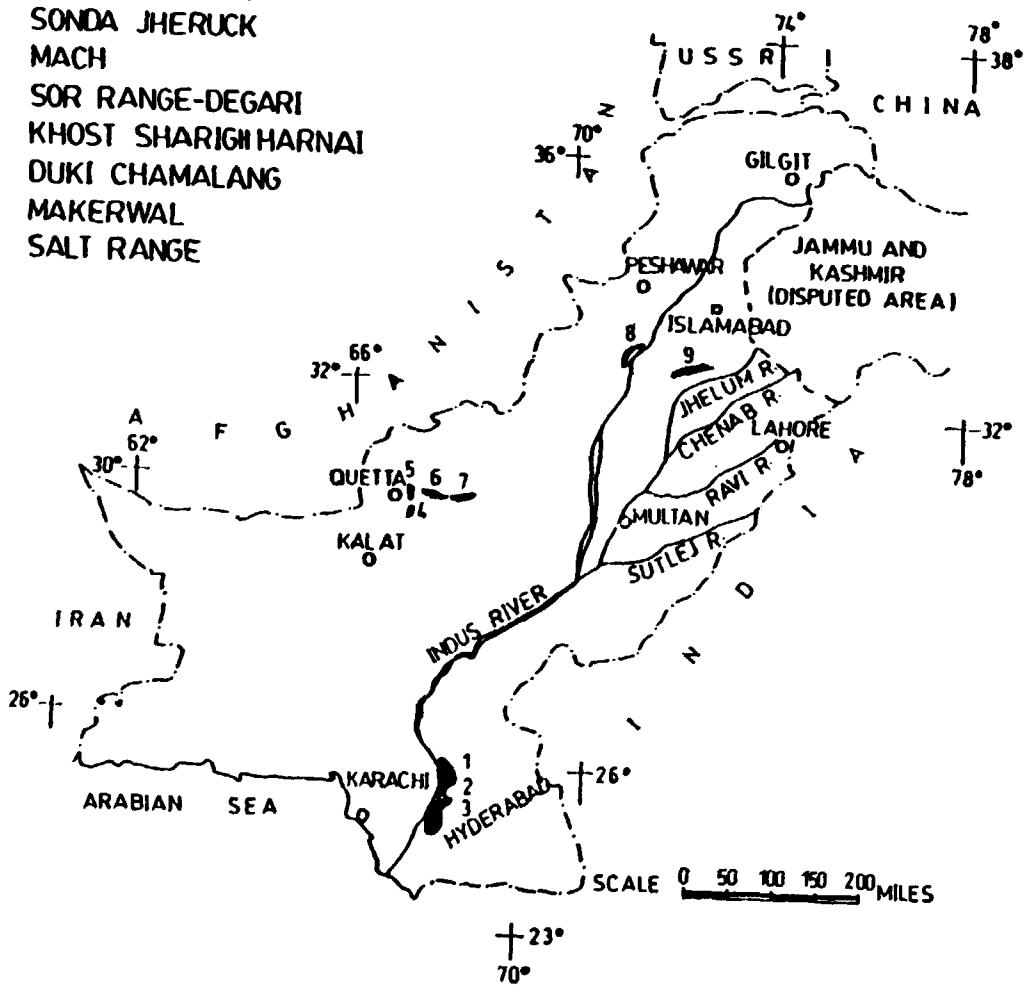


Fig. 1: Location of various coalfields in Pakistan.

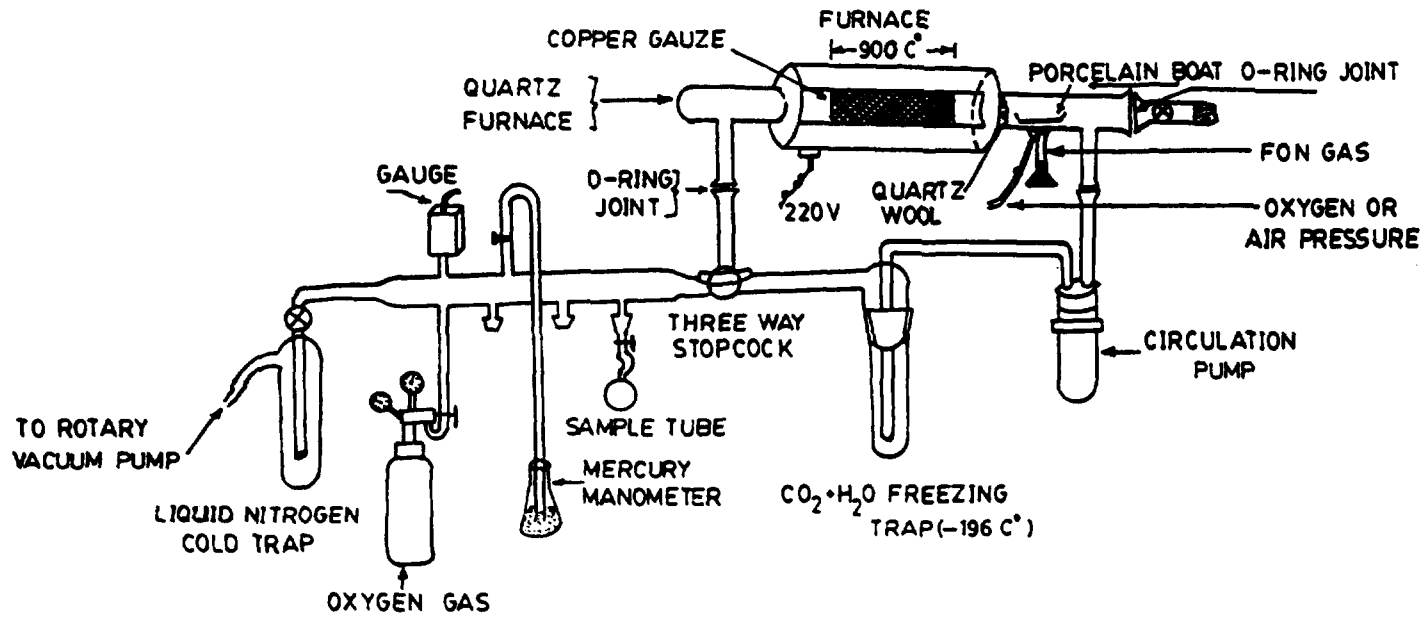
African Reference Materials) coal standards namely SARM-18, SARM-19 and SARM-20 (particle size: <106 micron) were purchased from South African Bureau of Standards, Pretoria, Republic of South Africa.

2.2. Experimental:

A. Stable Carbon Isotope Analysis:

For stable carbon isotope analysis on mass spectrometer, the organically bound carbon in coal was converted to CO₂ using the sample preparation system as shown in Fig. 2. About 15 - 20 mg moisture-free powdered coal sample was placed in a porcelain boat (8cm x 1cm x 0.8cm) and introduced into the quartz portion of the vacuum system. After preliminary evacuation (10⁻² torr), high purity oxygen was filled in the combustion part of the line at pressure slightly less than one atmosphere. The sample boat was externally heated with a gas burner (≈ 600 °C). The evolved CO/CO₂ were then circulated in the line with the help of a magnetically driven circulation pump. During this circulation, CO₂ gas and moisture was condensed in a trap held at liquid nitrogen temperature (-196°C). The CO gas was converted to CO₂ while passing over the heated copper gauze (940°C) in the presence of oxygen. After 5 minutes of circulation, all CO was converted to CO₂ and collected totally in the CO₂ trap. The temperature of this trap was then raised to -80°C with the help of liquid nitrogen-freon mixture in order to transfer the CO₂ in a suitable sample collector for mass spectrometric analysis. The

Fig. 2: CO₂ gas sample preparation system from coal.



stable carbon isotope data is expressed as $\delta \text{ ‰}$ (delta per mil) values relative to the international carbonate standard PDB. The reproducibility of $\delta^{13}\text{C}$ measurements was better than 0.1 ‰ for working standard.

B. Chemical Analysis:

Standards: The coal standard reference materials namely SARM-18, 19 and 20 were heated at 50 °C till a constant mass was obtained. Each standard (\approx 5g) was pelletized in a stainless steel mould of 35mm diameter at 30 kN for 20 seconds, using a Press Herzog Model HTP 40 (FRG).

Samples: Two samples obtained from the Makarwal coalfield were baked and pelletized as per procedure reported for standard. Minor difference remained in the size fraction of the sample and standard, the later containing much smaller particle size.

XRFS Procedure: The measurements were carried out in vacuum using a wavelength dispersive X-ray Fluorescence Quantometer model 8420, Applied Research Laboratories, Switzerland. The standards and samples were bombarded with primary X-rays from Rhodium anode X-ray tube operated at 50mA and 50kV. Samples were rotated during XRFS measurements to avoid any inhomogeneities present in the sample. The characteristic $K_{\alpha 1,2}$ lines except $L_{\alpha 1}$ line for Ba, Pb and U were measured for different intervals of time as given in Table-1. The intensities of the analyte lines were related to concentrations using calibration curves drawn with the help of SARM standards. Multivariable regression (MVR) analysis was carried out on the intensities and concentrations of standards.

TABLE -1: Operating conditions for XRF measurements using wavelength dispersive computerized XRF Quantometer-Model 8420⁺ (Applied Research Laboratories, Switzerland).

Element	Analyte line	Crystal	Detector	Counting time (s)
Al	K _a 1,2	PET*	FPC**	30
S	K _a 1,2	PET	FPC	30
K	K _a 1,2	PET	FPC	30
Ca	K _a 1,2	PET	FPC	30
Ti	K _a 1,2	LIF200	SC***	30
V	K _a 1,2	LIF200	FPC	40
Cr	K _a 1,2	LIF200	SC	50
Mn	K _a 1,2	LIF200	SC	40
Fe	K _a 1,2	LIF200	SC	20
Co	K _a 1,2	LIF200	SC	40
Ni	K _a 1,2	LIF200	SC	40
Cu	K _a 1,2	LIF200	SC	40
Zn	K _a 1,2	LIF200	SC	40
Cd	K _a 1,2	LIF200	SC	40
Ba	L _a 1	LIF200	SC	50
Pb	L _a 1	LIF200	SC	40
U	L _a 1	LIF200	SC	40

+ Rhodium X-Ray Tube (50 mA, 50 kV)

* PET = Pentaerythritol

** FPC = Flow proportional counter (10 % Methane + 90 % Argon)

*** SC = Scintillation counter

This MVR calculation provided mathematical algorithms to compute the base curve polynomials simultaneously. The first degree based polynomial coefficients (A_0 & A_1) were calculated by computer using multitask system (MTS) software programme.

The relationship: $C_i = A_0 + A_1 I_i$ was used to correlate concentration (C_i) with intensity (I_i) for obtaining calibration curves for all elements measured in this study. Three typical calibration curves thus obtained for example, for Al, Fe and Ba are shown in Figure-3. The calibration curves are linear over the entire concentration range. These calibration curves were then used to evaluate XRFs measurements on same standards treated as "test samples" and the two coal samples collected from Makarwal Collieries, Punjab. The analyses data of three coal standards run as test samples are listed in Table-2. The precision was expressed as one sigma value of replicate (three or five measurements). The accuracy was given in % deviation (\pm) as difference in measured and certified values expressed as percent of certified concentration.

3. RESULTS AND DISCUSSIONS:

3.1. Stable Carbon Isotope Characterization:

The stable carbon isotope composition of seven coalfields is shown in Figure-4. The $\delta^{13}\text{C}$ values fall in a very narrow range: -26.7 ‰ to -23.9 ‰ . Three of the seven coalfields namely, Katha-Pale, Lakhra and Cherat show a very consistent isotopic composition around $-24.9 \pm 0.2 \text{ ‰}$. The Makarwal and Sharigh coals have comparable carbon isotopic values and are 0.5 ‰

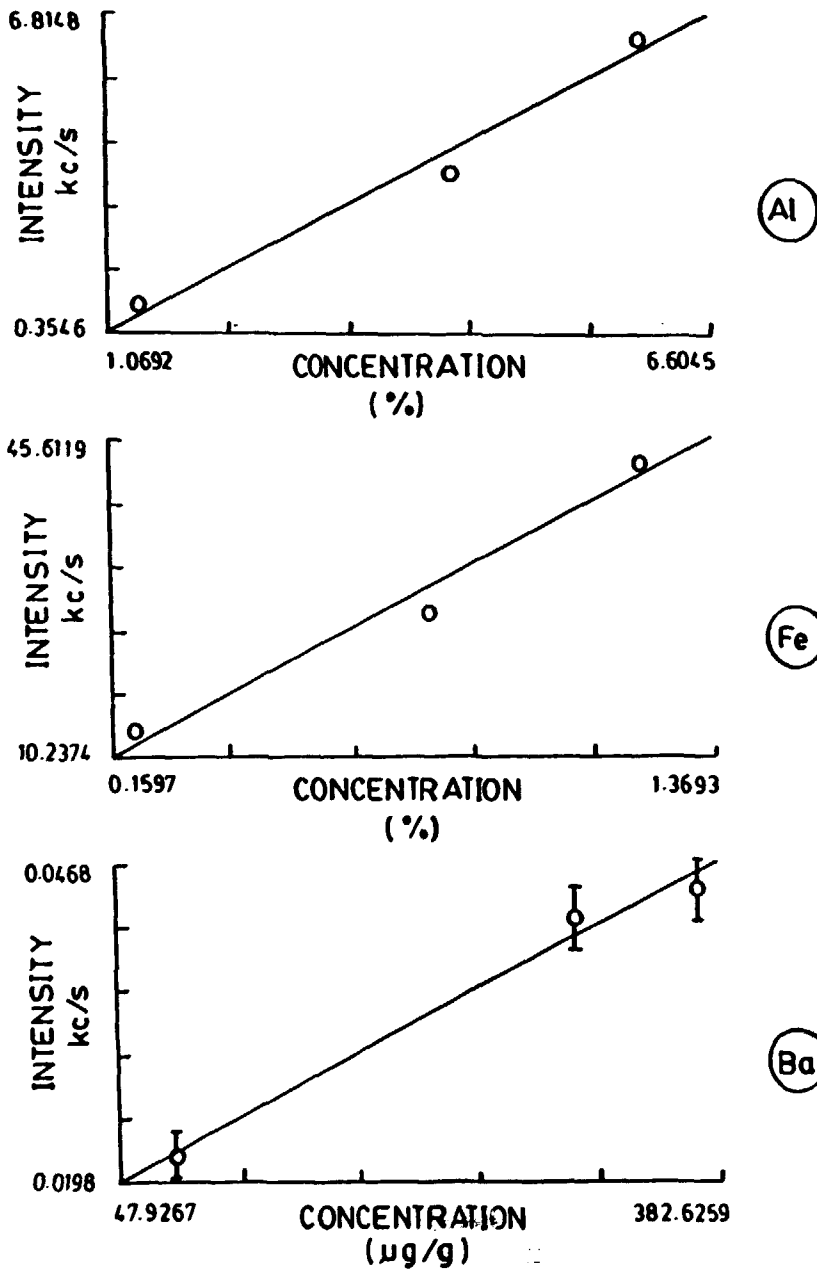
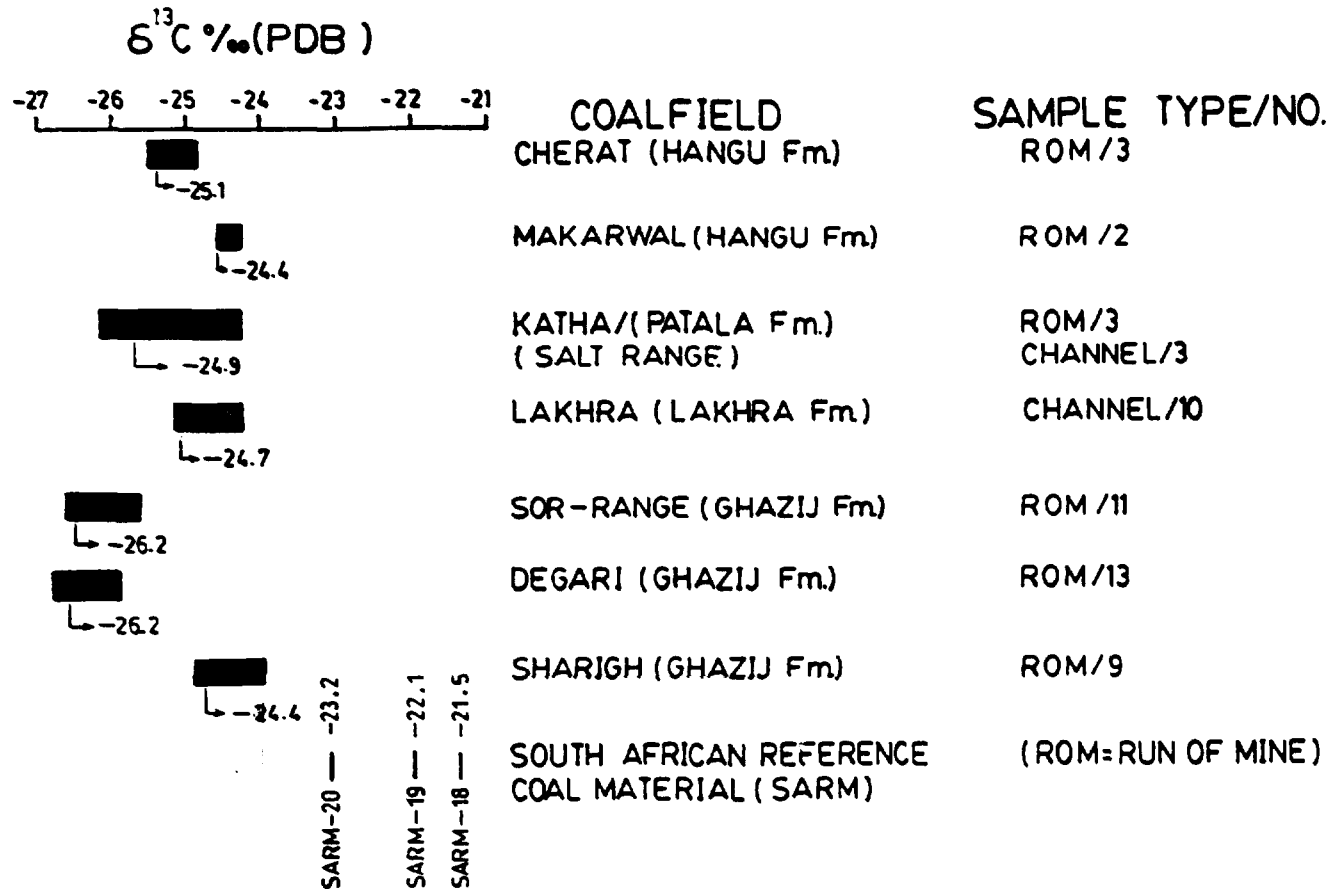


Fig. 3: Calibration curves for XRF analyses.

Fig. 4: Carbon isotope variations of various coalfields in Pakistan (Fm.= formation, ROM= run of mine, arrows indicate mean stable carbon isotope composition of respective coalfields).

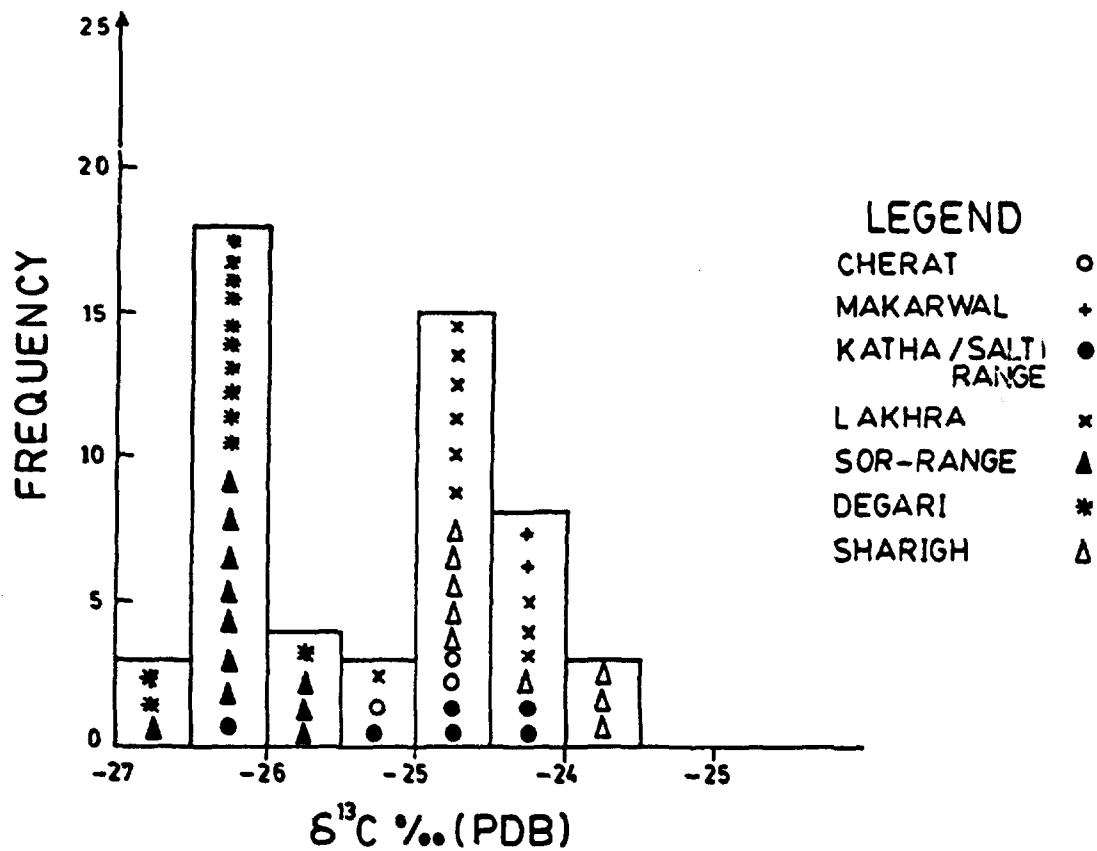


enriched in $\delta^{13}\text{C}$ than the Katha-Pale, Lakhra and Cherat coals. These values are in good agreement with those reported for Tertiary lignitic coals in Australia [Jeffery et.al., 1955]. Degari and Sor-Range coals have identical values (-26.2 ‰) and are depleted by about 1 to 1.5 ‰ than the rest of the coalfields.

Figure-5 shows the carbon isotope frequency histograms for seven coalfields. Notable is the fact that the carbon isotopic composition of all lignitic coals is comparable to that normally found for the starting material i.e. peat ($\delta^{13}\text{C} \approx -25 \text{ ‰}$). Coalification i.e. transition of peat (initial stage) through lignite (intermediate stage) to bituminous coal and anthracite, is activated by decomposition of plant debris through biochemical processes and later with increasing burial geochemical reactions. These reactions cause depletion in the C, H, O and N contents of the altering peat. These elements are given off in the form of water, CO_2 and CH_4 , higher hydrocarbons and nitrogen. Because hydrogen and oxygen that split off during this reaction are bonded to the carbon which is removed from the residual molecule through splitting of C - C bond, one might expect carbon isotope effects to occur during the process of coalification. However, these effects have been reported to be very small [Jeffery, et.al., 1955].

The observed variations in the stable carbon isotope composition of coal may then be discussed in view of the type of photosynthetic cycle for assimilation of environmental CO_2 in plants responsible for peat formation. For example, plants

Fig. 5: Carbon Isotope frequency histograms of coal samples.



following the Calvin or C₃ cycle of carbon fixation have a $\delta^{13}\text{C}$ variations around $-27 \pm 5 \text{ ‰}$. Those following the Hatch-Slack or C₄ cycle have variations around $-13 \pm 4 \text{ ‰}$. The CAM (Crassulacean Acid Metabolism) plants show a large spread around -17 ‰ . The terrestrial wood has variations around $-25 \pm 5 \text{ ‰}$. Thus, the observed range of $\delta^{13}\text{C}$ values between -23.9 ‰ to -26.7 ‰ (Fig. 5) indicate that Tertiary coals have been formed from burial of plants which mainly represent the Calvin Cycle of photosynthesis.

Significant carbon isotope difference is observed between Sharigh coals and the isotopically identical Degari and Sor-Range coals. The former is 1.8 ‰ enriched in $\delta^{13}\text{C}$ than the later two coalfields. All the three coalfields pertain to the Eocene age. The vegetation responsible for peat formation grew under deltaic to fluviatile conditions (Ahmed et. al., 1986). The isotopic differences in these coalfields which are widely separated may be explained from the existence of different plant-biotope or the depositional environments. Thus, the Sharigh coal may be expected to form from C₃ plants which were either isotopically heavier than the C₃ plants grown at Degari and Sor-Range fields at the time of peat formation. Another and rather more promising explanation for this difference may be the possibility that with similar plant biotope, the Degari/Sor-Range coal was formed in deltaic to fluviatile / terrestrial environments whereas the Sharigh coal was formed in marine / estuarine environments in which the plants assimilated marine bicarbonate ion or the CO₂ produced from hydrolysis of bicarbonate ion. A better

determination of spatial trends of $\delta^{13}\text{C}$ at these coalfields is required to validate the second hypothesis.

Figure- 6 shows a fairly constant distribution of carbon isotope composition on the geological time scale. This suggests that during the Tertiary regime, the carbon isotope composition of the carbon dioxide source of the plant material and that of the atmosphere did not occur. These observations are in agreement with those of Craig [1953] who found no time or spatial distribution in the analysis of a number of individual samples ranging through the upper Paleozoic and Tertiary.

3.2. Chemical Characterization:

Table-2 gives data of XRFs elemental analyses of three SARMS (reference coal materials) for elements namely Al, S, K, Ca, Ti and Fe at percent and for Cr, Co, Ni, Cu, Zn and Ba at $\mu\text{g/g}$ levels. In most cases, the precision is within $\pm 3\%$ except for light element Al in SARM-18 and 20, where precision is within $\pm >13\%$. Moreover, the accuracy is poorer for elements like S, K, Fe, Cr, Co, Ni, Cu and Zn whereas it is notably better than 6% for Ca, Ba and Ti. Nevertheless, except for Al, the standard deviation is less than 5% for all other elements for the three SARMS. This appears to be good enough for concentrations of the order of $\mu\text{g/g}$. The deviations from true or actual values are expected high at such small concentration levels. These high deviations may also be partly due to instrumental or matrix effects. Also higher standard deviations are expected for light elements like Al and S. Similar standard deviations are reported by other workers [Nadkarni, 1980].

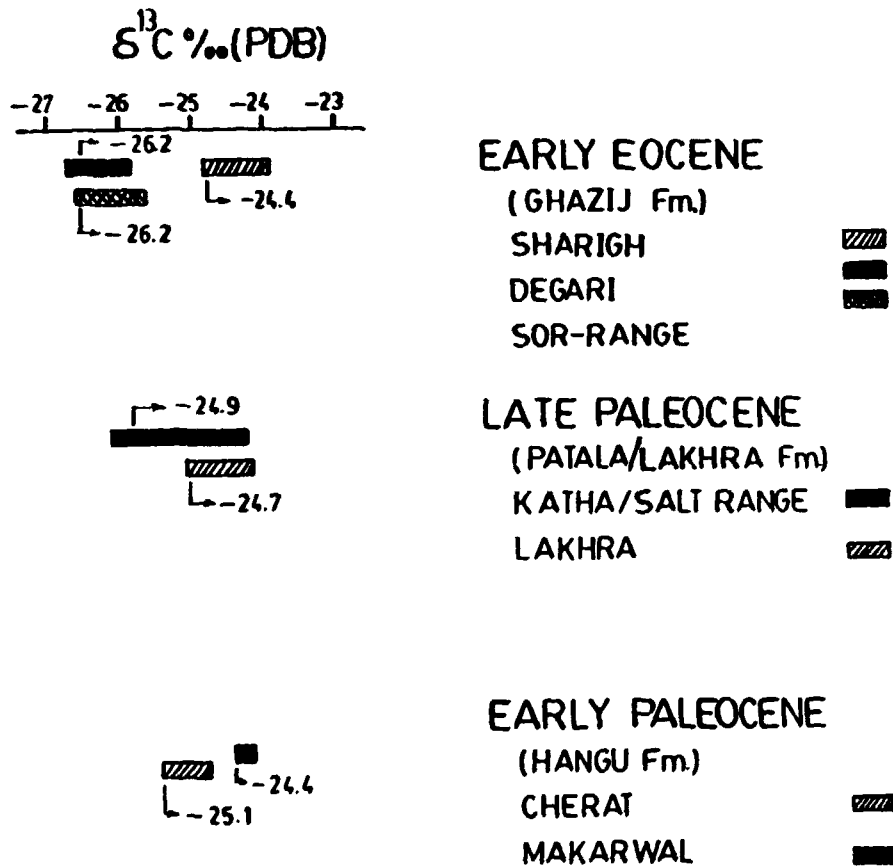


Fig. 6: Variations of carbon isotopic composition of coal in Tertiary period (Fm. = formation, arrows indicate mean stable carbon isotope composition of respective coalfields).

TABLE-2: XRF analyses of SARM (South African Reference Materials) coal samples

SARM 18 (Witbank)

Element	Certified value	Measured value	S.D. (±)	% Deviation
Al (%)	1.36	1.31 ± 0.18	13.7	- 3.68
S (%)	0.56	0.81 ± 0.01	1.23	+44.6
K (%)	0.12	0.165 ± 0.005	3.03	+29.1
Ca (%)	0.13	0.12 ± 0.003	2.5	- 7.69
Ti (%)	0.064	0.074 ± 0.001	1.35	+15.6
Fe (%)	0.203	0.265 ± 0.002	0.75	+30.5
Cr (µg/g)	16	13.8 ± 0.92	6.66	-13.7
Co (µg/g)	6.7	6.37 ± 0.002	0.03	- 4.92
Ni (µg/g)	10.8	16.7 ± 0.14	0.87	+54.6
Cu (µg/g)	5.9	11.76 ± 0.4	3.40	+99.3
Zn (µg/g)	5.5	9.92 ± 0.43	4.33	+80.3
Ba (µg/g)	78	65.9 ± 3.3	5.00	-15.5

SARM 19 (O.F.S)

Element	Certified value	Measured value	S.D. (±)	% Deviation
Al (%)	4.24	3.56 ± 0.03	0.84	-16.0
S (%)	1.49	1.00 ± 0.006	0.60	-32.9
K (%)	0.20	0.16 ± 0.008	5.0	-20.0
Ca (%)	0.99	1.01 ± 0.009	0.89	+ 2.02
Ti (%)	0.19	0.19 ± 0.002	1.05	0
Fe (%)	1.22	1.25 ± 0.006	0.48	+ 2.46
Cr (µg/g)	50	55.1 ± 1.5	2.72	+10.2
Co (µg/g)	5.6	7.0 ± 0.015	0.21	+25
Ni (µg/g)	16	17.8 ± 0.17	0.95	+11.2
Cu (µg/g)	13	10.63 ± 0.05	0.47	-18.2
Zn (µg/g)	12	8.5 ± 0.4	4.70	-29.2
Ba (µg/g)	304	22 ± 12	3.72	+ 5.92

(Table-2 continued)

SARM 20 (Sasolburg)

Element	Certified value	Measured value	S.D. (±)	% Deviation
Al (%)	5.96	5.34 ± 0.99	18.5	-10.4
S (%)	0.51	0.42 ± 0.002	0.48	-17.6
K (%)	0.116	0.121 ± 0.002	1.65	+ 4.31
Ca (%)	1.33	1.31 ± 0.006	0.46	- 1.5
Ti (%)	0.35	0.38 ± 0.002	0.52	+ 3.57
Fe (%)	0.82	0.7 ± 0.008	1.14	-14.6
Cr (µg/g)	67 *	65.3 ± 1.58	2.42	- 2.54
Co (µg/g)	8.3	7.22 ± 0.02	2.77	-13
Ni (µg/g)	25	17.0 ± 0.03	1.76	-32
Cu (µg/g)	18	15.22 ± 0.44	2.89	-15.4
Zn (µg/g)	17	14.24 ± 0.3	2.10	-16.2
Ba (µg/g)	372	362.6 ± 8.23	2.27	- 3.45

* Uncertified/ approximate property value

Two coal samples from Makarwal area were analyzed for same elements using SARM reference coal standards for calibration. The results of XRFS analyses are recorded in Table-3. The precision of the average of five measurements in most cases, like SARMS is within ± 3% except that higher values are obtained for Fe and Cr in sample-A and for S, Ca and Cu for sample-B but in no case it is > 8%. The accuracy of these measurements can be judged from the comparison of measured and certified values of SARMS reported in Table-2. V, Mn, Cd, Pb and U were analyzed in both the samples using single standard technique. The error is expected to be more as compared to those obtained using calibration curves drawn after intensity measurements of three standards. The amount of Al, S, K, V, Cr, Co, Ni, Cd, Ba and Pb in both the samples is of the same order of magnitude whereas Ca, Ti, Cu and U are more in

TABLE -3: XRFS elemental analyses[†] of two coal samples from Makarwal (Sample type: ROM, Lumshival cross-section)

Element	Sample - A		Sample - B	
	Measured value	± S.D.	Measured value	± S.D.
Al (%)	0.96(0.006)	0.62	1.31(0.034)	4.45
S (%)	7.41(0.23)	3.10	5.53(0.31)	5.60
K (%)	0.0682(0.0006)	0.88	0.113(0.002)	1.77
Ca (%)	0.114(0.003)	2.63	0.0137(0.001)	7.30
Ti (%)	0.89(0.012)	1.35	0.426(0.004)	0.95
Fe (%)	1.85(0.16)	8.65	3.92(0.006)	0.15
V (µg/g)*	<1		<1	
Cr (µg/g)	79.5(3.7)	4.65	96.0(4.45)	4.63
Mn (µg/g)*	8		23	
Co (µg/g)	6.65(0.19)	2.85	6.11(0.16)	2.62
Ni (µg/g)	18.4(0.06)	0.33	18.73(0.01)	0.05
Cu (µg/g)	23.24(0.2)	0.86	7.36(0.57)	7.74
Zn (µg/g)	<8		17.0(0.2)	1.17
Cd (µg/g)*	38		24	
Ba (µg/g)	<50		<50	
Pb (µg/g)*	18		20	
U (µg/g)*	9		<1	

One sigma value given in parentheses

* Measured against single standard.

† Average of five measurements.

Sample-A than in Sample-B. However, the concentrations of Fe, Mn, and Zn are higher in Sample-B. From environmental point of view, the percentage of ~~S~~ and 5 - 7 % is noteworthy in these coal samples. These values are in agreement with previously reported results [Ahmed et. al., 1986]. The qualitative XRD analysis on these samples indicates that sulfur is present in the form of pyrite. Moreover, the toxic elements like Cr, Cd and Pb are present at µg/g level. The concentration of Cr is > 80 µg/g and Cd is <39 µg/g and of Pb is around 20 µg/g. In the present

studies As, Se and Hg have not been quantified due to their absence in one of the three coal standards (SARMs) used for obtaining calibration curves for concentration measurements. The concentrations of the order of $<1\mu\text{g/g}$ of Se and Hg are reported as approximate property value (uncertified) in SARM-19 and as certified value in SARM-20. The concentration of As is reported for SARM-19 and SARM-20 of the order of 5 - 7 $\mu\text{g/g}$. In future, the concentrations of As, Se and Hg may be approximately measured for the local coal samples using single standard procedures.

The measured elemental concentrations in Makarwal coal are also compared with the NBS-Coal standards namely: SRM-1632 and SRM-1633 [Nadkarni, 1980] and with NBS-1635, KY # 9ASTM and IL # 6-ASTM [Lindahl, 1981]. The concentrations of Ti and U in Sample-A are in agreement with the best values of their concentrations reported for NBS coal standards, SRM-1633 and of Cu in SRM-1632. The concentrations of Al and U in Sample-B are in the same order of magnitude as the best value reported for these elements in SRM-1632 and of Cr in SRM-1633. Moreover, the concentration of Co, Ni and Pb in both Makarwal samples are similar to those reported for SRM-1632 and SRM-1633 coal standards. The concentration of Fe in Sample-B and of ~~Ti~~ in Sample-A are similar to their respective amounts analyzed in high Ca coal [Nadkarni, 1980]. Our value for Cu in Sample-B is comparable with those reported in KY # 9ASTM and in IL # 6ASTM and of Mn with NBS-1635 coal standard. The concentration of Zn in Sample-A is similar to that determined in NBS-1635 and in Eastern ASTM Coal [Lindahl, 1981].

4. CONCLUSIONS:

Carbon Isotope Variations: The $\delta^{13}\text{C}$ values of sampled Tertiary coals in Pakistan fall within a narrow range. Their mean stable carbon isotopic compositions close to the mean isotopic values of peat suggest that the coals are of lignitic grade. However, the range of carbon isotopic composition and the existence of any changes during the process of coalification in each coalfield can further be validated upon a detailed comparison of a large number of coal samples.

Paleo-vegetation: The observed range of variations in the carbon isotope composition of coal from various coalfields in Pakistan is indicative of C_3 type of vegetation / plants responsible for the formation of Tertiary coals.

Depositional Environments: It is speculated that the plants responsible for peat formation at Sharigh coalfield grew under marine/deltaic environments and thus used in addition to environmental CO_2 , the carbon of marine bicarbonate ion / CO_2 produced from hydrolysis of bicarbonates. The Degari and Sor-Range coalfields were formed under deltaic to fluvial / terrestrial environments.

Paleo-environments: No systematic carbon isotope changes are observed during the Tertiary regime thereby indicating consistent carbon isotope composition of atmospheric CO_2 during this period.

Environmental Pollution and Engineering Concerns: Based on the elemental and mineralogical analyses, it is observed that the

Makarwal coal matrix contains significant contents of toxic materials such as Pb, Mn, Cd, Cr and sulfur as pyrite. Thus, the use of this coal for thermal power plants may require significant purification processes for the safety of thermal power plants and to exclude possibilities of acid rain in surrounding environments from pyritic sulfur as it is between 5 - 7 percent in this coal.

5. ACKNOWLEDGEMENTS:

The authors are thankful to Mr. Abdul Mateen (PSO, Centre for Nuclear Studies, Nilore, Islamabad), Mr. Ahmed Hussain (Deputy Director, GSP, Peshawar), Mr. Rafiq Ahmed (Chief Executive, Katha Collieries), Mr. J. R. Das (Project Manager, PMDC Collieries, Sharigh), Mr. Abdul Majeed Zahid (PMDC, Sor-Range Collieries), Mr. Saifullah Khan Paracha (Managing Director, Habibullah Mines, Pvt. Ltd.), Mr. Muhammad Mobeen (Project Manager, Degari Collieries), Mr. Tariq Zamir (Project Manager, PMDC Collieries, Lakhra), Mr. Ghulam Abbas Shah (Chief Mining Engineer, PMDC Collieries, Makarwal) for provision of coal samples and related information about the sampling sites. Special thanks are due to the Chairman Pakistan Mineral Development Corporation (PVT) Ltd. for arrangement of coal samples from the PMDC Collieries. We are also thankful to Dr. N.M. Butt (Director PINSTECH) for providing financial assistance for this work.

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