Geochemical Characterization of Outcrop Sediments from Dharangi-Upper Indus Basin Pakistan

T. FAZEELAT* AND M. S. YOUSAF
*Department of Chemistry,
University of Engineering & Technology
Lahore-54890 Pakistan*

Summary: Three out crop samples from Dharangi area of Upper Indus Basin were investigated to determine hydrocarbon composition, thermal maturity, type of organic matter and generative potential. TOC values determined by both wet combustion titration and pyrolysis methods suggest good to excellent source rock potential for sediments namely B and C, whereas these values show marginal to fair source rock potential for sample A. Rock-Eval pyrolysis was carried out in order to determine maturity, type of kerogen and potential to generate liquid or gaseous hydrocarbons. Which suggest that samples A and B contain type III kerogen and is gas prone; while sample C shows excellent accumulation of free and pyrolyzable hydrocarbons. It contains type II kerogen and is oil prone.

Introduction

Biomarkers are organic compounds, preserved in sediments whose skeleton can be related to precursor molecules in living organisms [1,2]. A complex series of geochemical reactions convert the latter into former, hence the biomarkers can often be used to infer the particular type of organism contributing to petroleum. Many types of organic compounds in crude oils and sediments are not considered to be biomarkers because they cannot be related directly to biogenic precursors. They could be of biological origin, but their sources are simply no longer recognizable due to diagenetic and catagenic transformations. Small alkanes can be generated from a variety of precursors by cracking and skeletal rearrangements giving a tremendous variety of isomers having no obvious relationship to their biological precursors, however their relative distribu-tion can be used to infer informations about maturity and precursor organism. Many varied *n*-alkanes parameters have been used as possible indicators of thermal maturity [3,4]. Espitalie *et al* [5] and Peters and Moldowan [6] have developed standard pyrolysis methods for source rock characterization. In this study parameters based on GC and Rock-Eval pyrolysis have been applied for the assessment of thermal maturity, generatic potential and kerogen type of sediments.

Samples

Three outcrop samples described in this study belong to of Jatta Gypsum Formation of Upper Indus and were provided by Oil and Gas Development Corporation (OGDC) of Pakistan-Islamabad. The outcrop of Jatta Gypsum covers an area of about 130 km long and 15-30 km wide in the southern part of Kohat area. Its thickness ranges from 25-40m [7]. In Kohat area of the basin, shale is present in Jatta Gypsum of Eocene age with TOC of more than 25%. These oil shales are 6m thick and would have source rock potential, however their immaturity is reflected by low vitrinite reflectance values. Further to south the carbonate are associated with organic matter of low TOC and generally mature to marginally mature and therefore has insignificant source rock potential. No fossil study has been reported from this unit, however its comfortable contacts with the lower Eocene Formations above and below indicate an Early Eocene age.

Results and Discussion

The presence of sufficient quantity of organic carbon (excluding carbonate carbon) is the prerequisite for a potential source rock. For rocks at thermal maturity in the beginning of oil generative window, Peters and Moldowan [2] suggested TOC values as: poor (TOC<0.5wt%), fair (TOC 0.5-1 wt %), good (TOC 1-2 wt %) and very good (TOC >2 wt %). However TOC values decrease with thermal maturity. Very high levels of TOC could be due to dead carbon although TOC values of 10% or more in coaly sediments are common. Table 1 lists TOC values of the samples analyzed. The TOC values of sample A is fair (0.8, 0.85%), whereas high values of

---

*To whom all correspondence should be addressed.

Table-1:TOC and Rock-Eval Pyrolysis Data for Selected Samples from Dharangi.

Sample	TOC (wt. %)		S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	T_{max} (°C)	GP (kg/t)	PI	HI	OI
	Tit.	Pyr.								
A	0.85	0.85	0.47	1.36	0.18	435	1.83	0.26	160	21
A	0.85	0.85	0.49	1.31	0.23	435	1.80	0.27	154	27
B	13.56	13.56	9.43	20.94	0.04	438	30.37	0.31	154	0
B	10.00	10.00	8.12	21.00	0.05	438	29.12	0.28	210	1
C	22.06	22.06	28.43	124.32	0.52	436	152.75	0.19	564	2
C	19.31	19.31	25.34	121.92	0.56	437	147.26	0.17	631	2
C	19.36	19.36	24.48	123.68	0.52	438	148.16	0.17	639	3

Basic pyrolysis data are in mg/g of rock and hydrogen and oxygen indices (HI and OI) are in mg. of hydrocarbons. S_1 is a peak which represents the amount of free hydrocarbons (already generated) in a rock, the S_2 represents the amount of hydrocarbons formed by the breakdown of kerogen due to heating at high temperature and the ratio of $S_2 \times 100$/TOC is called the hydrogen index. S_3 is a measure of organic carbon dioxide generated from the kerogen at 390°C and the ratio of $S_3 \times 100$/TOC is called the oxygen index. The heating temperature (T_{max}) at which maximum hydrocarbons (S_2) are generated is related to the degree of thermal maturation of the sample. The ratio of S_1/S_1+S_2 characterizes the transformation or or generation of kerogen hydrocarbons to petroleum, this value will increase with maturation; unusually high values represent staining; S_1+S_2 represents the total possible generation potential of the kerogen.

this parameter for samples B and C (10.5, 13.56) and (18.5, 22.06) respectively show excellent organic richness and genetic potential and/or coaly sediments.

Rock-Eval Pyrolysis and other geochemical measurements have been used for the assessment of quality and quantity of source rock organic matter. The data from Rock-Eval pyrolysis for three selected samples is shown in Table1. Four basic parameters are generated by Rock-Eval. S_1 represents any free hydrocarbon in the rock that was either present at the time of deposition or were generated from the kerogen since deposition.

Heating at 300°C simply distill these hydrocarbons out of the rock. The carboxyl groups in the kerogen break off between 300° and 390°C, yielding CO_2 (S_3) which is trapped and analyzed during the cooling cycle using thermal conductivity detector (TCD). Between 350° and 550°C, hydrocar-bons (S_2) are generated by cracking the kerogen. S_1, S_2 and S_3 are measured in mg/g of rock. The tempe-rature at which maximum amount of S_2 hydro-carbons are generated is called T_{max}, values of 435°-438°C for this parameter shows that the sediments are thermally mature.

The production index (P1) represents amount of hydrocarbons generated relative to total amount of hydrocarbons present: S_1/S_1+S_2, it is a maturity para-meter. Values from 0.1 to 0.4 characterize the interval from onset to peak oil generation, while higher values are indicative of the gas generating stage (i.e. post oil generation stage) or from contami-nation by migrated oil and values of 0 to 0.1 have been described for thermal immaturity. On the basis

of above discussion and inspection of the PI data (0.17-3; Table 1) it is concluded that all the samples are within the oil window.

The indices, hydrogen index (HI) and oxygen index (OI) are qualitative rather than quantitative. Both parameters decrease in value with increasing maturity. High hydrogen indices indicate predomi-nantly oil-prone sediments; high oxygen indices indicate gas-prone source rocks. Hydrogen indices below 150mg HC/g TOC is indicative of the absence of significant amount of oil-generative lipid material and hydrogen indices above 150 reflect increasing amount of lipid rich material, have fair potential for the generation of gaseous hydrocarbons. The hydro-gen indices above 300 are considered to have good source potential for liquid hydrocarbons [6]. The organic mater type could be assessed on a hydrogen index versus oxygen index diagram; which shows that samples A and B in Table 2 contains type III kerogen and is gas prone; while sample C shows excellent accumulation of free and pyrolyzable hydrocarbons and falls in excellent source rock category. The sediment is thermally mature and contains type II kerogen and is oil prone [5,6,8].

Table-2:Bulk and *n*-Alkane Parameters of the Sediments

Samples	Satu-rates %	Aromatics %	NSO %	Resins +ASP %	CPI	OEP
A	22	45	17	16	0.96	0.97
B	33	49	7	11	0.97	1.0
C	35	40	15	15	0.91	0.94

CPI = $(C_{19}+C_{21}+C_{23}+C_{25})$ + $(C_{21}+C_{23}+C_{25}+C_{27})$
/2 $(C_{22}+C_{24}+C_{26}+C_{28})$ calculated using *n*-alkane data
OEP = + $(C_{21}+6C_{23}+C_{25})/(4C_{22}+4C_{24})$ calculated using *n*-alkane data
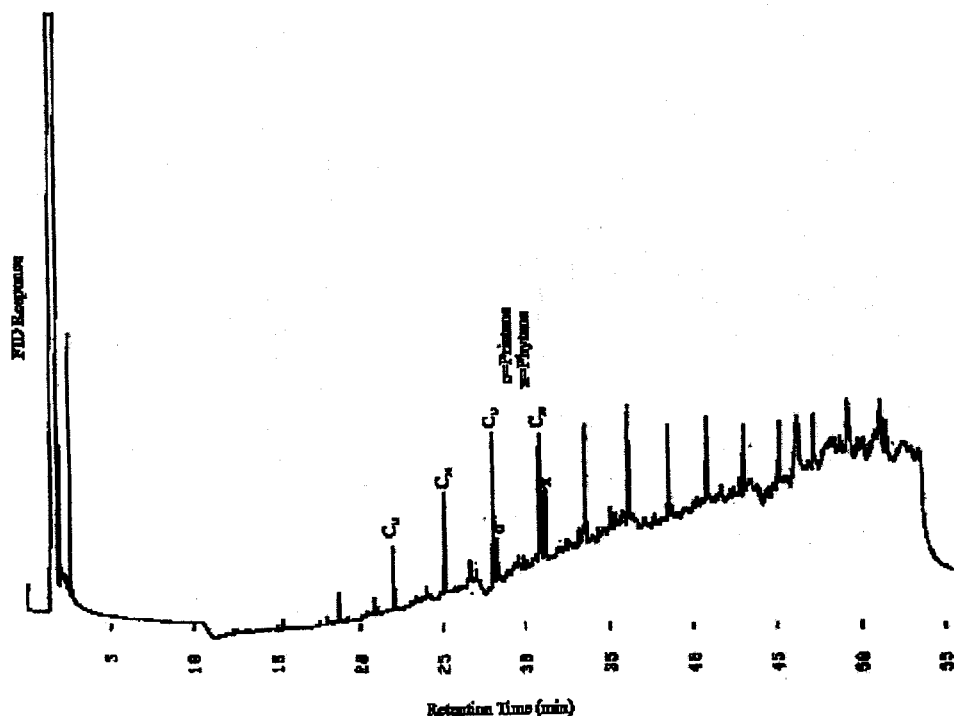
Fig. 1:   Capillary Gas Chromatogram of Dharangi A.

The hydrocarbon composition of sediments was determined using capillary gas chromatography. Prior to gas chromatography, soluble organic matter was fractionated into saturated, aromatics, NSO and resins + asphaltenes components using column chromatography on silica gel. Quantification of these fractions reveal a high percentage of saturated hydrocarbons in all the samples. However sample A contains less relative percentage of saturated hydrocarbons as compared to B and C which contain more than 30% saturated hydrocarbons. They can act as excellent source rocks as suggested by other geochemical parameters. The saturated fractions were subjected to capillary gas chromatography-FID analysis. The chromatograms are shown in Figures 1-3.

The predominance of odd (region C_{19}-C_{27}) versus even (C_{20}-C_{26}) n-alkanes has been used to characterize both the maturity and source input of the organic matter. The values significantly above 1.0 (odd preference) and below 1.0 (even preference) indicate thermally immature organic matter, whereas a value of 1.0 may indicates mature organic matter [2]. Bray and Evans [9] used CPI to obtain source

input information: an odd predominance in this carbon number region indicated contribution of organic matter from higher plants [9,4], however organic matter from other sources usually does not exhibit an odd preference. In this study the CPI value has been used as a thermal maturity indicator according to Peters and Moldowan [2], a value of 1.0 describes thermally mature sample, whereas values significantly greater or less than one indicate thermally immature samples. The values were calculated using the relative peak areas in the gas chromatograms as shown in Table 2. The Odd-Even preference (OEP) values were further calculated using C_{21}-C_{25} n-alkanes [4]. The values significantly greater than one has been described for thermally immature oil or extracts whereas values lower than one describe thermal immaturity. The OEP values (0.94 – 1.0) also show that the samples are mature.

Experimental

Determination of Total Organic Carbon (TOC)

The organic carbon was determined by both wet combustion titration [10] and pyrolysis methods.
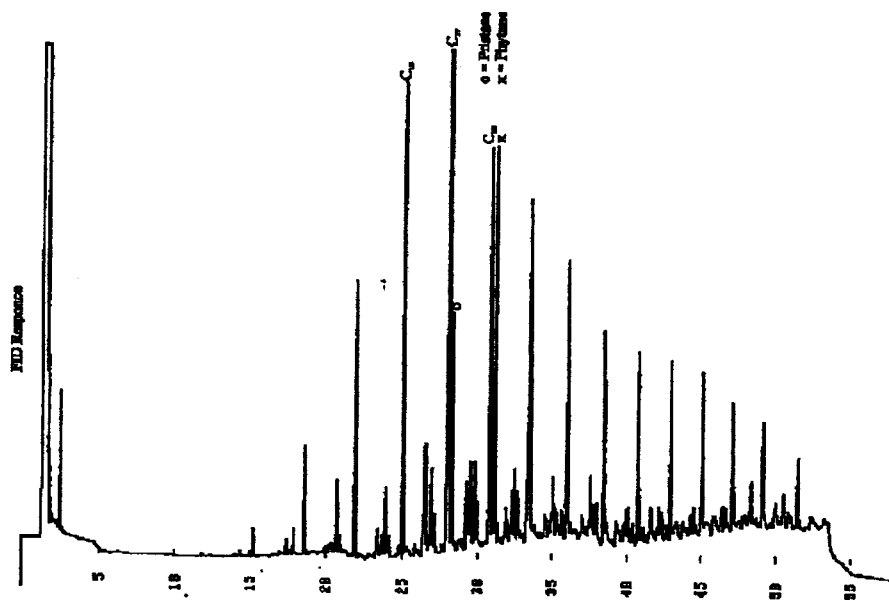
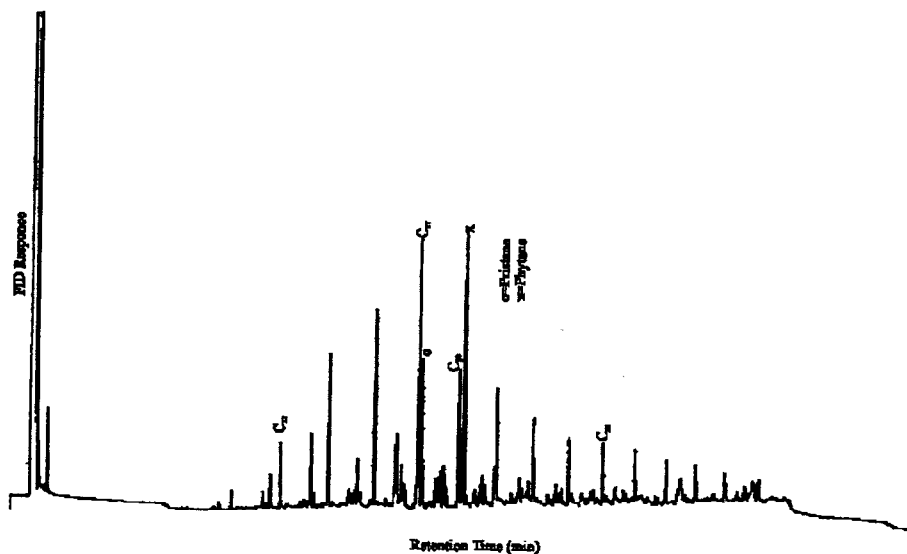Fig. 2: Capillary Gas Chromatogram of Dharangi B.

Fig. 3: Capillary Gas Chromatogram of Dharangi B.

Wet Combustion Titration Method

The crushed sediment (100 mg) was taken in a dry conical flask and solution of chromic acid (0.4N 10mL) was added to it. It was placed on a sand bath for digestion at approximately 175°C for 3 minutes. The volume was then made 100mL by adding disti-lled water. The contents of the flask were allowed to cool and 5 drops of diphenylamine indicator (prepared by dissolving 0.1 g diphenylamine in 50mL conc. H_2SO_4) were added. The contents of the flask titrated against ferrous ammo-nium sulphate (0.2N) to green end point. A blank titration was run containing the acid solution but omitting the sample.

$$\text{Total Organic Carbon (wt. \%)} = \frac{2.16 \text{ (Blank titer - Sample titer)}}{\text{Blank titer x Sample weight}}$$

TOC Determination by Leco Furnace

TOC was further determined using Leco, DC-12 Carbon Determinator, USA at OGDC Islamabad. In brief crushed sediment (100mg) was treated with HCl (6N) to remove carbonates followed pyrolysis at 1200°C in the atmosphere of oxygen. The amount of CO_2 evolved during pyrolysis was measured by a thermal conductivity detector.

Extraction of Soluble Organic Matter (SOM) from Sediments

The crushed sediments (5g) were extracted with dichloromethane (150mL) for about 24 hrs. in a Soxhlet extractor, The solvent was carefully removed from the filtrate by using rotary evaporator to afford the soluble organic matter.

Fractionation of Sediments Extract by Column Chromatography

The sediment extracts were fractionation of into alkanes, aromatics and NSO (nitrogen, sulphur and oxygen) fractions by column chromatography on Silica gel [11]. Glass column (40cm x 1.2 cm i.d.) packed with 3g. freshly activated silica gel (250°C for 24 hours) in n-hexane (20mL). The SOM (50mg) in n-hexane was introduced onto the column. The alkanes were eluted with three bed volumes of n-hexane, the aromatics with three bed volumes of 95:5 n-hexane:diethyl ether, and NSO with three bed volumes of methanol. The fractions were recovered by careful evaporation of the solvent on a sand bath followed by complete removal of solvent under nitrogen.

Capillary Gas Chromatography

The sample dilutions for capillary GC were made as follows:

For each mg. of saturated alkane, 50μL (micro liter) of n-hexane were added. Analysis of alkane fractions was carried out, using a Shimadzù 14B series (Japan) gas chromatograph with a 30m x 25 mm i.d. fused silica capillary column coated with methyl silicone (OV-1). The sample (1μL) was injected in a splitless mode at 60°C. Detector (FID) and injector temperatures were 300°C and 280°C respectively. The oven temperature was programmed from 60°C to 300°C at 4°C/min. Nitrogen at a linear velocity of 28cm/s was used ass the carried gas. The data was collected from 0-60 minutes.

Rock-Eval Pyrolysis

The Rock-Eval Pyrolysis was carried out using Rock-Eval II plus (Delsi, Inc.) with data acquisition workstation at OGDC Islamabad. Rock-Eval II combines pyrolysis analysis with the capability of determining total organic carbon. Ditch cutting rock samples were washed with deionized water, pulverized and sieved through 80 mesh sieve. Samples of ground sediment (100 mg) were pyrolyzed at 330°C for 3-4 minutes, followed by programmed pyrolysis at 25°C min to 550°C in helium atmosphere. The vapours were analysed with flame ionization detector (FID). The oven was allowed to cool; each analysis was completed in 20 minutes [6].

Acknowledgements

References

1. G. Eglinton, P. M, Scott, T. Besky, A. L. Burlingame and M. Calvin, Science, 145, 263 (1864).
2. K. E. Peters and J. M. Moldowan, The Biomarker Guide. Prentice Hall, New Jersey, 209 (1993).
3. E. E. Bray and E. D. Evans, AAPG Bulletin, 49, 248 (1965).
4. R. S. Sclan and J. E. Smith, Geochim. Cosmochim. Acta, 34, 611 (1970).
5. J. Espitalie, M. Madec, B. Tissot and P. Leplat, Offshore Technology Conference, OTC 2935, Houston Texas, May 2-5, 439 (1977).
6. K. E. Peters, AAPG Bulletin, 70, 318 (1986).
7. I. B. Kadri, Petroleum Geology of Pakistan Pub: PPL Karachi-Pakistan, 275 (1995).
8. K. E. Peters, J. K. Whelan, J. M. Hunt and M. E. Tarafa, AAPG Bulletin, 67, 2137 (1983).
9. E. E. Bray and E. D. Evans, Geochim. Cosmochim. Acta, 22, 2 (1961).
10. H. J. Atkinson, G. R. Giles, A. J. Maclean and J. R. Wright, Chemical Methods of Soil Analysis, Contrib. No. 169 (revised), Chem, Div, Serv., CDA, Ottawa (1985).
11. T. Fazeelat, Research Journal, 8, 55 (1994).