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Source-rock Potential and Origin of Hydrocarbons in the Cretaceous and Jurassic Sediments of the Punjab Platform (Indus Basin, Pakistan).

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ABSTRACT

A better understanding of the petroleum systems, including source rock characterization, is needed to enhance the success rate of exploration in the Punjab Platform of Pakistan. Bulk geochemical data and biomarker composition are used here to characterize the environment of deposition and the source rock potential of the strata, drilled in the Ali Sahib and Amir Wali wells. Rock-Eval pyrolysis data classify the organic matter in Jurassic to Eocene strata as Type-III kerogen with transition to Type-II. A few samples from the Chichali Formation (Fm) of Cretaceous age and the Datta Formation (Jurassic) have a fair generative potential for oil and gas.

An algal/microbial origin is proposed for the organic matter present in the samples from the Cretaceous Chichali Fm, whereas a mixed algal/bacterial and land plant origin is proposed for the organic matter of the Cretaceous Lumshiwal, as well as the Samana Suk and Datta Fms (both Jurassic). An anoxic/reducing marine environment during deposition of the Chichali and the Lumshiwal Fms. (Cretaceous) is indicated, whereas the Samana Suk and Datta/Kingriali Fm (Jurassic to Triassic) were deposited under oxic to dysoxic conditions. Urs-12-ene, a biomarker for angiosperms, wasidentified in the Chichali Fm of the Ali Sahib well. All samples are immature to marginally mature. An average vitrinite reflectance (Rr) between 0.5 and 0.6 is estimated from Tmax and the isomerisation of 17α21β (H) C31 hopanes.

A condensate sample from the Sarai Sidhu well indicates elevated biodegradation of light hydrocarbons that were derived from the cracking of petroleum. Based on the presence of rearranged drimanes in the condensate, probably originating from pentacyclic triterpenoids originating in angiosperms, and of urs-12-ene in the Chichali Fm, an origin of the condensate in this Fm is proposed. Oil and condensate must have been formed deeper in the Basin, most probably from mature sediments of the Chichali or Datta Fm. The investigated condensate may represent the degraded residue of methanogenic biodegradation responsible for the gas accumulations in the study area.

INTRODUCTION

Despite growing insights from geophysical investigations and drilling activities, the success rate of hydrocarbon exploration in the Punjab Platform of the Indus Basin in Pakistan is still unsatisfactory. Due to the lack of systematic studies, numerous wells have been drilled for exploration of hydrocarbons but were abundoned.

The Ali Sahib well in the Khanewal district and the Amir Wali well in the Jhang district of the Punjab province were drilled up to 2050 m by Oil and Gas Development Company Limited in 2005 (Figure 1). Both the wells were dry; whereas natural gas has been discovered in the Nandpur and Punjpir fields, which are situated between Ali Sahib well and Bahu well. Gas-condensate has been found in the Sarai Sidhu well(Figure 1).

To enhance the success rate of exploration, a better understanding of the oil-gas system is needed. Until now, only bulk geochemical data (total organic carbon, Rock-Eval pyrolysis) are available for source-rock characterization. However, the number of suitable samples for organic matter type characterization and thermal maturity evaluation by Rock-Eval data is limited in the sedimentary series of the Punjab Platform, due to low organic carbon content (TOC) and associated mineral matter matrix effects. The fossil record together with TOC content and kerogen-type characterization provide information regarding the environment of source rock deposition and maturity. However, the interpretation of TOC, hydrogen index (HI) and oxygen index (OI) is insufficient to identify potential hydrocarbon source rocks because of difficulties to distinguish indigenous and migrated hydrocarbons. Biomarkers (e.g. alkanes, steranes, hopanes), biomarker ratios (such as pristane/phytane and dibenzothiophene/phenanthrene), vitrinite reflectance, and carbon isotope studies are important tools to characterize potential source rocks.

In this study, the interpretation of TOC and maturity parameters in combination with biomarker data are used to characterize the environment of deposition and the source rock potential of the strata drilled in the Ali Sahib and Amir Wali wells. The aim of the study is to increase our knowledge for further exploration in this area of the Punjab Platform.

2. GEOLOGICAL SETTINGS

The Punjab Platform, a westward dipping monocline of the Indian Shield (Kazmi and Jan 1997), is part of the Indus Basin (Figure1). In the North and in the Northwest of the Punjab Platform, the Kohat-Potwar Depressions are situated. Proterozoic basement rocks (Kirana Group) crop out in Sargodha-Shahpur region of the Punjab province, Northeast of the study area (Figures1 and 2). The Punjab Platform is subdivided in a smaller northern part and a larger southern part by the Sargodha High (Kirana Group), which is formed by buried ridges of the Indian Shield, extending eastwards where it is named as Rajasthan Shelf (Verma, 1991). The Punjab Platform is bounded by the Sulaiman Depression in the West and by the southern Indus Basin in the south which is extending into the Arabian Sea (Figure 1). The studied wells

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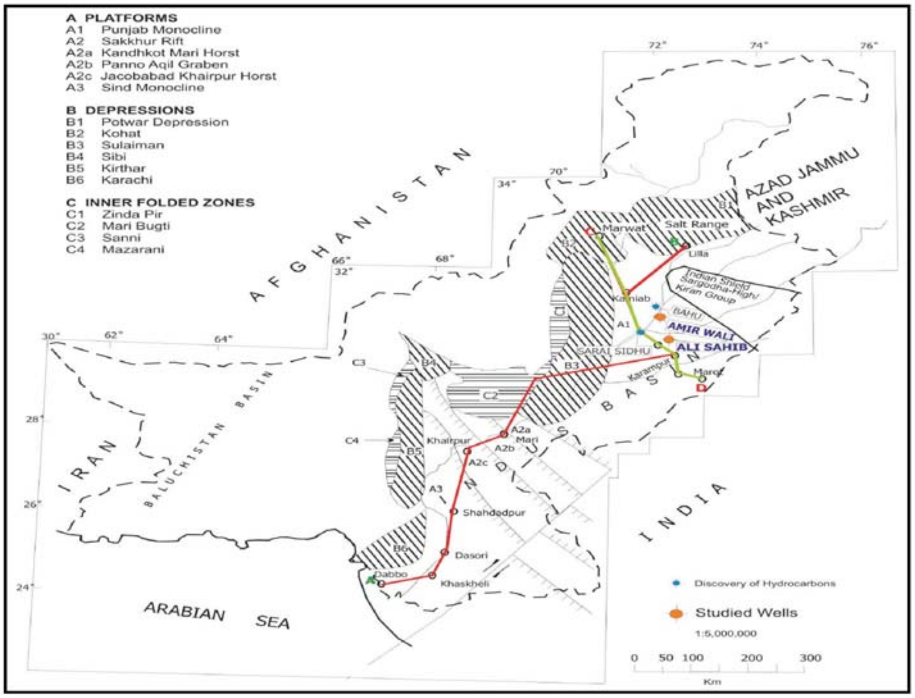

Figure 1 - Geological sketch map of Pakistan showing position of studied wells (Ali Sahib and Amir Wali drilled by OGDCL in 2005) and of cross section lines A-B and C-D.

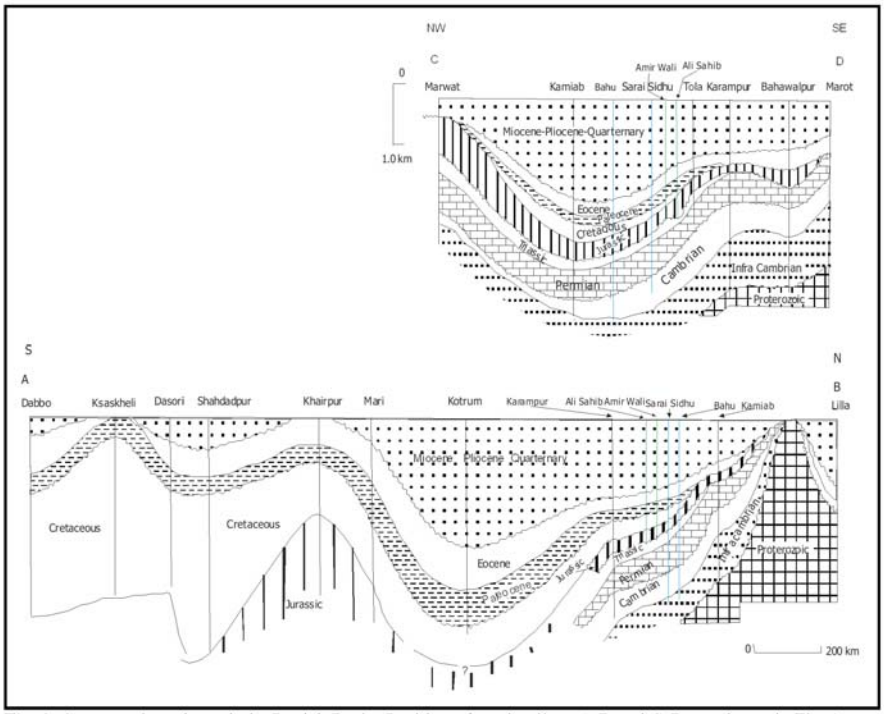

Figure 2 - Cross sections through the Punjab Basin. Position of section lines A-B and C-D are shown in Figure 1. (modified after Kazmi and Jan 1997).

are located in the alluvium covered plains of the Punjab Platform. The rocks of Kirana Group, are comprised of meta-sediments (e.g. Phyllites, quartzites) and meta-volcanics. Some of these rocks have been dated by Rb-Sr (isochrone) to 870 ± 40 Ma (Davies and Crawford 1971). NW-SE and N-S trending cross sections (Figure 2) illustrate the geological situation in the study area. The studied wells (Ali Sahib and Amir Wali) and the Bahu well have been projected to the section lines (A-B and C-D).

Geophysical surveys (Balakrishnan 1977; Farah, et al., 1977; Seeber, et al., 1980; Malik, et al., 1988) and remote sensing studies (Kazmi 1979; Kazmi and Rana 1982) indicate that the basement is extensively traversed by NNE to NE, NNW and E-W trending faults. Kemal, et al., 1992 outlines the Precambrian/Cambrian basin as a NW-SE trending (excluding Potwar Basin) region. Potwar Basin is situated northwards of the Sargodha High and contains a well developed Precambrian to Cambrian succession. Gravity and seismic surveys, supported by limited bore-hole data, indicate that in the eastern part of the Punjab Platform Precambrian rocks form a gentle westward dipping monocline, covered by Mesozoic to Cenozoic marine to deltaic sediments (Kazmi, and Jan 1997).

The sediments of the Punjab Platform represent several tectono-sedimentary cycles starting from the Infra-Cambrian Salt Range Formation and followed by the Cambrian clastic-carbonate-evaporite cycle. The Cambrian cycle is followed by Permian tillite-clastic-carbonate cycle after a long hiatus (as Ordovician to the Carboniferous strata have not been deposited). A thin Mesozoic succession is also present. Then early Tertiary clastics and carbonates exist. Finally, the Siwalik molasse covers this entire succession (Kazmi and Jan 1997). As the Punjab Platform represents a stable continental margin of the Indo-Pakistani Plate, Late Eocene to Early Oligocene orogenesis resulted in little compressive deformation. The tectonic structures in the study area are most probably due to the episodic movements of salt in Infra-Cambrian Salt Range Formation.

3. LITHOLOGY AND STRATIGRAPHY OF THE WELLS

Post-Eocene sediments (Chinji Fm., Nagri Fm., and Dhok Pathan Fm.) were not included into this study, as these sediments are less prospective as potential source rocks. The lithological successions in the area of the two wells are derived from the study of cuttings.

In the Ali Sahib well (Figure 3), 23 lithofacies were distinguised in the Eocene to Jurassic sequence. At the depth of 1250 m, the 35 m thick Sakesar Limestone of Eocene age consists mainly of limestone with sub ordinate shale. The underlying Nammal Fm (1285 1460 m;) comprises mainly of shale and limestone. An early Eocene age is inferred by the occurrence of NP 11 biozone (Paleogene nannoplankton zonal scheme; (Martini 1971). At the depth of 1460 m, the Nammal Fm is underlain by the late Paleocene (NP 9) Dungan Fm. The Dungan Fm comprises mainly of limestone with subordinate shale and it is 30 m thick. Below the Dungan Fm, the Ranikot Fm consists dominantly of shale with subordinate sandstone (1490 1520 m). The lower contact of the Ranikot Fm is with the Lumshiwal Fm of Cretaceous age. The lithology of the Lumshiwal Fm is sandstone with thin bands of shale and limestone. The Lumshiwal Fm is 100 m thick in the drilled sequence and it rests upon the Chichali Fm at the depth of 1620 m. The Chichali Fm is 60 m thick and it comprises shale with traces of sandstone. Early Cretaceous age has been assigned to the Chichali Fm in this well on the basis of Nannofossils species found. Gakkhar et al. 2010 concluded that the upper part (limestone) of the Samana Suk Formation is basically lower part of the Chichali Formation comprising the Late Jurassic. According to them the Chichali Fm has its lower contact with the Middle Jurassic sequence comprising the Samana Suk Fm. The thickness of the Samana Suk Fm is 142 m and it comprises dominantly of oolitic limestone with subordinate shale, claystone and sandy beds. The upper contact of the Datta is with the Samana Suk Fm. The Datta Fm comprises mainly of sandstone, shale and claystone. The thickness of the Datta Fm is 128 m up to target depth (i.e. 2050 m).

In the Amir Wali well (Figure 3), there are 20 lithofacies in the drilled sequence from Eocene to Jurassic age. The Sakesar Fm of Eocene age starts at 1315m depth and consists mainly of limestone. The thickness of the Sakesar Fm is 25 m. The lower contact of the Sakesar Fm is with the Nammal Fm at the depth of 1340 m. The 85 m thick Nammal Fm (1340-1525 m) comprises mainly of limestone and shale. The lower contact of the Nammal Fm is with the Dungan Fm. The 10 m thick Dungan Fm comprises mainly of shale. At the depth of 1535 m, the Dungan Fm is underlain by the Ranikot Fm. The lithology of the Ranikot Fm is dominantly sandstone with subordinate shale and marl and has a thickness of 85 m. In the Amir Wali well the thickness of the underlying Lumshiwal Fm is only 40 m (1620 -1660 m) as compared to 100 meters in Ali Sahib well. The lithology of the Lumshiwal Fm is mainly sandstone with streaks of shale. The Lumshiwal Fm overlies the Chichali Fm at the depth of 1660 m. The Chichali Fm comprises marl, sandstone and shale. The Chichali Fm is 100 meter thick in the Amir Wali well as compared to 60 m in the Ali Sahib well (Figure 3). The age of the Chichali Formation has been described as Late Jurassic to Early Cretaceous by Gakkhar, et al., 2010. The underlying Samana Suk Fm of Jurassic age comprises dominantly of limestone and has the thickness of 140 m. The upper contact of the Datta Formation is with the Samana Suk Fm at the depth of 1890 m. The Datta Fm comprises mainly sandstone, claystone and shale and has thickness of 160 m up to target depth of 2050 m.

4. ANALYTICAL METHODS AND MATERIALS

Four sections up to 9 meters from each well were cored. The recovery of the cores, from sandy intervals was not good and only 2.5 meters have been recovered from 9 meters. The recovery from limestone horizon was 100 % . Formations are named according to (Shah 1977; Kazmi and Jan 1997) and geological data of the company.

Based on high TOC data, samples for biomarker studies were selected from studied wells (Ali Sahib and Amir Wali), The sample positions are marked in the profiles of the wells. Thirty samples from Paleocene to Jurassic strata of Amir Wali well were selected (Table 1). Ten samples were from cores (extension C in sample no.) and twenty were from cuttings (extension D). From Ali Sahib well, three samples from cores and nine samples from cuttings from Cretaceous and Jurassic strata were selected (Table 2, Figure 3). But some of the samples have been lost, that is why the number of samples in tables 1 and 2 are showing the less quantity of the samples as

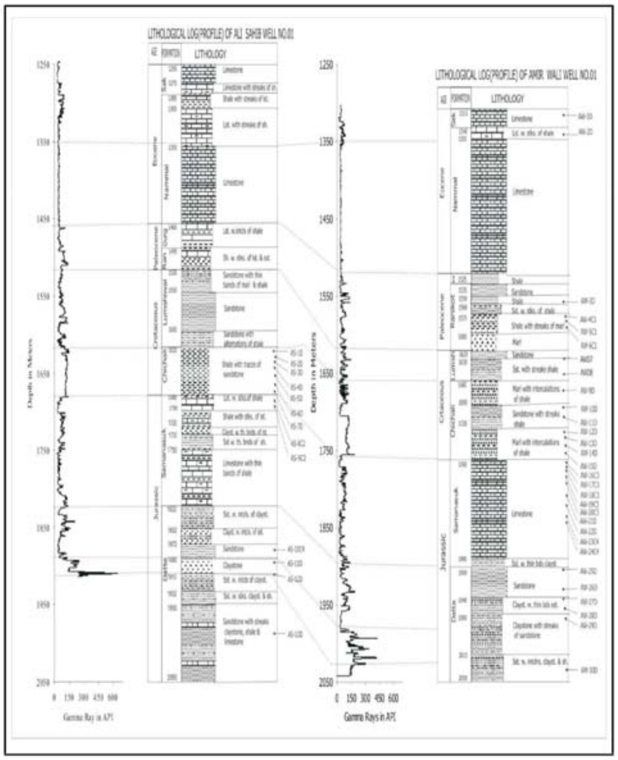

Figure 3 - Stratigraphic columns and well logs of the Ali Sahib and Amir Wali wells.

Table 1 - Bulk organic geochemical data of samples from Ali Sahib and Amir Wali wells

Sample	Formation	TOC[a] (wt.%)	PI[b]	HI[c] (mg HC/ g TOC)	OI[d] (mg CO_2/ g TOC)	T_{max}[e] (° C)	EOM[f] (mg/g TOC)	Sat. HC[g] (%, TOC)	Aro. HC[h] (%, TOC)	NSO (%, TOC)
Ali Sahib Well										
AS1D	Chichali	1.16	0.23	32	5	425	8	49	27	25
AS2D	Chichali	1.62	0.07	106	2	431	9	39	15	47
AS3D	Chichali	1.15	0.04	212	5	428	52	24	14	62
AS4D	Chichali	1.08	0.09	114	5	432	90	26	14	60
AS6D	Chichali	1.14	0.09	107	35	433	44	25	13	63
AS7D	Chichali	1.64	0.05	137	39	433	81	18	10	73
AS8C2	Samana Suk	1.25	0.64	4	70		11	30	6	64
AS9C2	Samana Suk	2.26	0.40	5	39		6	14	16	59
AS10C4	Datta	0.84	0.39	36	62	387	14	48	14	38
AS11D	Datta	1.55	0.06	251	57	429	6	23	19	58
AS12D	Datta	0.79	0.32	16	15	426	163	24	12	64
AS13D	Datta/Kingriali	0.90	0.25	27	29	430	22	35	14	52
Amir Wali Well										
AW1D	Nammal	1.25	0.19	41	42	412	12	39	11	50
AW2D	Nammal	0.88	0.24	48	59	414	18	40	10	50
AW3D	Ranikot	2.33	0.08	62	38	425	14	28	10	63
AW4C1	Ranikot	0.82	0.16	39	22	414	14	9	7	84
AW6C1	Ranikot	0.92	0.62	17	48	418	6	29	13	58
AW7D	Lumshiwal	1.30	0.18	64	68	423	9	20	6	74
AW8D	Lumshiwal	2.00	0.39	28		423	13	15	9	76
AW9D	Chichiali	1.51	0.20	37	40	425	14	4	38	58
AW10D	Chichiali	1.80	0.21	29	49	426	7	41	28	69
AW11D	Chichiali	1.70	0.17	43	35	423	11	36	14	26
AW12D	Chichiali	1.20	0.14	88	50	417	10	36	8	53
AW13D	Chichiali	1.00	0.14	141	80	419	12	58	16	56
AW14D	Chichiali	1.20	0.19	123	80	419	29	36	9	47
AW15D	Chichiali	1.60	0.16	52	38	419	12	45	11	40
AW16C3	Samana Suk	0.62	0.31	58	116	421	17	44	7	48
AW17C3	Samana Suk	0.59	0.50	39	88	419	23	20	15	64
AW20C3	Samana Suk	1.00	0.20	37	56	422	7	55	13	32
AW21D	Samana Suk	0.68	0.26	46	118	422	39	28	9	63
AW22D	Samana Suk	0.70	0.38	26	91	421	12	63	19	19
AW23C4	Samana Suk	2.19	0.36	7	23	416	26	67	3	30
AW24C4	Samana Suk	1.38	0.50	3	12		14	36	26	38
AW25D	Datta	1.50	0.07	215	32	421	46	39	35	26
AW26D	Datta	1.00	0.29	35	72	422	12	40	54	6
AW27D	Datta	1.60	0.09	191	38	420	28	40	7	53
AW29D	Datta	1.00	0.09	220	52	424	13	2	15	83
AW30D	Datta/Kingriali	0.90	0.18	83	80	422	36	39	22	39

[a] Total organic carbon content; [b] Production Index (S1/(S1+S2)); [c] Hydrogen index; [d] Oxygen Index; [e] Temperature of maximum pyrolysis yield; [f] Extractable organic matter; [g] Saturated hydrocarbon fraction; [h] Aromatic hydrocarbon fraction

it is mentioned here. The drill cutting samples have been washed to remove the drilling mud and subsequently dried at room temperature.

The total organic carbon was determined after the removal of carbonate by 6N hydrochloric acid, using a Leco Carbon 412, Elemental Analyzer. Pyrolysis measurements were performed using a "Rock-Eval 2+" instrument at G and R Labs. (Islamabad, Pakistan). The S1 and S2 peaks (mg HC/g rock) were used to calculate the Hydrogen-Index (HI = S2*100/TOC [mg HC/g TOC]) and the Production-Index (PI = S1/(S1+S2) (Espitalié, et al, 1977). The Oxygen Index was calculated from the S3 peak areas (OI = S3*100/TOC [mg CO2/g TOC]). As a maturation indicator, the temperature of maximum hydrocarbon generation (Tmax) was measured.

Solvent extraction and biomarker studies have been carried out at University of Leoben, Austria. For organic geochemical analyses, representative portions of selected samples were extracted for approximately 1 h using dichloromethane in a Dionex ASE 200 accelerated solvent extractor at 75°C and 50 bar. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichloromethane solution (80:1) and separated by centrifugation. The fractions of the hexane-soluble organic matter were separated into NSO compounds, saturated hydrocarbons, and aromatic hydrocarbons by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (Radke, et al., 1980).

The saturated and aromatic hydrocarbon fractions were analysed on a gas chromatograph equipped with a 30-m DB-1 fused silica capillary column (i.d. 0.25 mm; 0.25-μm film thickness) and coupled to a Finnigan MAT GCQ ion trap mass spectrometer. The oven temperature was programmed from 70° to 300°C at a rate of 4°C min-1 followed by an isothermal period of 15 min. Helium was used as carrier gas. The sample was injected splitless with the injector temperature at 275°C. The mass spectrometer was operated in the EI (electron impact) mode over a scan range from m/z 50 to m/z 650 (0.7 s total scan time). Data were processed with a Finnigan data system. Identification of individual compounds was accomplished based on retention time in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different compound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas from the gas chromatograms in relation to those of internal standards (deuterated n-tetracosane and 1,1´-binaphthyl, respectively). The concentrations were normalised to the total organic carbon content.

5. RESULTS AND DISCUSSION

5.1. Total Organic Carbon (TOC) and Rock-Eval Analysis

The samples are characterized by low to moderate TOC contents (between 0.79 and 2.26 wt.%) in the Ali Sahib well, and comparable TOC values (0.59 to 2.33 wt.%) in the Amir Wali well (Table 1). The sampled Formations do not show systematic differences in TOC. Enhanced TOC contents are found in shaly and marly horizons of the Chichali Fm and in the limestones of the Samana Suk Fm.

Hydrogen Index versus Oxygen Index (Figure 4A) or HI versus Tmax (Figure 4B) values classifies the organic matter in the selected samples from Ali Sahib and Amir Wali wells as Type-III kerogen with transition to Type-II. According to (Hunt J.M., 1996), it is difficult to discriminate among and to evaluate source rocks with HI values between 100 and 400 mg HC/g TOC. In our case, most of the samples have HI value in the range of 3-250 (Figures 4A and 4B, Table 1). All samples are immature to marginal mature (Figure 4B). Because of relatively low TOC contents, a mineral-matrix effect cannot be excluded. In order to test this assumption, S2 is plotted versus TOC in Figure 5 (Langford and Blanc Valleron 1990). The equation of the correlation line for the Datta/Kingriali Fms suggests that the "true" HI is 420 mg HC/g TOC. No correlation has been found for the other Fms (Figure 5), probably due to variations in S2 caused by differences in kerogen-type beside the mineral matrix effect.

After correction for the maximum mineral matrix effect in the TOC versus S2 diagram (Figure 5), only few of the samples from the Datta and Chichali Fms reach the geochemical parameters describing a fair generative potential for gas and oil (Peters 1986). Seven samples including shales, sandstone and marly series of the Chichali Fm (Cretaceous), have TOC values ranging from 1.0 to 1.7 wt.% and HI values ranging from 50 to 212 mg HC/g TOC, are encouraging for a hydrocarbon source rock perspective. The Rock-Eval data of these samples are indicative of a mixture of marine and terrestrial material and are suggested as oil and gas prone. The occurrence of condensate in the Sarai Sidhu well from the Samana Suk Fm raised the idea that this formation can also be considered as a source rock for gas. However, based on the studied samples no source rock potential can be attested to this formation. Seven samples of the Datta Formation (Jurassic) show comparatively high HI values of 97 to 251 mg HC/g TOC are relatively low to very low when these values are compared with the prospective horizons of hydrocarbons. The OI ranges from 15 to 75 mg CO2/g TOC (Figure 4A, Table 1) which indicates terrestrial influence (Hunt 1996). The TOC value of the Datta Formation ranges from 0.57 to 1.60 wt. %, indicating a fair hydrocarbon source potential.

Davis et al., (1989) demonstrated that oil fields can be formed from source rocks lacking high HI values. Distinguishing between type III (potential gas) and type IV (non- generative) kerogen is particularly difficult at low TOC values, because of the mineral matrix effect. He further argued that pyrolysis of low TOC samples (<1.5%) often results in lower HI and higher OI values. Oxygen Index values of samples low in TOC (< 2 wt.%) tend to be higher in high carbonate rocks containing siderite arguing for a contribution of carbonate to OI(Orr 1983). In the light of the above discussion, the Chichali Formation and the Datta Formation are considered as potential source rocks for hydrocarbons (oil and gas prone). Higher HI values are observed from the cuttings in comparison to the HI measured in the cores of the same Formation. One possibility to explain the higher HI values of cutting samples is the possible contamination by materials from other Formations.

Kerogen maturity can be determined by plotting HI versus Tmax (Radke, et al., 1980). The petroleum generating range is considered between 430˚C to 465˚C Tmax. The Tmax varies with the type of kerogen as well as maturity, particularly in immature samples. It has been reported by (Peters 1986) that the variation in the Tmax of immature samples would be up to 20˚C due to difference in the type of organic matter. In

Table 2 - Characteristic biomarker ratios of samples from Ali Sahib and Amir Wali wells.

Sample	*n*-C_{15-19}/ *n*-Alkanes	*n*-C_{21-25}/ *n*-Alkanes	*n*-C_{27-31}/ *n*-Alkanes	CPI[a]	Pr[b]/ *n*-C_{17}	Ph[c]/ *n*-C_{18}	Pr/Ph	S/(S+R) - C_{31} Hopanes	MPI 1[d]	R_c[e] (%)	DBT[f]/ Phen.[g]
Ali Sahib Well											
AS1D	0.35	0.23	0.28	0.79	0.35	0.48	0.53	0.50	0.44	0.66	0.23
AS2D	0.59	0.18	0.12	1.62	1.54	0.31	3.53	0.50	0.52	0.71	0.27
AS3D	0.33	0.25	0.31	1.40	0.61	0.76	0.74	0.54	0.40	0.64	0.23
AS4D	0.15	0.54	0.17	1.24	0.77	0.94	0.83		0.57	0.74	0.65
AS6D	0.39	0.30	0.20	2.51	0.32	0.54	0.56	0.47	0.55	0.73	0.71
AS7D	0.34	0.29	0.25	1.60	0.71	0.50	1.14	0.50	0.56	0.74	0.52
AS8C2	0.12	0.17	0.59	0.90	0.80	0.28	1.22	0.46	0.61	0.77	0.18
AS9C2	0.12	0.17	0.59	0.90	0.28	0.05	1.57				
AS10C4	0.17	0.24	0.47	0.95	0.28	0.05	1.57	0.50			
AS11D	0.29	0.39	0.21	1.65	0.63	0.61	0.80		0.58	0.75	0.19
AS12D	0.21	0.35	0.31	1.51	1.23	0.60	1.50	0.60	0.68	0.81	0.56
AS13D	0.23	0.39	0.24	0.90	0.72	0.23	2.34	0.56	0.56	0.74	0.17
Amir Wali Well											
AW1D	0.78	0.18	0.04	0.97	0.27	0.17	2.82	0.56	0.69	0.81	0.18
AW2D	0.53	0.33	0.10	1.08	0.63	0.63	1.46	0.57	0.69	0.81	0.56
AW3D	0.49	0.18	0.16	1.05	0.78	0.54	1.32	0.50	0.52	0.71	0.22
AW7D	0.34	0.21	0.22		0.37	0.44	1.03	0.53	0.43	0.66	0.13
AW8D	0.43	0.27	0.21	0.86	0.52	0.62	1.14				
AW10D	0.45	0.20	0.26	0.84	0.82	0.70	1.43	0.59	0.73	0.84	0.12
AW11D	0.35	0.23	0.34	0.81	0.44	0.51	0.81	0.59			
AW12D	0.53	0.22	0.15	0.92	0.79	0.74	1.69	0.49			
AW13D	0.43	0.27	0.19	0.97	0.28	0.37	0.46				
AW14D	0.57	0.24	0.08	0.97	0.47	0.44	1.20	0.50	0.52	0.71	0.23
AW15D	0.59	0.17	0.12	1.11	1.21	0.43	2.02	0.47	0.47	0.68	0.18
AW16C3	0.27	0.25	0.32	1.13	0.28	0.15	1.86	0.45	0.53	0.72	0.20
AW17C3	0.39	0.23	0.26	1.19	0.38	0.18	2.48	0.49	0.51	0.70	0.15
AW19C3	0.20	0.34	0.32	1.08	0.80	0.72	1.17				0.27
AW20C3	0.25	0.37	0.24	0.97	0.71	0.51	1.16	0.46			
AW21D	0.53	0.20	0.16	0.79	0.58	0.39	1.73		0.52	0.71	0.10
AW22D	0.32	0.19	0.38	0.97	0.63	0.45	1.53	0.49			
AW23C4	0.47	0.37	0.03	1.03	0.47	0.36	1.10	0.51			
AW24C4	0.40	0.42	0.02	1.91	0.48	0.52	0.83	0.47	0.76	0.86	0.13
AW26D	0.27	0.16	0.43	0.99	0.63	0.66	0.87	0.56	0.48	0.69	0.22
AW27D	0.36	0.18	0.36	1.74	0.66	0.47	1.06	0.52			0.20
AW28D	0.59	0.14	0.14	1.24	0.66	1.00	0.51	0.58	0.57	0.74	0.15
AW30D	0.39	0.26	0.21		0.89	0.40	1.79	0.53	0.65	0.79	0.21

[a] Carbon preference index (according to Bray and Evans, 1961); [b] Pristane; [c] Phytane; [d] Methylphenanthrene Index (according to Radke et al., 1982); [e] Calculated vitrinite reflectance equivalence from MPI 1 (Radke and Welte, 1983); [f] Dibenzothiophene; [g] Phenanthrene

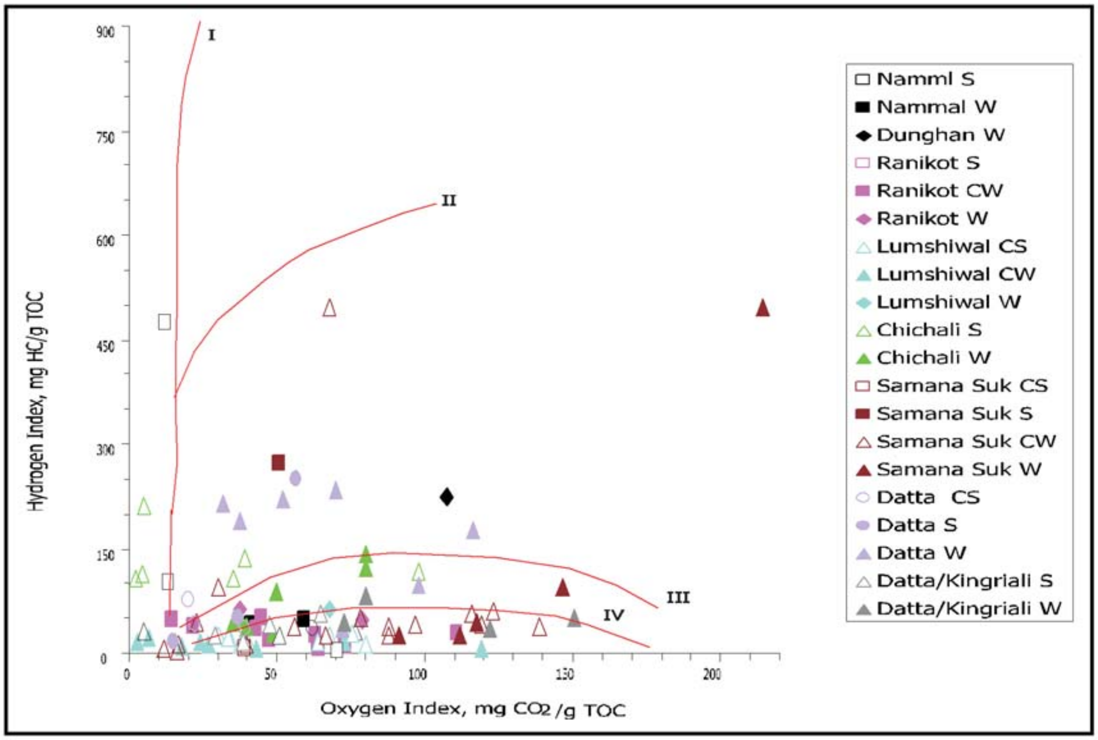

Figure 4A - Hydrogen Index versus Oxygen Index of the Ali Sahib and Amir Wali wells. W:Ditch cuttings of the Amir Wali Well, CW: Core of the Amir Wali Well, S: Ditch cuttings of the Ali Sahib Well, CS: Core of the Ali Sahib Well.

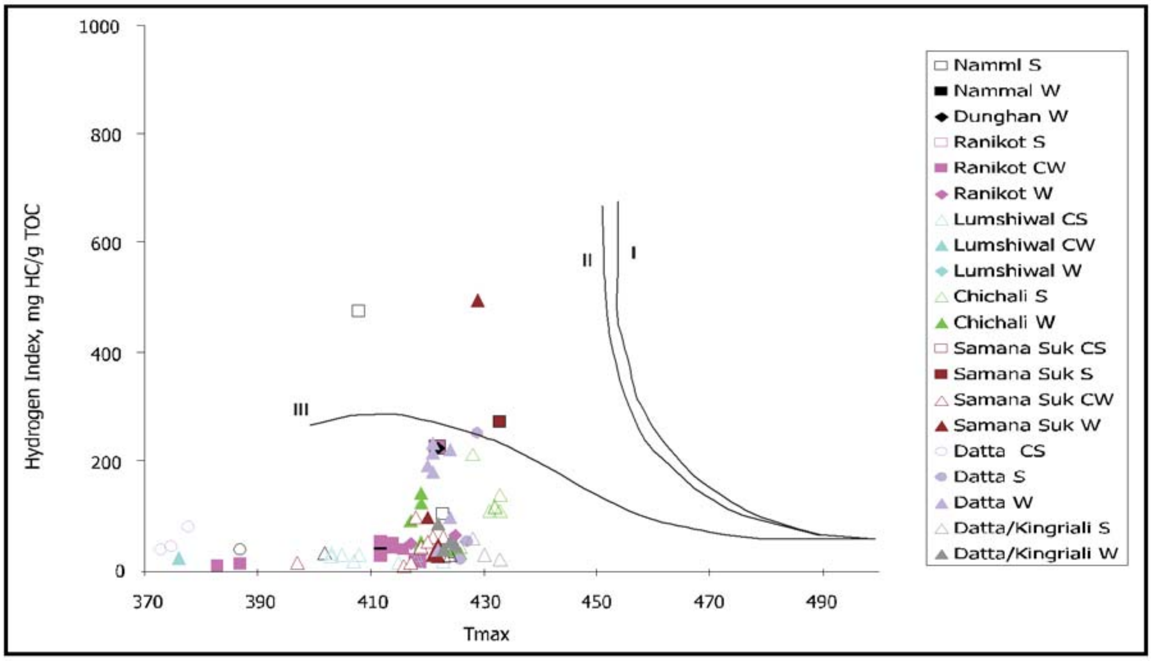

Figure 4B - . Hydrogen Index versus Tmax of the Ali Sahib and Amir Wali wells. W: Ditch cuttings of the Amir Wali Well, CW: Core of the Amir Wali Well, S: Ditch cuttings of the Ali Sahib Well, CS: Core of the Ali Sahib Well.

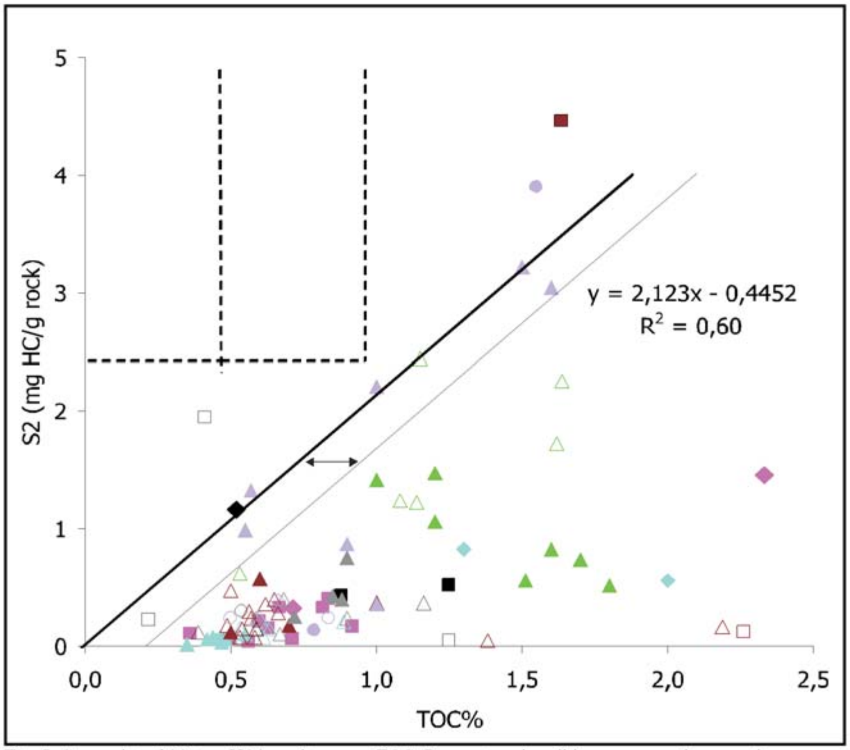

Figure 5 - Cross-plot of S2 (mg HC/g rock) versus TOC. Parameters describing source rock generative potential are outlined (according to Peters, 1986).

Figure 4B, it is obvious that no core sample lies in the range of 430˚C to 465˚C. This is an indication that all the samples are immature. The petroleum generating tendency is not good as the kerogen is of type III or IV and the Tmax (419-433˚C) is less than required for the onset of hydrocarbon generation.

A cross plot of TOC versus S1 was introduced by (Radke, et al., 1980) to distinguish between indigenous and non indigenous hydrocarbons. From Figure 6, it is obvious that all the organic matter can be considered as indigenous and there is no indication for migrated hydrocarbons in the samples of the Amir Wali and the Ali Sahib wells. However, the Production Index (PI) of several samples exceeds 0.2 (Table 1), a value normally observed in mature source rocks or in the presence of migrated hydrocarbons.

5.2. Bitumen Content and Composition

The normalized yields of the extractable organic matter (EOM) from the selected samples of the Ali Sahib well (12 samples), and from the Amir Wali well (26 samples) vary from 6 mg/g TOC (0.6 % in the Samana Suk Formation) to 163 mg/g TOC (16.3% in the Datta Formation)Table 1. In general, the lithology of the samples with high contents of bitumen extracted is claystone and the lithology of the samples with low contents of extracted bitumen is limestone.

The bitumen content (EOM yield in % of TOC) of the Nammal Formation of Eocene (two samples) is 1.2 % to 1.8 % of TOC. The Ranikot Formation of Paleocene age (four samples) has the bitumen content from 0.6 % to 1.3 %. From the Lumshiwal Formation of Cretaceous age (two samples); we got 0.9 % to 1.3 % of TOC. We selected 13 samples from the Chichali Formation of Cretaceous age. Six shaly samples (from the Ali Sahib Well) show bitumen contents from 0.8 % to 9.0 %, comparable to the normal bitumen content range (5-15 %, (Radke, et al., 1980). While the other seven samples (from the Amir Wali Well), consist of sandstone, shale and marl and have lean to moderate extracted bitumen quantity (0.7 % to 2.9 %). The EOM yields from the rest of the sample set are lean to moderate (0.6 to 3.9 % of TOC). The bitumen content of the Datta Formation (8 samples) is moderate to good (0.6 % to 16.3 % of TOC).

The relative proportions of hydrocarbons of the EOM of the samples are highly variable (between 16 and 94%), and most samples yield relatively high proportions of hydrocarbons (> 25%) taking into account the low maturity (Tmax < 430°C) of the organic matter (Table 1). The saturated hydrocarbon fractions predominate in most samples over the aromatic hydrocarbons. The NSO componds (polar compounds plus asphaltenes) contribute between 6 and 84 % of the EOM (> 40% in most samples).

5.3. Molecular Composition of Hydrocarbons n-Alkanes, isoprenoids

The n-alkane patterns of most of the samples from the Chichali Fm are dominated by short to mid-chain n-alkanes (< n-C25). The long-chain n-alkanes (> n-C27) contribute to less than 30 % of the total n-alkanes and do not show a marked odd over even predominance, as indicated by values of the Carbon Preference Index (CPI) close to 1.0 (Table 2; Figure 7). The CPI was calculated from the concentrations of individual n-alkanes using the formula according to (Bray and Evans 1961). Some samples show higher CPI values exceeding 1.5, but the long-chain n-alkanes in these samples are of low abundance that may have resulted in erroneous CPI values (Figure 8). Furthermore, these samples are characterized by an even over odd predominance in the C15 to C31 range. Together with the high relative contents of short-chain n-alkanes (<C20), which are predominantly found in algae and microorganisms (Bray and Evans 1961), an algal/microbial origin is proposed for the organic matter present in the samples (Figure 8). Abundant branched alkanes (iso-, anteiso-, isoprenoidal-) argue for a high contribution of microbial biomass (Cranwell, et al., 1987).

The relative proportions of long-chain n-alkanes in samples from the Samana Suk and Datta Formations are highly variable (Figures 9 and 10) but on average higher as compared to the samples from the Chichali Fm (Figures 7and 8). High proportions of long-chain C27-C31 n-alkanes relative to the sum of n-alkanes are typical for vascular plants, where they occur as the main components of plant waxes (Eglinton and Hamilton 1967). However, samples with higher amounts of long-chain n-alkanes do not show a marked odd over even predominance (Figure 9). Enhanced CPI values are usually found in samples with immature terrestrial organic matter input (Cranwell 1977). A mixed algal/bacterial and land plant origin is proposed for the organic matter in samples from Samana Suk and Datta Fms, as well as in samples from the Lumshiwal Fm (Figure 11). CPI values are considered to have been possibly affected during bacterial reworking and/or maturation (Tissot and Welte 1984).

Taking into account the low abundance of the acyclic isoprenoids pristane (Pr) and phytane (Ph) in several of the samples, which resulted in considerable errors in peak integration (standard deviation in the range of 0.2 to 0.3), the Pr/Ph ratios (between 0.5 and 3.5; Table 2) must be interpreted with care. According to (Didyk, et al., 1978), Pr/Ph ratios exceeding 3.0 are diagnostic for oxic environments, values between 1.0 and 3.0 indicate dysaerobic conditions during early diagenesis, and values below 1.0 were interpreted as reflecting anaerobic environments. Pristane/phytane ratios are also known to be affected by maturation (Eglinton and Hamilton 1967) and by differences in the precursors for acyclic isoprenoids (i.e. bacterial origin; (Volkman and Maxwell 1986; (ten Haven, et al., 1987). An influence of different ranks on pristane/phytane ratios can be ruled out for the sample set. The Pr/Ph values between 1.0 and 3.0 of most samples are interpreted to be consistent with suboxic bottom water conditions and the input of terrestrial organic matter into the basin. However, an archaeal origin of phytane as well as a contribution of tocopherols to pristane formation (Goossens, et al., 1984) cannot be excluded.

Shanmughan 1985; Connon and Cassou1980 and Talukdar, et al., 1993 classified the kerogen by cross plotting pristane/n-C17 versus phytane/n-C18 (Figure 12). The mixed terrestrial marine source of organic matter in different Fms is supported from the cross plot. It is obvious from Figure 12, that the Chichali Formtion and the Lumshiwal Formation (Cretaceous) were deposited in anoxic/reducing marine environment, whereas the Samana Suk and Datta/Kingriali Fms (Jurassic to Triassic) were deposited in oxic environment. Low Pr/n-C17 and Ph/n-C18 ratios are most probably due to the immature character of organic matter, as comparable values have been found in low-rank coal seams (Bechtel, et al., 2007).

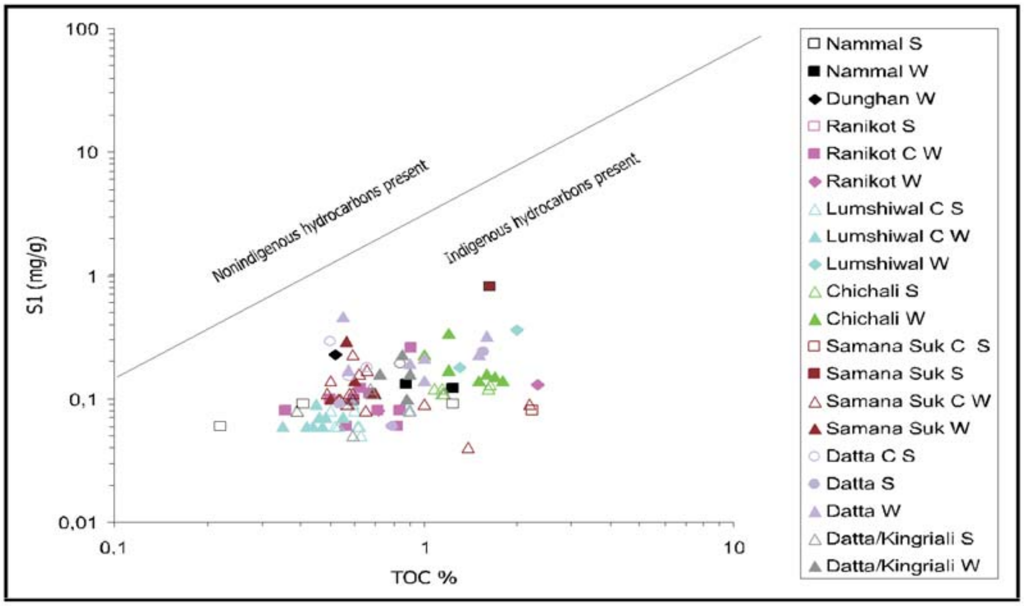

Figure 6 - Cross-plot of S1 (mg free HC/g rock) versus TOC for the distinguishing of indigenous and nonindigenous hydrocarbons (Radke et al, 1996). W: Ditch cuttings of the Amir Wali Well, CW: Core of the Amir Wali Well, S: Ditch cuttings of the Ali Sahib Well, CS: Core of the Ali Sahib Well.

Steroids, Triterpenoids

Only in few samples 5α,14α and 17α, (H) C27 to C29 steranes dominating over the 5α, 14β, 17β (H) steranes are found in low concentrations insufficient for peak integration. The C27, C28 and C29 pseudo homologues are present in variable relative concentrations. The corresponding diasteranes could not be detected. The results are consistent with a mixed algal-terrestrial organic matter source. Algae are the predominant primary producers of C27 sterols, while C29 sterols are more typically associated with land plants (Volkman 1986). However, numerous results from recent biomarker studies add to the growing list of microalgae that contain high proportions of 24-ethylcholesterol (Volkman, et al., 1999) which is a C29 sterol.

Hopanoids are the predominant constituents of the non-aromatic cyclic triterpenoids in all samples. The samples show similar patterns, characterized by the occurrence of 17α, 21β (H)-type hopanes from C27 to C33. The 17β, 21α (H) hopanes (moretanes) from C29 to C31 are present in low amounts. The predominant hopanoid is the αβ -C30 hopane (Figures 7-11). The most probable biological precursors of the hopanes are bacteriohopanepolyols (Ourisson, et al., 1979), (Rohmer, et al., 1992). These compounds have been identified in aerobic bacteria and fungi, as well as in cryptogames (e.g. ferns, moss) and most recently, sulfate-reducing bacteria (Blumenberg, et al., 2006). The ratio of the 22S/(22S + 22R) isomers of the 17β, 21α (H) C31 hopanes vary between 0.45 and 0.60 (Table 2), close to the equilibrium value of 0.6 (Mackenzie, et al., 1982). These values argue for a minimum thermal maturity equivalent to vitrinite reflectance values of 0.5% Rr (Mackenzie and Maxwell 1981), consistent with the measured Tmax values. A pentacyclic triterpenoid of the ursane type was found in the saturate hydrocarbon fractions of the samples from the Cretaceous Chichali Fm from the Ali Sahib well (Figure 8C). The compound was tentatively identified as urs-12.-ene (Philp 1985). Non-hopanoid triterpenoids containing the structures typical of the oleanane skeleton, the ursane skeleton, or the lupane skeleton are known as biomarkers for angiosperms (Karrer, et al., 1977; Sukh Dev, 1989). These compounds are significant constituents of wood, roots, and bark (Karrer, et al., 1977).

Aromatic Hydrocarbons

In most samples, individual aromatic hydrocarbons are detected in considerable concentrations. The chromatograms are dominated by dimethyl- and trimethyl-naphthalenes, as well as methyl- and dimethyl-biphenyls (Figure 13). Further constituents are alkyl-benzenes, phenanthrene, dibenzothiophene and methyl-phenanthrenes. Napthalene, phenanthrene and their methylated analogues derive from a variety of non-specific precursor compounds such as sesquiterpenoids, steroids and triterpenoids (Tissot and Welte 1984). Increasing amounts of isopropyl-methyl-phenanthrene (retene; (Philp 1985) towrds the Jurassic Datta Fm (Figure 13) indicate increasing contributions of resinous organic matter, derived from species of coniferales families Cupressaceae/Taxodiaceae, Podocarpaceae and/or Araucariaceae (Otto and Wilde 2001).

The dibenzothiophene (DBT) / phenanthrene ratio (Table 2) reflects the amount of free hydrogensulfide in the environment during organic matter deposition and/or early diagenesis. Information about the depositional environment of the respective source rocks can be provided from crude oil samples using a DBT/phenanthrene versus pristane/phytane diagram (Figure 14; Hughes, et al., 1995). All samples fall into the fields characteristic for lacustrine sulphate-poor (Zone 2) or marine shales (Zone 3) as source rocks. As the organic matter has been also extracted from marine limestone and marl, some data points should plot into Zone 1b (Figure 14).

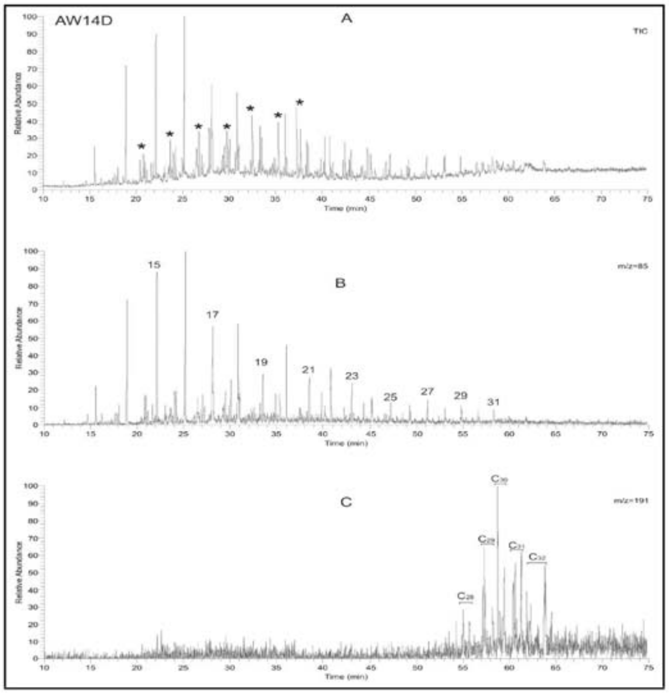

Figure 7 - (A) Gas chromatogram (total ion current) of the saturated hydrocarbon fraction of sample AW14D (Cretaceous Chichali Fm.). n-Alkanes are labelled according to their carbon number; branched alkanes are marked by asterisks. (B) Mass chromatogram (m/z = 85) for n-alkanes. (C) Mass chromatogram (m/z =191) for triterpenoids. Characteristic hopanes are labelled.

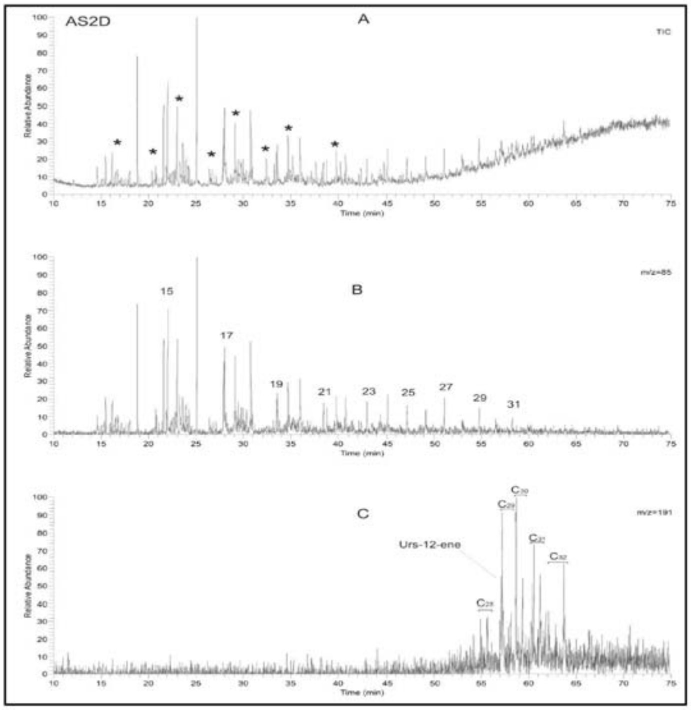

Figure 8 - (A) Gas chromatogram (TIC) of the saturated hydrocarbon fraction of sample AS2D (Cretaceous Chichali Fm.). n-Alkanes are labelled according to their carbon number; branched alkanes are marked by asterisks. (B) Mass chromatogram (m/z = 85) for n-alkanes. (C) Mass chromatogram (m/z = 191) for triterpenoids. Characteristic hopanes are labelled

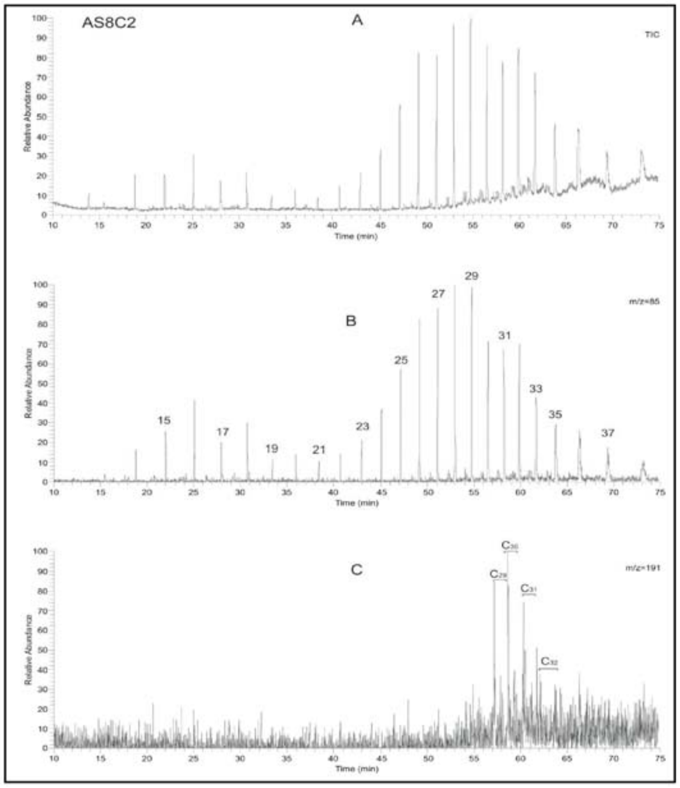

Figure 9 - (A) Gas chromatogram (TIC) of the saturated hydrocarbon fraction of sample AS8C2 (Jurassic Samana Suk Fm.). (B) Mass chromatogram (m/z = 85) for n-alkanes (labelled according to their carbon number). (C) Mass chromatogram (m/z = 191) for triterpenoids.

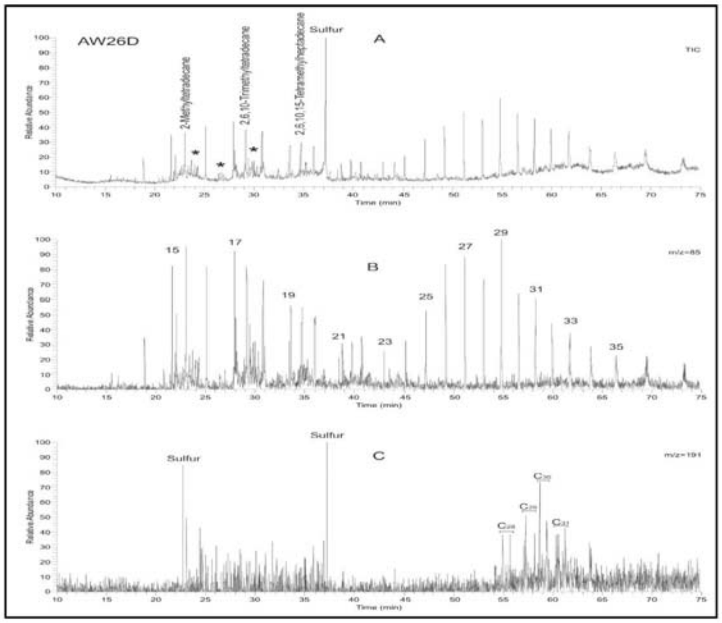

Figure 10 - (A) Gas chromatogram (TIC) of the saturated hydrocarbon fraction of sample AW26D (Jurassic Datta Fm.). (B) Mass chromatogram (m/z = 85) for n-alkanes (labelled according to their carbon number). (C) Mass chromatogram (m/z = 191) for triterpenoids.

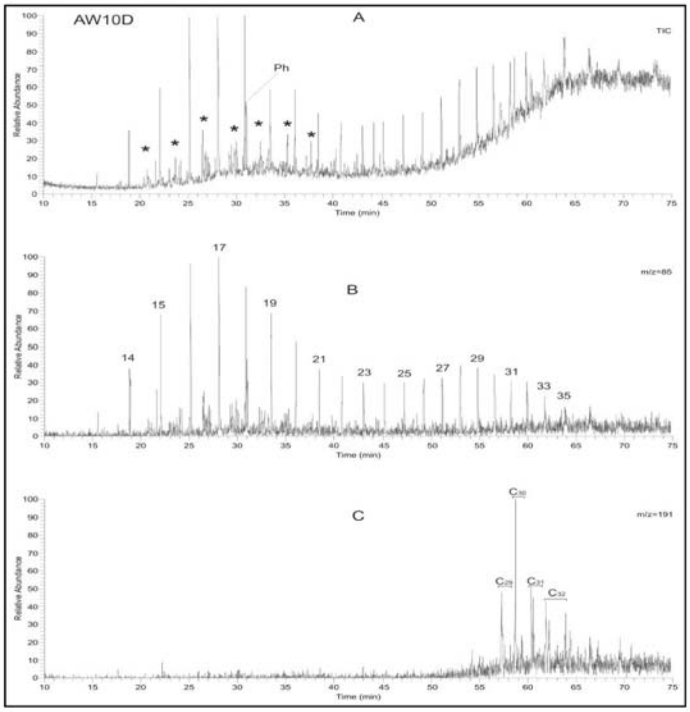

Figure 11 - (A) Gas chromatogram (TIC) of the saturated hydrocarbon fraction of sample AW10D (Cretaceous Lumshiwal Fm.). Branched alkanes are marked by asterisks. (B) Mass chromatogram (m/z = 85) for n-alkanes (labelled according to their carbon number). (C) Mass chromatogram (m/z = 191) for triterpenoids.

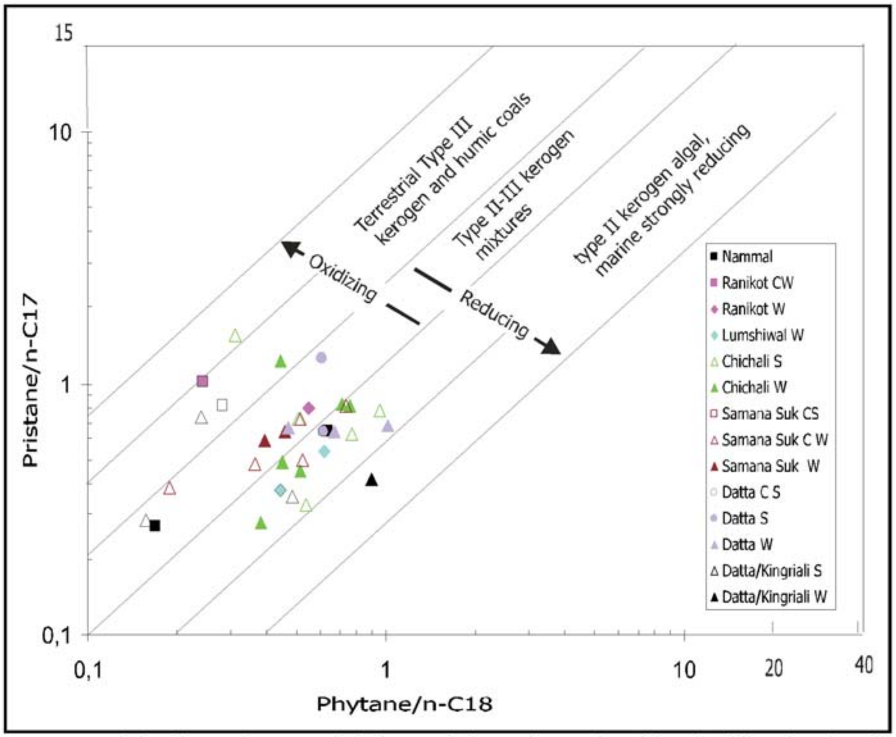

Figure 12 - Correlation diagram between pristine/n-17 and phytane/n-18 ratios of the Ali Sahib and Amir Wali wells (Connan and Cassou, 1980). W: Ditch cuttings of the Amir Wali Well, CW: Core of the Amir Wali Well, S: Ditch cuttings of the Ali Sahib Well, CS: Core of the Ali Sahib Well.

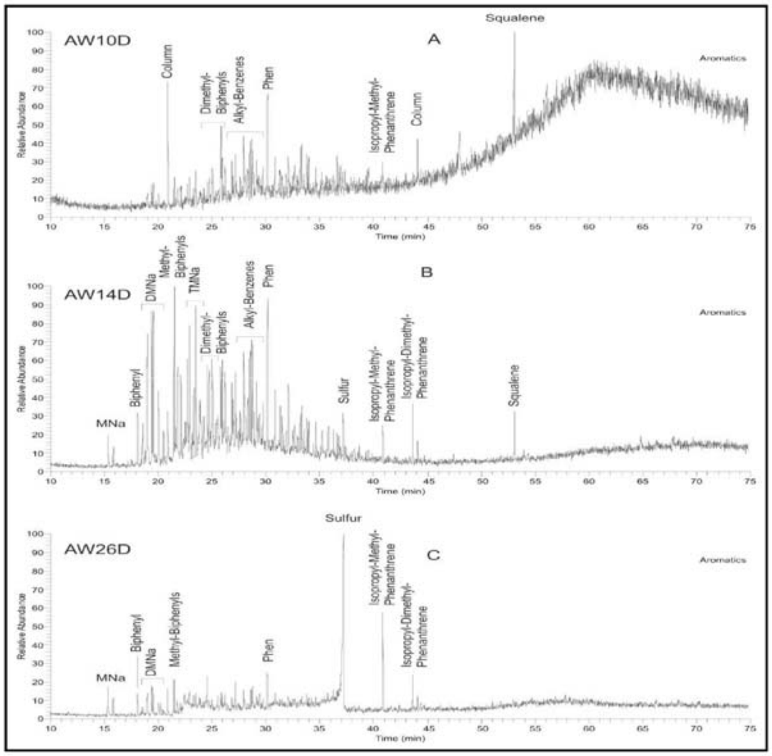

Figure 13 - Gas chromatograms (TIC) of the aromatic hydrocarbon fractions of (A) sample AW10D (Cretaceous Lumshiwal Fm.), (B) sample AW14D (Cretaceous Chichali Fm.), and (C) sample AW26D (Jurassic Datta Fm.). MNa = Methyl-Naphthalenes; DMNa = Dimethyl-Naphthalenes; MNa = Trimethyl- Naphthalenes; Phen = Phenanthrene.

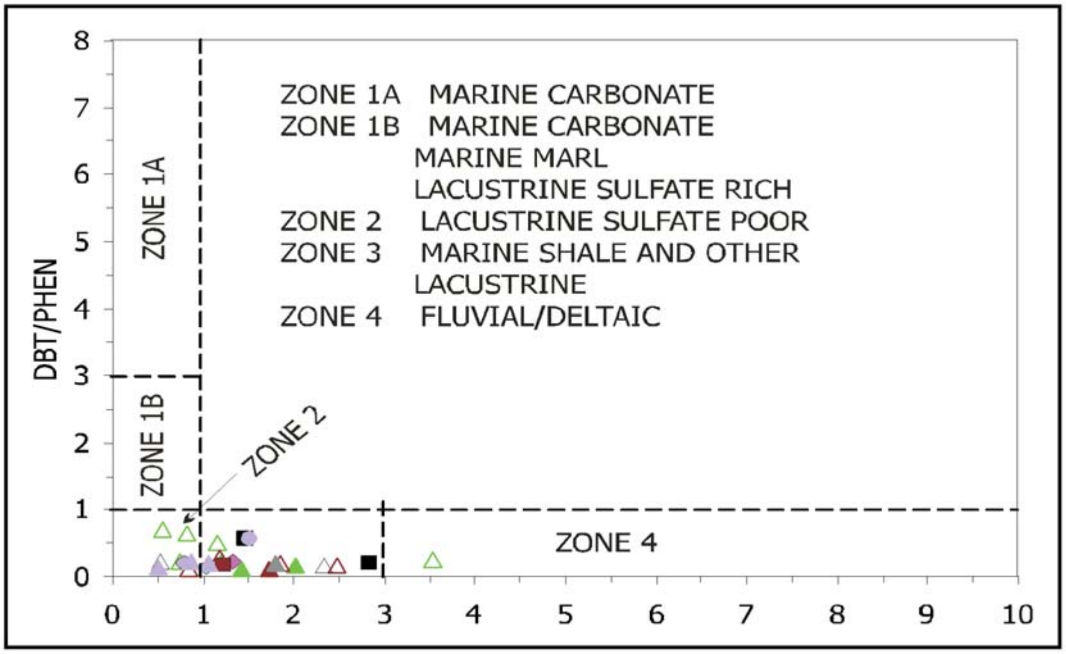

Figure 14 - Cross-correlation of dibenzothiophene/phenanthrene versus pristine/phytane ratios of samples from the Ali Sahib and Amir Wali wells. Zones characteristic for oil samples from specific source rocks are outlined (according to Hughes et al., 1995).

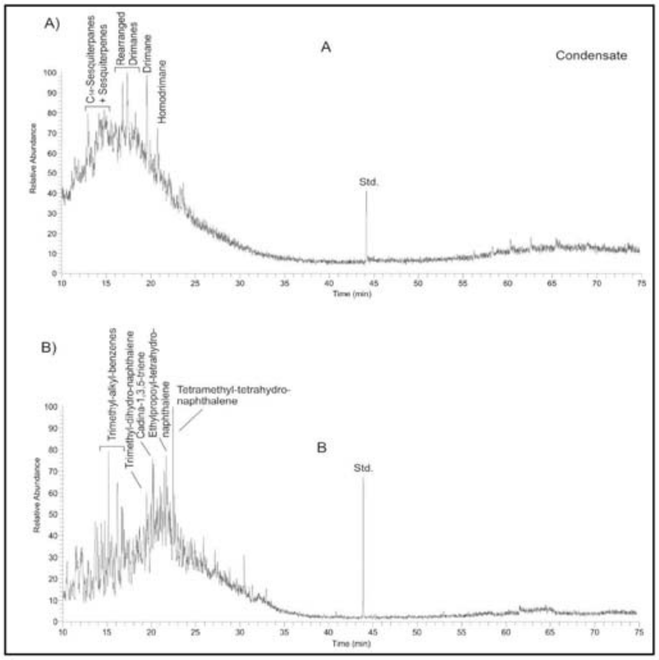

Figure 15 - Gas chromatograms (TIC) of (A) the saturated hydrocarbon fraction and (B) the aromatics of the condensate sample from the Sarai Sidhu well. Identified sesquiterpenoids are labelled. Std. = Standard (deuterated n-tetracosane for saturated HC; 1,1´-binaphthyl for aromatic HC).

This discrepancy may indicate the presence of free iron in the environment sufficient to bind the H2S formed during bacterial sulphate reduction. However, the diagram was developed for the characterisation of possible source rock lithologies from oil samples, and care must be taken when applying these relationships for classification of extractable organic matter from sediments (Figure 14; Hughes, et al., 1995).

A well established maturity proxy used for type III kerogen is the methylphenanthrene index (MPI-1 = 1.5*[((2-MP) + (3-MP))/ ((P) + (1-MP) + (9-MP))]; (Radke, et al., 1982). For organic matter of low thermal maturity (Rr <1.35%) the equation Rc = 0.6*MPI-1 + 0.4 allows calculation of equivalent vitrinite reflectance (Radke and Welte 1983). In the samples investigated, the MPI-1 values range between 0.40 and 0.68 (Table 2). The average calculated vitrinite reflectance of Rc = 0.73% is higher than the values estimated from Tmax and the isomerisation of 17α, 21β (H) C31 hopanes (Rr in the range of 0.5 to 0.6%). This discrepancy most probably results from problems in peak area integration due to low intensities of methylphenanthrenes and overlapping peaks.

5.4. Condensate and Gas Composition of Neighboring Wells

For the comparison with the molecular composition of hydrocarbons from EOM, the saturated and aromatic hydrocarbon fractions of a condensate sample from the Sarai Sidhu well (Figure 1) were included into this study. Beside a hump in the low boiling point range (9 30 min) of the chromatogram, sesquiterpenoids predominate the saturated hydrocarbon fraction of the condensate (Figure 15A). No n-alkanes could be detected. Identified compounds are drimane, homodrimane (Philp 1985), and re-arranged drimanes (Nytoft, et al., 2009). These compounds are most probably derived from drimenol of microbial origin (Alexander, et al., 1983), or reflect a higher plant contribution (Philp 1994 ; Nytoft, et al., 2009). Additional C14-sesquiterpanes and sesquiterpenes are present, but remain unidentified.

Beside a high contribution of unresolvable hydrocarbons in the low boiling point range (Figure 15B), the aromatics consist of dimethyl- and trimethyl-1-alkylbenzenes, as well as trimethyl-dihydro-naphthalenes and the trimethyl- and tetramethyl-tetrahydro-naphthalenes possibly formed through the degradation of pentacyclic precursor molecules (Püttmann and Villar 1987) The presence of the hump, as well as the absence of n-alkanes in the condensate is interpreted as a result of elevated biodegradation of light hydrocarbons derived from the cracking of petroleum. Sesquiterpenoids are known to be resistent against biodegradation and have been found in biodegraded crude oils (Bendoraitis 1974).

Natural gas from the Bahu well was found in Jurasic (Samana Suk) and Cretaceous (Lumshiwal) Formations. The gas composition is different in both lithologies; a higher wettness of the gas is observed in Jurassic strata (C1/(C2+C3) around 125) as compared with its composition in Cretaceous strata (C1/(C2+C3) = 560 to 650). Recently, the close association of dry gas with severely degraded oils has been explained by a common methanogenic biodegradation mechanism in subsurface degraded oil reservoirs (Jones, et al., 2008). Wet gas biodegradation results in gases becoming dryer and oils heavier (Larter and di Primio 2005). In the present case, the condensate may represent the degraded residue of methanogenic biodegradation responsible for the gas accumulations in the study area. What is the isotope value of hydrocarbon gas components.

6. SUMMARY AND CONCLUSIONS

Rock-Eval pyrolysis data classify the organic matter of selected samples from Jurassic to Eocene strata, drilled in the Ali Sahib and Amir Wali wells (Punjab Platform, Pakistan), as Type-III kerogen with transition to Type-II. Samples from the Chichali (Cretaceous) and the Datta Formation (Jurassic) reach the parameters describing a fair generative potential for oil and gas. However, all samples are immature to marginal mature outlining a low petroleum generating tendency. No indications for migrated hydrocarbons are present. The bitumen content of some samples from the Chichali and Datta Formations is moderate to good.

Based on the high relative contents of short-chain n-alkanes (<C20), an algal/microbial origin is proposed for the organic matter present in the samples from the Chichali Fm. Abundant branched alkanes (iso-, anteiso-, isoprenoidal-) argue for a high contribution of microbial biomass. A mixed algal/bacterial and land plant origin is proposed for the organic matter in samples from Lumshiwal, Samana Suk and Datta Fms. Low CPI values of these samples are considered as a result of bacterial reworking. The cross plot of pristane/n-C17 versus phytane/n-C18 ratios, suggests an anoxic/reducing marine environment during deposition of the Chichali and the Lumshiwal Fm (Cretaceous), whereas the Samana Suk and Datta/Kingriali Fm (Jurassic to Triassic) were deposited under oxic to dysoxic conditions.

Hopanes, derived from bacteriohopanetetrol found in bacteria and fungi, are the predominant constituents of the non-aromatic cyclic triterpenoids in all samples. The isomerisation of the 17α, 21β (H) C31 hopanes is close to the equilibrium value of 0.6 arguing for a minimum thermal maturity equivalent to vitrinite reflectance values of 0.5% Rr (yes, the equilibrium value becomes insensitive to further maturation). The pentacyclic triterpene urs-12.-ene, a biomarker for angiosperms, was identified in the Cretaceous Chichali Fm from the Ali Sahib well. what about Cretaceous biomarker of other well.

Based on the DBT/phenanthrene versus pristane/phytane diagram, all samples fall into the fields characteristic for lacustrine sulphate-poor or marine shales, regardless of the origin of the EOM including marine limestones this I understand to be Free Iron poor environment. and marly sequences. Probably, sufficient free iron was present in the environment to bind the H2S formed during bacterial sulfate reduction. The methylphenanthrene index (MPI-1) ranges between 0.40 and 0.68. The average calculated vitrinite reflectance of Rc = 0.73% from MPI-1 is higher than the values estimated from Tmax and the isomerisation of 17α, 21β (H) C31 hopanes (Rr in the range of 0.5 to 0.6%).

The presence of a hump in the saturated and aromatic hydrocarbon fractions of a condensate sample from the Sarai Sidhu well, as well as the absence of n-alkanes and the presence of high relative amounts of sesquiterpanes, are interpreted as a result of elevated biodegradation of light hydrocarbons derived from the cracking of petroleum. Sesquiterpenoids are known to be resistent against biodegradation and have been found in biodegraded crude oils. Rearranged drimanes are considered to have been derived from the degradation of pentacyclic triterpenoids found in angiosperms has been identified in the Chichali Fm, what about other wells a possible origin of the condensate from this Fm is proposed.

Based on the present data, oil and condensate must have been formed in deeper parts in the Punjab Platform, most probably from mature sediments of the Chichali or Datta Formation.

The composition of natural gas derived from Jurrasic (Samana Suk) and Cretaceous (Lumshiwal) Formations in the Bahu well reflects a higher wetness (C1/C2+C3) in the Jurrasic strata. Based on recent concepts about a common methanogenic biodegradation mechanism in subsurface oil reservoirs, including wet gas biodegradation, the condensate may represent the residue of biodegradation responsible for the gas accumulations in study area.

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