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Relationship between Ratio of Pristane to Phytane, Crude Oil Composition and Geological Environment of South Cambay Basin, Ankleshwar, Gujarat, India

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Abstract

The ratios of di-benzo-thiophene to phenanthrene and pristane to phytane joined together suggests the easiest way to know the crude oil source rock depositional environments of the particular area. This type of studies signify identification of the source formation(s) in a basin thereby providing valuable guidance for further exploration of oil wells. The ability to interpret this information from the data analyzed of a crude oil is much valuable during drill stem test of the samples collected from exploratory wells which are characteristically drilled on structural heights, stratigraphically remote from the source formation(s). The ratio of these two compounds is usually interpreted to be an indicator of the oxicity of the environment of deposition[3,4]. Recent advances in organic geochemistry in combination with geological constraints lead us to suggest that the Pr/Ph ratio cannot be used as an indicator for oxygen levels. However, in hypersaline environments of deposition the rationale behind a low Pr/Ph ratio is easier to understand, and in these environments application of the Pr/Ph ratio can be expected to be successful.

In the present endeavor the ratio of pristane and phytane of Ankaleswar oilfield has been evaluated to know the relationship of other parameters. The Ankaleswar oilfield is one of the promising field of Gujarat state and contributing 10% of the total production of the Indian oilfields.

Introduction

The term "*petroleum*" was first used in the treatise *De Natura Fossilium*, published in 1546 by the German mineralogist *Georg Bauer*, also known as *Georgius Agricola*. *Petroleum* or *Crude Oil* is a naturally occurring, inflammable liquid consisting of a complex mixture of hydrocarbons of various molecular weights, and other organic compounds, that are found in geologic formations beneath the earth's surface.

Phytane is a diterpenoid alkane where as pristane is formed from the decarboxylation of phytol, it has one extra carbon to phytane. Phytanyl is the corresponding substituent. Phytanyl groups are frequently found in phospholipids in membranes of thermophilic Archaea. These include caldarchaeol, a compound which contains two fused phytanyl chains.

The Ankaleswar oilfield area has been taken under investigation to know the quality and mode of origin of the field looking into its contribution to nation.

Methodology:

The physical and chemical property and Gas Chromatographic analyses have been done at Central Drug Research Institute, Lucknow, (U.P.) India, using a Chemito model 9610 GC with the option of a flame ionization detector. The GC columns were DB-5, 30m, 0.25 capillaries. The initial column temperature was 40^{o}C with a hold time of four minutes. The temperature programmed at 5^{o}C per minute with a final temperature of 300^{o}C. The tests were performed according to ASTM procedures where possible.

Pristane and Phytane Ratio :

Gas Chromatographic analysis is used to carry out the amount of the saturated hydrocarbon fractions of crude oils and bitumens. The research of petroleum geochemistry shows that pristane (pr) and phytane (ph) are the main ingredients for bio-mark. They possess of obvious property of geochemistry. Different oil origins have different content. The content of pristane and phytane in various kinds of oil sample has been analyzed, and the different characteristic peak area has been compared and contents of pristane and phytane were found different from different oil samples of the area. Very high Pr/Ph ratios are suggestive of terrestrially influenced sediments including coals whereas Pr/Ph ratios substantially less than 1.0 are suggestive of highly reducing depositional environments (Table 9.4).

Identification of the compounds represented by the various peaks is carried out by comparison of retention times (times required for components to emerge from the column) with authentic standards. Quantification is performed either by measuring peak heights (if all peaks in question are the same shape) or, more correctly, by measuring the areas under the peaks using an automatic integrator attached to the detector.

The gas chromatograph and peak area ratio of oil samples of Ankleshwar oilfields has been presented in the following plot and tables.

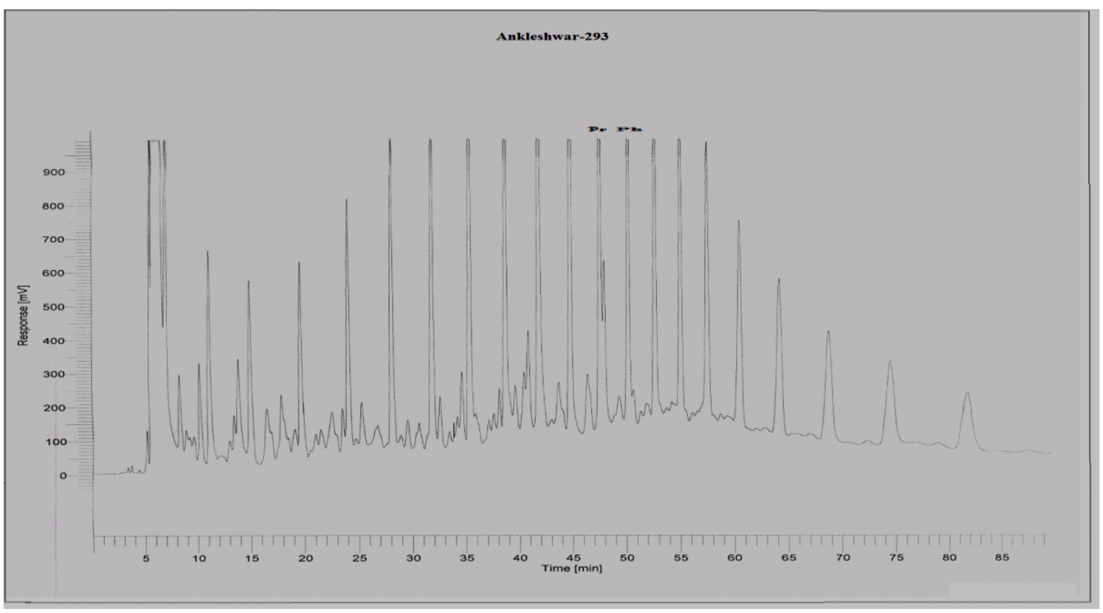
Analytical methods :

Quantitative comparisons based upon chromatographic peak heights or peak areas have been used for pr/ph ratio. The major peaks of the chromatogram have been characterized for comparison in between C17, C18 and C19, C20 peaks. A variety of normalization methods have been used over the years to determine concentration or relative concentration profiles of components in the oil sample. Normal paraffin profiles (plots of peak size versus normal paraffin carbon number) have been calculated by normalizing one or sum of the normal paraffin (e.g. C-13). The later method has two primary advantages. First, the numbers calculated for normal paraffin have some physical significance in that they represent a relative distribution in terms of a fraction of the total. Second, and even more important for comparisons between oils, the numbers obtained are not distorted by excessive errors in the peak which may be used for the normalization.

Other quantitative comparisons, in addition to the normal paraffin and isoprenoid profiles, are based on ratios of pairs of peaks (one peak is normalized by another). The most common ratios considered are the normal C- 17/pristane (the C-19 isoprenoid) ratio and the C-18/phytane (the C-20 isoprenoid). The ratios of other normal paraffin to their nearest isoprenoid also may be considered and in fact this is suggested by the IP method for fingerprint analysis. The advantage of these ratios of the compounds that are close to each other on the chromatogram will undergo similar weathering and hence these ratios may be preserved in spite of weathering. Jackson, *et al.*[7] calculated the ratios of each paraffin C14 with C18 and Ni/V along with isoprenoid oil spill sample and suspect Bunker fuel oil and found that there result are very close to each other. Additionally, the pristane to phytane ratio has been used to characterize oil samples.

The Gas Chromatographs values are as follows.

Figure 1. Gas Chromatograph Plot of Oil A.

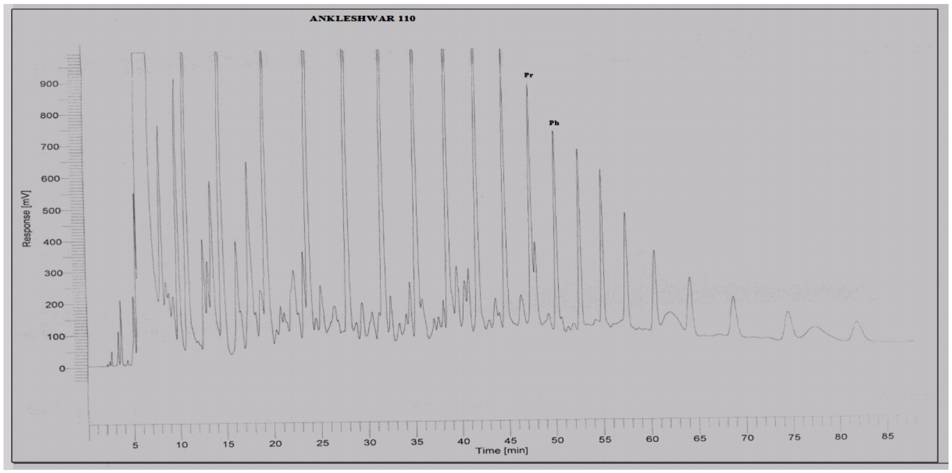


Peak	Time	Area
#	Min	%
1	9.567	0.16
2	10.156	1.11
3	11.061	2.69
4	11.961	0.01
5	12.911	0.26
6	13.368	0.56
7	13.805	1.78
8	14.863	2.74
9	16.456	0.48
10	17.793	0.37
11	19.055	0.4
12	19.559	2.62
13	19.886	0.22
14	20.469	0.05
15	20.967	0.27
16	21.427	0.35
17	22.505	0.54
18	23.474	0.51
19	23.967	3.47
20	24.686	0.11
21	25.247	0.67
22	26.729	0.22
23	27.707	0

Peak	Time	Area
#	Min	%
24	27.994	4.16
25	28.913	0.08
26	29.513	0.4
27	30.585	0.51
28	31.714	4.95
29	32.564	0.71
30	33.448	0.13
31	33.837	0.02
32	34.17	0.3
33	34.614	0.89
34	35.229	5.3
35	35.888	0.38
36	37.137	0.21
37	37.569	0.33
38	38.126	0.54
39	38.56	5.49
40	39.615	0.78
41	40.437	0.84
42	40.483	1.42
43	41.694	5.84
44	43.023	0.01
45	43.695	0.43
46	44.667	5.01

Peak	Time	Area
#	Min	%
47	46.381	1.2
48	47.449	4.68
49	47.965	2.34
50	49.332	0.79
51	50.109	4.58
52	50.684	0.27
53	51.384	0.08
54	51.892	0.02
55	52.602	4
56	54.247	0.04
57	54.98	3.79
58	56.155	0.05
59	56.614	0.03
60	57.524	4.19
61	58.782	0.01
62	60.503	3.71
63	64.158	3.54
64	68.723	3.13
65	74.472	2.88
66	81.722	2.36

Figure 2. Gas Chromatograph Plot of Oil B.

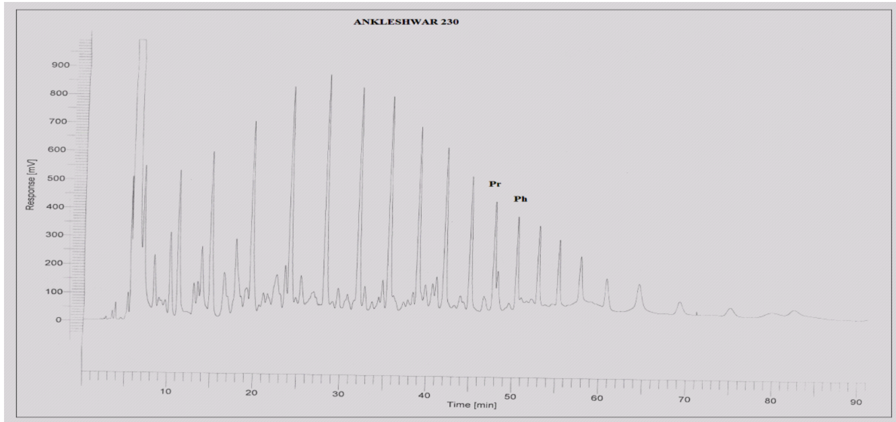


Peak	Time	Area
#	min	%
1	9.96	3.07
2	10.84	5.1
3	12.002	0.04
4	12.699	1.38
5	13.15	1.13
6	13.65	3.15
7	14.56	5.44
8	16.277	1.72
9	16.625	0.49
10	17.59	3.88
11	18.195	0.23
12	18.739	1.2
13	19.287	5.33
14	20.361	0.11
15	20.844	0.3
16	21.216	0.12
17	22.301	1.6
18	22.712	0.25
19	23.328	1.07
20	23.727	5.13
21	24.556	0.25
22	25.117	0.89
23	26.125	0.17

Peak	Time	Area
#	Min	%
24	26.569	0.58
25	26.606	0.12
26	27.282	0
27	27.84	5.04
28	28.815	0.21
29	29.471	0.57
30	30.527	0.6
31	31.263	0.32
32	31.654	5.1
33	32.526	0.64
34	33.427	0.26
35	34.152	0.43
36	34.598	0.8
37	35.22	5.32
38	35.873	0.53
39	37.12	0.29
40	37.577	0.31
41	38.136	0.45
42	38.614	5
43	39.623	1.18
44	40.449	0.85
45	40.872	0.91
46	41.789	4.31

Peak	Time	Area
#	Min	%
47	43.004	0.13
48	43.713	0.49
49	44.117	0.19
50	44.813	3.78
51	46.446	0.69
52	47.602	3.3
53	48.04	1.29
54	49.378	0.38
55	50.256	2.62
56	50.753	0.13
57	51.444	0.05
58	51.992	0.02
59	52.758	2.25
60	54.33	0.02
61	55.126	2
62	56.258	0.01
63	57.626	1.7
64	60.628	1.44
65	62.262	0.11
66	64.329	1.3
67	68.938	1.16
68	74.735	0.94
69	82.092	0.05

Figure 3. Gas Chromatograph Plot of Oil C.

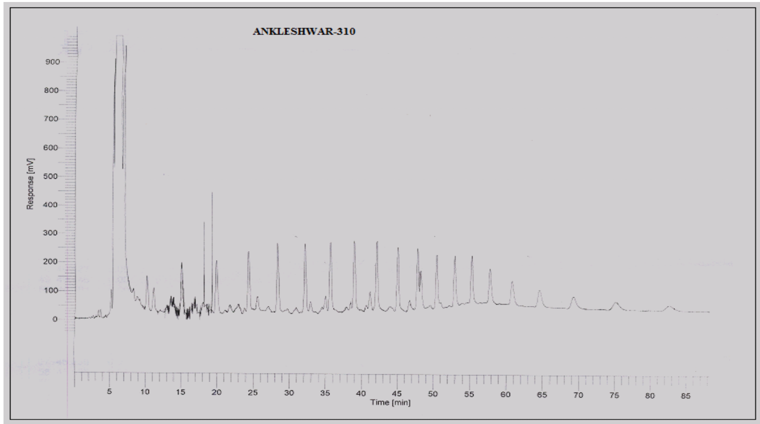


Peak	Time	Area
#	min	%
1	8.276	1.25
2	8.797	0.34
3	9.08	0.26
4	9.532	0.36
5	10.119	2.06
6	11.056	3.83
7	12.866	0.82
8	13.337	0.85
9	13.797	2.49
10	14.822	4.92
11	16.421	0.85
12	17.753	2.97
13	18.358	0.36
14	18.995	1.04
15	19.517	5.78
16	20.458	0.13
17	20.948	0.54
18	21.391	0.63
19	22.471	1.86
20	22.848	0.29
21	23.454	1.04
22	23.948	6.39
23	24.655	0.2
24	25.252	0.97

Peak	Time	Area
#	Min	%
25	26.542	0.22
26	26.729	0.14
27	27.331	0
28	27.614	0.01
29	28.042	6.55
30	28.913	0.19
31	29.54	0.62
32	30.645	0.64
33	31.387	0.19
34	31.852	6.31
35	32.65	0.67
36	33.501	0.25
37	34.263	0.43
38	34.724	0.86
39	35.424	6.11
40	35.972	0.47
41	37.197	0.3
42	37.689	0.36
43	38.252	0.49
44	38.788	5.44
45	39.711	0.98
46	40.259	0.91
47	40.989	1.04
48	41.945	4.81

Peak	Time	Area
#	Min	%
49	43.098	0.24
50	43.808	0.58
51	44.189	0.23
52	44.914	3.69
53	46.557	0.62
54	47.696	2.95
55	48.148	1.12
56	49.474	0.27
57	50.346	2.39
58	50.892	0.14
59	51.522	0.03
60	52.076	0.15
61	52.845	2.02
62	53.643	0.02
63	54.425	0.01
64	55.21	1.7
65	56.345	0.01
66	57.727	1.66
67	60.756	1.12
68	64.485	1.5
69	69.162	0.75
70	71.12	0
71	75.011	0.54
72	82.468	0.04

Figure 4. Gas Chromatograph Plot of Oil D.



Peak	Time	Area
#	min	%
1	10.111	4.09
2	10.692	0
3	10.977	0.59
4	11.046	1.8
5	11.309	0.01
6	19.766	1.58
7	21.167	0.01
8	21.205	0
9	21.252	0
10	21.596	0
11	21.61	0.01
12	21.624	0.01
13	21.81	0.01
14	22.249	0
15	22.272	0
16	22.332	0
17	22.363	0.01
18	22.378	0
19	22.647	0
20	22.796	0
21	22.882	0.01
22	22.97	0
23	24.205	8.69
24	24.845	0

Peak	Time	Area
#	min	%
25	25.086	0
26	25.231	0.01
27	25.257	0.02
28	25.364	0.06
29	25.411	0.03
30	27.821	0.03
31	28.238	10.3
32	30.185	0
33	30.868	0.01
34	32.033	9.55
35	32.835	0.14
36	34.546	0
37	34.897	0.14
38	35.57	9.09
39	37.045	0.01
40	37.16	0.01
41	37.711	0.01
42	38.388	0.05
43	38.424	0.02
44	38.907	9.55
45	39.684	0.01
46	40.342	0.01
47	40.388	0.01
48	40.427	0

Peak	Time	Area
#	Min	%
49	40.446	0
50	40.781	0
51	40.792	0
52	41.128	0.14
53	42.045	9.9
54	43.671	0.17
55	44.998	8.93
56	46.214	0.22
57	46.296	0.01
58	46.528	0.02
59	46.606	0.04
60	46.809	0.01
61	47.757	6.17
62	48.064	0.11
63	48.215	3.02
64	50.406	6.99
65	52.899	0.35
66	55.259	6.1
67	57.489	0.01
68	57.774	1.63
69	60.819	0.39
70	64.567	0.29
71	70.968	0.01
72	79.35	0.01

The chromatograph of oil samples and their value evaluated based on Waples (1945) are as follows.

OIL A
C17/C18 22.505/23.474 = 0.958 0.958/0.970 = 0.99
C19/C20 23.967/24.686 = 0.970

OIL B
C17/C18 22.505/23.474 = 0.981 0.981/0.983 = 0.99
C19/C20 23.967/24.686 =0.983

OIL C
C17/C18 22.505/23.474 = 0.979 0.979/0.983= 0.99
C19/C20 23.967/24.686 = 0.983

OIL D
C17/C18 22.505/23.474 = 0.992 0.992/0.992= 1
C19/C20 23.967/24.686 = 0.992

Composition of Crude oil

Table 1. Chemical Composition of Organic Material and Petroleum.
(After Levorsen, 1958).

	Organic Material	Petroleum
Carbon	52-71 Percent	83-87 Percent
Hydrogen	7-10 Percent	11-15 Percent
Oxygen	15-35 Percent	Trace to 4 Percent
Nitrogen	4-6 Percent	Trace to 4 Percent
Sulphur	Traceable	Trace to 4 Percent

Table 2. Chemical Properties of Crude Oil of Ankleshwar Oilfield

S. No.	Well No.	Carbon %	Hydrogen %	Sulphur %	Oxygen %	Nitrogen %	Mineral Matter %
1	AW- 310	81.26	14.06	Nil	Nil	Nil	4.68
2	AW- 311	61.28	10.32	Nil	Nil	Nil	28.4
3	AW- 234	46.71	9.52	Nil	Nil	Nil	43.77
4	AW- 293	63.06	10.86	Nil	Nil	Nil	26.08
5	AW- 12	65.87	10.59	Nil	7.89	Nil	15.65
6	AW- 110	58.37	10.06	Nil	2.97	Nil	28.6
7	AW- 173	40.37	6.81	Nil	3.68	Nil	49.14
8	AW- 230	63.30	10.55	Nil	3.50	Nil	22.65
Average		**60.02**	**10.34**	**Nil**	**2.25**	**Nil**	**27.37**

Ankleshwar oils as evident from the chemical examination, the carbon content varies between 40.37% and 81.26% (average: 60.12%), hydrogen content varies between 6.81% and 14.06% (average: 10.5%), oxygen compound varies between Nil to 7.89% (average: 3.84%), nitrogen and sulphur compounds are absent in all the oil samples, and metallic constituents varies between 4.68% and 49.14% (Average: 24.59%). The chemical composition of crude oil of Ankleshwar area is very close to the chemical composition of petroleum as given by Levorsen; but the carbon % is slightly less than the suggested one. The reason behind this is that the carbon percentage does not include the metallic contents where as Levorsen has included the metallic content in his studies.

Petroleum System and Depositional Environment :

The Cambay Basin is a fairly rich petroleum province as the basin has generally favourable combination of source sediments, reservoir rocks, regional seals and traps. The Cambay Shale - Hazad-Kanwa is the main petroleum system in the Ankleshwar oilfield. This sub-system is present in the southern part of the basin in the Broach-Jambusar and Narmada blocks. Oil generated and expelled mainly from the source rock in the upper parts of the Cambay Shale (and partly from source rock within Ankleshwar and Dadhar Formations) in Broach-Jambusar block accumulated in the sandstone reservoir of the Hazad Member of the Ankleshwar Formation, which were, in turn, sealed by the Kanwa Shales.

The Cambay basin has witnessed different environmental condition and sedimentation from its inception. According to Sudhakar and Basu[3] the frequent occurrence of plant remains, laminated nature of shale and absence of fossils in Cambay Shale shows that these sediments were deposited in lagoons and paludal swamps.

Pandey *et al*., (1989) have suggested that the deposition of Ankleshwar formation (Reservoir Rocks) in the axial part of the Broach depression have started in the later phase of Middle Eocene time resulting in the deposition of ***Hazad member as delta front and distributory channels environment.*** This deltaic sequence overlies the marine shale (Kanwa shale) and presence of planktonic foraminifera ***indicates a transgressive activity*** in these ***shales during Late-Middle Eocene times.*** The Middle Eocene and Late Eocene sequence (Ardol Member) exhibit decrease in foraminifera concentrati on and becomes sandy upwards suggesting a reworked ***deltaic progradation.*** This sand unit is in turn, overlain by a marine Late Eocene shale (Telwa Shale) evidenced by presence of *Globorotalia-Lenticulina* ***biofacies indicating an upper marine influence and destructive phase in deltaic progradation.***

Occurrence of *Nummulites-Discocyclina* assemblage in the lower part of ***Dadhar formation (Cap rocks) represents a wide transgressive phase*** indicating inner-middle shelf environment with warm water conditions in the South Cambay basin. In this area the large input of coarser clastics brought in by the Proto Narmada river system, was deposited as widespread sheet sandstones and was reworked by marine agencies. Thus, the major part of ***Dadhar formation represents*** the sediments deposited at the ***Proto-Narmada delta system*** during the ***destructive phase.***

Result and Discussion

The Calculation of Pristane and Phytane value shows that the Pr/Ph ratio is in between 1 and 3. It is suggesting the oxic marine sediments origin of crude oil in the investigated area. (Table 9.4)

Table 3. Pristane / Phytane ratios as indicators of depositional environment (Powell T. G., 1988).

Sediment Type	Pristane/Phytane
Anoxic marine sediments	<1
Oxic marine sediments	1-3
Coals	>3

Sulphur and Nitrogen are elements of organic compound and if both are absent from oil, the oil becomes light crude oil. The present oil sample's chemical composition shows absence of Sulphur and Nitrogen. Pr/Ph ratio of the investigated sample envisaged the oxic marine origin of sediment.

Acknowledgment

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