

The Geochemical Composition of Oils and Sediments From Ahmedabad-Mehsana Block of North Cambay Basin, India

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Summary

Porphyryns and perylene biomarkers have attracted considerable attention as important constituents of source rocks and crude oils, in recent years. These biomarkers provide significant information on depositional environments, origin, and maturity of the oils in petroliferous basins. During present studies, both porphyryns and perylene pigments in oils from different structures and sediment samples belonging to Cambay Shale Formation from age Late -Early Eocene of North Cambay basin were analysed and quantified. The results indicate that distribution and preservation of both petroporphyrins and perylene pigments are mainly controlled by the redox conditions experienced by different sub units of the Cambay Shale Formation. The anoxic events identified by the distribution of these pigments during Early to Late Eocene times can be correlated with the sea level changes, which occurred during this period. The abundance of vanadyl porphyryns and perylene in the Younger Cambay Shale sequences suggests that high anoxic condition with low pH during deposition. On the contrary the enrichment of nickel porphyryns in Older Cambay Shale sediments indicate suboxic conditions with high pH and Eh. Furthermore, the enrichment of etioporphyryn (ETIO) series of nickel porphyryns with vanadyl porphyryns as well as low concentrations of vanadium in the oils of North Cambay basin suggests that these oils are mainly derived from the Older Cambay Shale (OCS) and Olpad Formation deposited under suboxic conditions.

Introduction

Accumulation and generation of hydrocarbons is a complex process dependent on preservation of organic matter and its maturation in space and time. These processes involve diagenesis and catagenesis of various organic facies, which lead to the formation of petroleum. The diagenetic products of chlorophyll such as 'Petroporphyrins' found generally in the form of complexes of nickel and vanadium in sediments and oils are important biological markers to study and fine-tune the hydrocarbon occurrence models. Similarly, another biomarker 'perylene', a polycyclic aromatic hydrocarbon preserved under identical depositional conditions as those of porphyryns has also been used to decipher the mechanisms involved in the genesis of petroleum (Aizenshtat, 1973). The presence of both these pigments in a wide variety of sediments, sedimentary products (petroleum) and terrestrially derived peats and coals is well documented in the literature (Baker and Louda, 1986). Both porphyryns and perylenes have also been reported to be extremely sensitive indicators of time-temperature history of sedimentary organic matter (Baker and Louda, 1986). Present work deals with the isolation and quantification of both porphyryns and perylene pigments in oils from different structures and pay zones and sedimentary source sequences of Ahmedabad- Mehnsana block, North Cambay basin to evaluate the source organics, depositional environment and maturity.

Geological settings

The Cambay basin, situated in the northwestern part of Indian craton is a rift graben, which came into existence in the earliest Paleocene. Basin is divided into five tectonic Blocks, which resulted as a sequel to rifting along the west coast of India. These blocks are Narmada, Jambusar-Broach, Cambay-Tarapur, Ahmedabad-Mehnsana and Sanchor-Patan blocks (Pandey et al., 1993). In the Ahmedabad- Mehnsana block, two longitudinal axial trends parallel to the axis of the basin are conspicuous. These are Sobhasana- Kalol-Ahmedabad trend in the east and Mehnsana- Kadi- Viraj-Jhalora- Sanand- Dholka trend in the west. The longitudinal up-lifts and depressions are (i) Eastern margin depression (ii) The eastern anticline zone (Sobhasana in North and Ahmedabad- Bakrol in south) (iii) The Central depression (iv) The Western anticline zones (v) The Western margin depression. The lithostratigraphy of different blocks of the Cambay Basin has been described by various authors (Chandra and Chaudhary, 1969, Bhandari and Chaudhary, 1975, Pandey et al., 1993). In Mehnsana block the Deccan trap forms the technical basement, which is overlain unconformably by Olpad Formation. It is further subdivided into two units designated as Older and Younger Cambay Shale formations. The Younger Cambay Shale has unconformable relationship with overlying Kalol Formation and underlying Cambay Shale Formation. The Kadi



Formation restricted to Ahmedabad-Mehsana block is the stratigraphic equivalent of the younger Cambay Shale. The Kalol Formation has conformable relationship with overlain Tarapur Formation. The formation has been deposited in alternating regressive and transgressive marine influence in a deltaic depositional regime, its thickness is about 150-200m in Mehnsana block. The location map and generalized stratigraphy of North Cambay basin is shown in Fig. 1 & 2.



Fig.1: Location map of Cambay basin

Methodology

Crude oil samples (9-10 gms) were extracted with 100 ml dimethyl formamide (DMF) on water bath. The DMF extracts were reextracted with ether and was concentrated after the removal of DMF with distilled water. The extract of metalloporphyrins was purified by column chromatography using neutral alumina. The finely ground cutting/core samples (100-150 gms) were Soxhlet extracted with methanol + benzene (1:9 v/v) mixture. The extract was concentrated and metalloporphyrins (MPP) were purified by alumina column chromatography by using sequential elution with 100% toluene, a 20-80% gradient of toluene and chloroform and 100% chloroform. The fraction eluted with 100% chloroform contained MPP as ascertained by UV/VIS spectrometry.

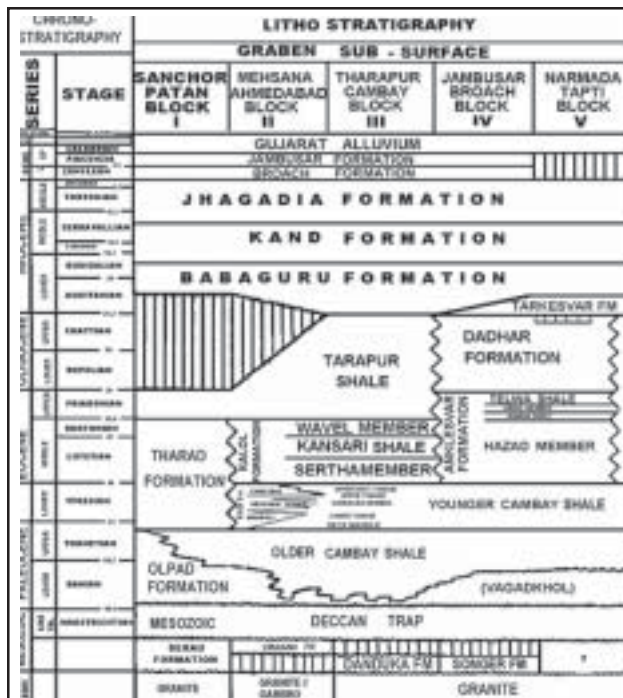


Fig. 2: Generalised stratigraphy

The mixture of nickel and vanadyl chelated MPP isolated from alumina column was concentrated and were applied to silica gel (100-200 mesh) column. Elution with hexane/toluene (1:1v/v) separated nickel complexes whereas elution with mixture of toluene/chloroform (1:1 v/v) isolated vanadyl complexes. Perylenes were fractionated from the oils and bitumen on silica gel column by using toluene as mobile phase (Louda and Baker, 1984). HPLC (Waters 840 HPLC) was used to isolate different structural isomers of MPP. The solvent system acetonitrile + methanol (10:90v/v) was used on reverse phase C18 column (Waters 5i, 150 mm, Synergy RPC18 column) with a flow rate of 1.5ml/min. The detection of nickel porphyrin isomers was done at a fixed wavelength detector set at 546nm. Structural isomers of nickel porphyrins were identified by using commercially available standards. Thin layer chromatographic (TLC) analyses of demetallated free base petroporphyrins were carried out on Silica gel G plates using dichloromethane: hexane (1:2) as mobile phase.

Results and discussion

The geochemical data and the distribution of perylene and porphyrins in oils and sediments are listed in tables-1 and 2 and the distribution pattern of ETIO (C23-C34) and DPEP series of porphyrins of oils and sediments are given in table-3.

Table 1 : Geochemical data and concentration of metalloporphyrins in oils

Well No.	Formation	Depth (m)	Density (gm/l)	Asphltene %	Sulphur %	Nip µg/g	Nickel µg/g	Vanadium µg/g	V/V+Ni
LN-A	Olpad	1606-09	0.9120	1.34	-	0.18	12.3	0.5	0.038
LN-B	Kalol	968-82	0.9655	3.68	-	1.26	33.0	2.5	0.071
KL-A	Kalol	1558-70	0.8658	1.02	0.115	0.60	18.0	0.72	0.039
JT-A	L.Kadi	1466-69	0.8047	0.17	-	1.40	6.0	0	0
JT-B	U.Kadi	1409-22	0.8243	0.16	-	12.5	14.0	0	0
SK-A	CMBS	2042-45	0.8265	0.34	0.094	5.60	18.0	0	0
SK-B	CMBS	2034-43	0.8309	0.23	0.096	0.24	4.5	0.05	0.011
SD-A	Kalol	1558	0.9355	2.48	0.132	8.00	92.0	0.67	0.007
VJ-A	Kalol	1303-30	0.9281	7.18	0.540	2.14	128	0.16	0.001
NW-A	Olpad	1985-99	0.8625	0.30	0.174	-	28.0	0.03	0.001
NW-B	CMBS	1881	0.8608	0.38	0.125	1.80	5.10	0.04	0.008
NW-C	Kalol	1426-35	0.8841	8.09	0.238	2.6	36.5	0.40	0.011
BL-A	Kalol	1039-59	0.9629	2.52	0.096	25.0	128	1.70	0.013
BL-B	Kalol	1050-65	0.9542	2.34	0.093	18.5	86.0	1.28	0.014
SN-A	Kalol	983-1027	0.9427	2.52	0.174	20.7	133	0.50	0.004
SN-B	Kalol	868-985	0.9387	1.89	0.157	15.0	102	0.85	0.008
SB-A	Kadi	1582-86	0.9213	0.14	0.610	0.30	10.0	0.18	0.016
SB-B	Kalol	1267-73	0.8210	1.06	0.047	5.60	8.00	0	0
JH-A	Kalol	1351-59	0.8810	1.80	0.099	2.00	22.0	0.75	0.032
KH-A	Olpad	1408-22	0.8711	2.46	-	6.31	24.0	0.04	0.011
NK-A	Kalol	1035.5	0.9688	4.93	0.165	1.42	10.0	0.79	0.073
BE-A	Kalol	921-35	0.9755	5.85	-	3.67	10.4	1.20	0.01

CMBS-Cambay Shale; L. Kadi-Lower Kadi; U.Kadi-Upper Kadi; Nip-Nickel porphyrin

Perylenes and porphyrins as indicators of source organics

Terrestrial source input is indicated by low concentration of petroporphyrins, generally less than 100 ppm (Lewan and Maynard, 1982). These are predominantly nickel complexed and are associated with low sulphur content (HajiIbrahim et al. 1981). Presence of perylene and dominance of nickel porphyrin as compared to vanadyl porphyrin in both oils and sediments indicate the terrestrial source input in the studied samples of Ahmedabad–Mehsana block (Table-1 & 2). Yang & Cheng (1988) also reported presence of perylene in crude oils and sediments from continental Salt Lake in China, derived from terrigenous organisms.

Depositional environment

The high concentration of nickel porphyrins in all the oils from different structures and pay zones in north Cambay Basin suggests that suboxic to oxic conditions prevailed during diagenesis. The nickel porphyrin concentration in oils increases from central part of the basin to western margins but decreases towards eastern margins, which seems to be the combined effects of redox and thermal conditions. It appears that these source rocks were deposited

in lacustrine/brackish environment with high pH and Eh (suboxic) conditions. The oils accumulated in the margin areas at Sanand, Jhalora, Kadi, Balol, Lanwa, Santhal and Indrora and also part of Jotana and Nawagam fields originated from source rock equivalent of SR-7 in KL-B at 2670-2710m. The enrichment of Vop and absence of Nip in SR-8/9 (2845-2990m.) of KL-C indicates more anoxic influence, which is in contrast to the freshwater depositional environment. The predominance of ETIO Nip in Cambay Shale further confirms the diagenesis of source organics in a sub-oxic to oxic conditions (Barwise & Roberts 1984).

Oil-to-oil correlation

The Kalol, Kadi and Cambay Shale oils of Mehnsana-Ahmedabad block are only enriched in nickel chelated tetrapyrrole pigments. The visible spectral analysis of demetallated free base porphyrin of all the samples studied indicate the presence of ETIO porphyrin as dominant structural type as reported earlier by Chandra et al. (1983). These oils also show very poor V/Ni ratios. Distribution pattern of metal porphyrin as analysed by HPLC also show the dominance of C31 and C32 structural isomers of ETIO-Nip with poor DPEP-Nip contents. Thin layer chromatography of demetallated porphyrins also gives similar results. All these studies indicate that oils are derived



Table 2 : Geochemical data and distribution of metalloporphyrin and perylene pigments in sediments

Well No.	Formation	Depth (m)	TOC %	EOM %	Tmax °C	Nip ng/g	VOp ng/g	Perylene ng/g	VQ VO+Ni	Ni Ni+V
SK-B	OCS	2001-09	3.66	0.29	436	266	116	184	0.3	0.20
VJ-A	KALOL	1310-19	42.9	1.44	423	85.0	42.0	180	0.33	0.21
JT-C	YCS	1512-14	4.82	0.76	425	43.0	19.0	29	0.30	0.20
BL-C	KADI	1343-52	9.99	0.81	427	138	96.0	15	0.41	0.22
SB-C	YCS	1420-26	4.15	2.72	423	0	73.0	100	1.0	0.15
SB-C	YCS	1576-82	6.49	0.07	431	210	0	7	0	0.26
SB-C	YCS	1582-88	5.69	0.13	429	2.0	36.0	30	0.95	0.19
SB-C	OCS	1960-64	2.84	0.15	435	16.0	0	0	0	0.24
SB-C	OCS	2360-63	2.34	0.17	440	24.0	0	0	0	0.25
KL-B	OCS	2139-44	2.83	1.26	430	0	23.0	68	1.0	0.18
KL-C	YCS	1839-44	3.04	0.09	444	0	0	9	0	0.13
KL-C	OCS	2791-2800	1.88	0.79	488	5.0	0	2	0	0.26
KL-C	YCS	2110-2200	1.65	0.30	436	0	0	10	0	0.19
KL-C	OCS	2670-2730	3.69	0.72	442	98.0	0	0	0	0.24
KL-C	OCS	2950-3120	1.90	0.19	443	0	29.0	0	1.0	0.18
KL-C	OCS	4280-4365	0.55	0.07	455	5.0	0	3	0	0.26
NW-A	OCS	1560-1655	2.24	0.18	441	0	39.0	86	1.00	0.17
NW-A	OLPAD	1927-30	22.36	1.80	429	30.0	0	106	0.22	0.46
SD-G	YCS	1156-66	2.56	0.94	425	0	0	23	0	0.20
SD-G	OCS	2030-2080	3.18	0.58	440	40.0	32.0	0	0.44	0.24
SD-G	OCS	2280-2305	1.18	0.17	446	15.0	14.0	0	0.48	0.24
UN-A	YCS	1320-26	1.87	1.32	435	0	13.6	186	1.00	0.13
UN-A	YCS	1558-64	3.25	0.45	431	36.0	17.0	89	0.32	0.18
UN-A	OCS	1576-82	1.34	0.14	441	12.0	0	15	0	0.20
UN-A	OCS	2480-84	1.06	0.11	435	65.0	0	0	0	0.26
SN-C	OCS	1842-49	0.97	0.23	425	0	0	114	0	0.27
SB-F	YCS	1584-93	7.58	0.154	430	50.0	0	45	0	0.30
SB-F	YCS	1878-73	6.97	0.165	435	52.0	0	42	0	0.28
SB-F	YCS	1720-29	7.57	0.24	431	56.0	0	54	0	0.26
SB-E	YCS	1414-23	3.8	6.62	412	0	16.0	33	1.0	0.16
SD-B	OCS	2031-39	6.86	0.724	454	166	20.0	298	0.1	0.21
SD-C	OCS	2191-96	6.31	0.27	385	0	0	104	0	0.32
SD-C	OLPAD	2481-89	1.77	0.045	436	0	0	5	0	0.36
SD-D	YCS	1292-97	5.36	0.18	429	110	0	46	0	0.30
SD-F	OCS	1955-60	1.47	0.72	430	0	0	320	0	0.26

from similar source organics. Variation in porphyrin contents in oils is mostly attributed to redox conditions during diagenesis

Oil to source correlation

The sediments of Older Cambay Shale from Paleocene to Early Eocene are enriched mostly in nickel porphyrins in depressional wells UN-1 & SB-C of Mehsana block and in KL-C & SD-G of Ahmedabad block. Whereas the Younger Cambay Shale sediments of Middle to Late Eocene are mostly enriched in either perylene or vanadyl porphyrins. The low concentration of vanadyl porphyrins in Kalol, Kadi and Cambay Shale pay oils and the dominance of ETIO- Nip indicates that the source rocks at the bottom

of Older Cambay Shale, specially sediments at the bottom of 'Sequence II' is the main source rocks which might have filled the axial as well as the basinal reservoirs of North Cambay Basin. The presence of Vop in SR-8/9 and its complete absence in oils of North Cambay Basin further negates the contribution of hydrocarbons from this source sequence to any of the reservoirs.

Distribution of nickel porphyrins from both oils and sediments of Older and Younger Cambay Shale indicate that C31&C32 alkylated ETIO porphyrins and other higher homologues are predominantly enriched in Older Cambay Shale of SK-B and SR-7 of KL-C than in Younger Cambay Shale sediments of JT-C & SB-F (Table-3). Similarly, the oils of BL-B, SN-B and NK-A are enriched mainly in C31

Table 3 : Concentration of ETIO and DPEP isomers of porphyrins in oils and sediments

Well	C28 μg/g	C29 μg/g	C30 μg/g	C31 μg/g	C32 μg/g	C33 μg/g	C34 μg/g	C35 μg/g	DPEP μg/g
Oils									
VJ-A	0.50	0.75	0.50	1.20	1.40	0.65	0	0.25	0
BL-B	0.75	0	0	0.30	2.50	0	0	0.25	0
SN-B	0.65	0	0	1.00	1.25	0.25	0.35	0	0
NK-B	0	0	0.25	1.00	2.00	0.50	0.50	0.25	0
Younger Cambay Shale Sediments									
UN-A	0.25	0.15	0.15	0.15	0.10	0.05	0	0	0
SB-C	0.45	0.65	0.85	0.15	0.05	0.05	0	0.05	0
SB-F	0.50	1.00	1.25	0.25	0.15	0.05	0	0	0
Older Cambay Shale Sediments									
UN-A	0.25	0.05	0.25	0.75	1.00	0.50	0.50	0.10	0.25
SB-C	0.15	0.15	0.55	1.00	1.25	1.25	0.50	0.35	0.25
SK-B	0.10	0.25	0.85	1.25	1.50	0.75	0.5	0	0.40

&C32 ETIO Nip. Further, the similarities between Nip from oil of NK-A and source sequences SR-7 of KL-C and SK-B (2001-2009m) almost conclusively prove that the sediments belonging to 'Sequence II' of Cambay Shale are the main prolific source rocks. However, contribution from Younger Cambay Shale source sequences wherever they have attained sufficient maturity in some oil pools of North Cambay basin cannot be ruled out.

Maturity

On the basis of porphyrin maturity parameter, the ratio of DPEP/ETIO porphyrins the maturity of Kalol pay oils decreases in the order VJ-A> BE-A> KL-A> NK-A= JH-A>BL-A= SN-B> LN-B>. SB-A oil is less mature than JT-A and even less than KL-A oil. In Older Cambay Shale sediments there is high concentration of higher carbon isomers with small concentration of DPEP in all samples. But in SD-G of SR-11/12 there is high concentration of DPEP. The presence of DPEP in all the samples show that with increasing thermal stress DPEP/ETIO ratio decreases because of transformation of DPEP into ETIO. The alkylation index of petroporphyrins increases with increasing Tmax (Baker and Louda, 1986). The distribution of nickel porphyrins in Younger Cambay Shale and Older Cambay Shale sediments suggest that the degree of alkylation of porphyrin increases with increasing Tmax (425-442°C). Whereas at Tmax value of 455°C (KL-C, SR-11/12) nickel porphyrins probably start dealkylating and therefore, showing the presence of only C32 and C33 ETIO isomers. It can also be inferred from these observations that Younger Cambay Shale sediments are now in late diagenetic stage,

whereas Older Cambay Shale sediments are in the past peak oil generation stage.

Conclusions

1. The distribution of petroporphyrins and perylene biomarkers in the oils and sediments (Cambay Shale) of North Cambay basin is the function of redox conditions. The dominance of ETIO series of nickel porphyrins and absence of vanadyl porphyrins in the oils indicates that the source sequences of these oils are deposited in suboxic conditions.
2. Dominance of higher carbon homologs of ETIO-Nip in all the oils suggests it to be sourced from mature source. In Younger Cambay Shale, the presence of vanadyl porphyrins and perylene shows their deposition in anoxic conditions. The dominance of lower carbon homologs of ETIO series of nickel porphyrins suggests them to be immature.
3. The sediments of Older Cambay Shale are enriched in nickel porphyrins in Mehsana block, indicating the prevalence of suboxic conditions during deposition. The predominance of higher homologs shows Older Cambay Shale to be matured sediments.
4. The presence of ETIO series of nickel porphyrins, both in oils and source sequences at the base of Older Cambay Shale and upper part of Olpad suggests these are the most prolific source rocks, which might have contributed to most of the oil reservoirs of north Cambay Basin.
5. The oil of VJ-A is the most mature, BL-A and SN-B oils are of similar maturity and NK-A and JH-A oils



are of similar maturity and the LN-B is the least mature oil among the studied oils of Kalol pay from different structures of North Cambay basin.

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References

- Aizenshtat, Z., 1973, Perylenes and its geochemical significance; *Geochimica et Cosmochimica Acta*, 37, 559-567.
- Baker, E.W. and Louda, J.W., 1986, Porphyrins in the geological record, In "Biological Markers in the Sedimentary Record" (ed. R.B. Johns) *Methods in Geochemistry and Geophysics*; 24, Elsevier Amsterdam 125-225.
- Barwise, A.J.G. and Roberts, I., 1984, Diagenetic and catagenic pathways for porphyrins in sediments; *Organic Geochemistry*, 6, 167-176.
- Bhandari, L.L. and Chaudhary, L.R., 1975 Stratigraphic analysis of Kadi and Kalol formations, Cambay Basin, India; *AAPG Bulletin*, 59, 5.
- Chandra, P.K. and Chaudhary, L.R., 1969, Stratigraphy of Cambay Basin; *ONGC Bulletin* 6, 37-50.
- Chandra, K. Kumar, P., Prakash, C., Mali, M.R. Dwivedi, P, Sharma, M.C., Datta, G.C. Rao, S. And Gupta, V., 1983 Geochemistry and genesis of Cambay Basin oils and their geochemical interpretation; ONGC Report Unpublished.
- Hajibrahim, S.K., Quirke J.M.E. and Eglington, G., 1981, Petroporphyrins Structurally related porphyrin series in bitumen, shales and petroleums- evidence from HPLC and mass spectrometry; *Chemical Geology*, 32, 173-188.
- Lewan, M.D. and Maynard, J.B., 1982, Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks; *Geochimica et Cosmochimica Acta*, 46, 2547-2560.
- Louda, J.W. and Baker, E.W. , 1984, Perylene occurrence, alkylation and possible sources in deep ocean sediments; *Geochimica et Cosmochimica Acta*, 48, 1043-1058.
- Pandey, J., Singh, N.P. Krishna, B.R. Sharma, D.D., Parikh, A.K. and Nath, S.S., 1993, *Lithostratigraphy of Indian petroliferous Basins*, Vol I, KDMIPE, ONGC, Publications.
- Yang, Z and Cheng, Z., 1988, Isolation, Identification and correlation of porphyrins from continental crude oils, source rocks, oil shales and coals of China, In *Geochemical Biomarkers*. Ed. T.F. Yen and J.M. Moldowon. Harward, Academic Publications. 117-131.