

Evaluation of Organic Matter, Hydrocarbon Source, and Depositional Environment of Onshore Warkalli Sedimentary Sequence from Kerala-Konkan Basin, South India

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ABSTRACT

Multidisciplinary analysis of the carbonaceous sediments of Warkalli Formation (Mio-Pliocene) from the Warkalli cliff section has been done to assess the source of organic matter, palaeo-depositional settings and the hydrocarbon potential. The *n*-alkane distribution from *n*-C₁₂ to *n*-C₃₃ along with bimodal distribution indicates significant organic matter contribution from microbial activity and higher plants. The contribution from angiosperm source vegetation is indicated by the oleanane type of triterpenoids. The hopanes distribution indicates the immature stage of the organic matter, which is in agreement with the T_{max} (av. 401 °C) and huminite reflectance (av. 0.28% R_p) values. The total organic carbon (TOC) contents vary between 0.8 and 6.72 wt. % in the studied sediments. Hydrogen index and oxygen index values range from 16 to 106 mg HC/g TOC, and 113 to 344 mg CO₂/g TOC, respectively. The maceral content is low, being dominated by the detrohuminite submaceral and the mineral matter accounts for 68 to 77% of the total composition. The phytoclast group (63-87%) is dominant with subordinate amorphous organic matter (4-35%). The study shows that the sediments were deposited in a marginal suboxic basin with intermittent variations. All the parameters unequivocally suggest that the studied sequence holds the potential to generate gaseous hydrocarbons.

INTRODUCTION

Miocene period marks the drastic changes in the palaeogeography of the Indian subcontinent. The period subsequent to the collision of Indian plate and Eurasian plates (~53 Ma) witnessed the changes in the denudation and sedimentation patterns in the western margin of the Indian subcontinent (Campanile et al., 2008). The Kerala-Konkan basin is located at the trailing edge of the Indian subcontinent, went through a major siliciclastic sedimentation starting from Miocene period. The strong tectonic reactivation due to Himalayan orogeny is considered as the reason of this sedimentation (Shah et al., 2009). Among these, the Mio-Pliocene sequences have been grouped as Warkalli Formation, consisting chiefly of sand and clay alternations with highly carbonaceous horizons. Although a major part of the Kerala-Konkan Basin is in the offshore region, some part is exposed in the onshore region mainly on the beach cliffs of the northern and southern Kerala.

The source vegetation aspects of Warkalli sequence, have been discussed by various workers (Awasti and Srivastava, 2005; Dutta et al., 2010; Kern et al., 2013; Reuter et al., 2013 and many others). Apart from this, the Kerala-Konkan basin has also been a locus of discussion and studies concerning the probable hydrocarbon resources. However, most of these studies were based on the offshore Mesozoic sub-basalt sequences (Shah et al., 2009; Mishra et al., 2011; Gorain, 2012; Fainstein et al., 2012). According to Singh and Lal (1993), the

basin consists of well defined structures, abundant reservoir bodies and possible source areas adequate enough for petroleum exploration. But even after several attempts, only few minor gas shows were identified (Kasargod -1 and KK-OS-II/B=1 wells, DGH report) and no economically viable deposits were found. For the first time, a multidisciplinary approach based on geochemical (Rock-Eval pyrolysis and biomarker analyses) and visual kerogen analysis (through palynofacies and maceral studies) have been performed to characterize the highly carbonaceous sedimentary rocks of Warkalli Formation, exposed at the beach cliff near Varkala. The aim of the study is to characterize the organic matter and providing valuable inputs about their morphological types, identifying the source of organic matters and maturation, and assessing the hydrocarbon potential of the sequence, besides distinguishing the depositional setting and its tempo-spatial variations.

GEOLOGICAL SETTING

The Kerala-Konkan Basin is the southernmost basin on the western continental margin of India. The basin lies to the south of the Bombay offshore basin, which is the major hydrocarbon producer of India (Singh and Sen, 2012). The structure, stratigraphy and facies distribution in the basin is largely controlled by the NNW-SSE trending fault parallel to the coastline and a NNE-SSW fault oblique to the Miocene shelf edge (Varadarajan and Nair, 1987; Singh and Sen, 2012). These faults also played a significant role in shaping the present day coastline (Varadarajan and Nair, 1987). On the continental part of the basin, the coastal cliffs are a prominent geomorphic feature formed intermittently over a cumulative length of 63.5 km along in the southern and northern tracts on the coastline of Kerala State (Kumar et al., 2009). These cliffs stand out as major outcrop sections of the Cenozoic sediments in the landward extension of Kerala-Konkan basin. This landward extension is also known as south Kerala sedimentary basin (SKSB; Nair et al., 1998). The cliff section near Warkalli (latitude: 8° 43' N, longitude: 76° 42' E) of Thiruvananthapuram in southern Kerala is occupied by Cenozoic siliciclastic sediments which unconformably overlies the Precambrian rocks (Krishnan, 1982; Soman, 1997: Fig.1a). These sediments uplifted during Mio-Pliocene to form the present-day cliffs (Krishnan, 1982). The location of Kerala-Konkan Basin is shown in Fig.1b.

The sediments on the Warkalli cliff section mainly composed of sandstones and clay alteration with carbonaceous horizons. The carbonaceous horizons with lignitic wood and resins are interbedded with sand and clay, and belong to the Warkalli Formation of Mio-Pliocene age (Poulose and Narayanaswami, 1968). However, it is also considered as Ambalapuzha Formation (Raha et al., 1983, Raha, 1996). Recently, Reuter et al. (2013) suggested an early to middle Miocene age to the sediments of Warkalli cliff section. The Warkalli Formation is considered as the equivalent of Cuddalore Formation of Cauvery

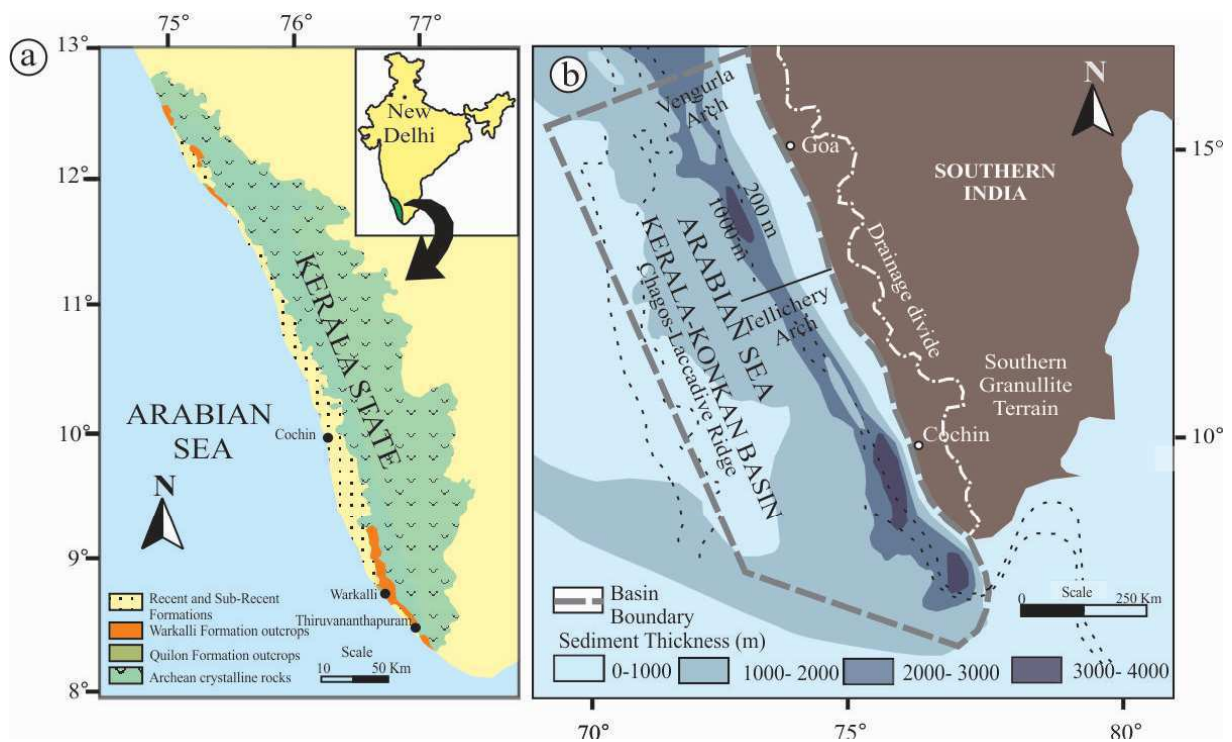


Fig.1. (a) Location of Warkalli in Kerala State, and (b) Kerala-Konkan Basin (modified from Campanile et al., 2008).

Basin. The Warkalli Formation extends over an area of 2,000 km². The sedimentary sequences of this formation are encountered in the offshore region as well (Prabhakar Rao, 1968). The siliciclastic sediments are overlain by the laterites of approximately 5 m thickness in the region.

SAMPLING AND METHODOLOGY

The total thickness of the studied Warkalli coastal cliff section is approximately 29 m. Based on pillar sampling method, 17 samples were collected from the section (Fig.2) and subjected to the following studies:

Gas Chromatography-Mass Spectrometry (GC-MS)

The soluble organic matter was extracted with dichloromethane:

methanol (9:1) mixture from the oven-dried powdered samples using ultrasonication for 30 minutes. Excess of *n*-pentane (40 ml) was used to precipitate asphaltenes. Consecutively, various fractions were separated and analyzed using an Agilent 7890A GC connected to Agilent 5975C MS. The GC is equipped with HP-5MS column (30 m×0.25 mm i.d., 0.25 μm film thicknesses) fused silica capillary column. Carrier gas used was the Helium (He) at a flow rate of 1 ml/min. Initially, the oven temperature in GC was held at 40 °C (5 mins), then ramped at a rate of 4 °C/min to 310 °C which was held for a final 5.5 mins. The 70 eV mass spectra were obtained in full scan (*m/z* 50-550) mode. Data processing is done using Chemstation software. Peak assignments were based on GC retention time and mass spectral data including comparison to MS library and published mass spectra.

Rock-Eval Pyrolysis

Rock-Eval pyrolysis was conducted using a "Turbo" Rock-Eval-6 pyrolyser manufactured by Vinci Technologies®. The pyrolysis method consists of a programmed temperature heating (in a pyrolysis oven) in an inert atmosphere. The procedure of the analysis is elaborated by Lafargue et al. (1998). The samples were first pyrolysed under an inert N₂ atmosphere, and the residual carbon was subsequently burnt in an oxidation oven. The amount of hydrocarbons released during pyrolysis was detected with a flame ionisation detector, while online infrared detectors measure continuously the released CO and CO₂. The samples were first pyrolysed from 100°C to 650°C at a rate of 25°C/min. The oxidation phase starts with an isothermal stage at 400°C, followed by an increase to 850°C at a rate of 25°C/min to burn out all the residual carbon.

Palynofacies

For palynofacies analysis, the samples were treated with HCl (to remove carbonates) and HF (to dissolve silica) acids, following the method of Batten and Stead (2005). The prepared slides were observed under transmitted white light, and 300 counts of particulate organic matter were taken. The degree of preservation, the colour of maturation and size of the organic matter (OM) were taken into consideration for qualitative analysis. The counted OM was categorized under phytoclast,

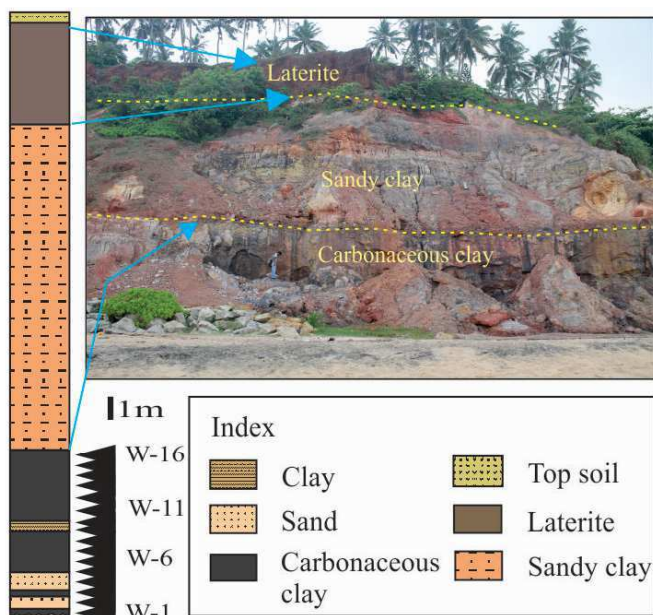


Fig.2. Lithology, sample distribution and photograph of the studied Warkalli cliff section.

amorphous OM and palynomorph groups based on the classification suggested by Mendonça Filho et al. (2012). Phytoclasts constitute tissues of higher plant origin, cuticles and membranes, wood derived materials (structured and non-structured) and fungal hyphae. Palynomorphs include pollen, plant spores and fungal spores, dinoflagellate, and foraminiferal linings, whereas AOM comprises of structureless plant matter which are severely degraded (seen as fluffy mass), and marine algae.

Organic Petrography

For microscopic examination, pellets were prepared following the recommendations of International Committee for Coal and Organic Petrology (ICCP). First, the lignite fragments of ± 18 mesh size (between $\pm 1-2$ mm grain) were embedded in Buehler's epoxy resin and hardener mixture in the ratio 5:1 and polished. ISO 7404-2, ISO 7404-3, and ISO 7404-5 (2009) standards were followed in the preparation of samples, maceral analyses, and reflectance measurements respectively. The petrographic study was performed on Leica DM 4500P microscope. Normal reflectance and fluorescence (blue light excitation) modes were simultaneously used during the microscopic observation adopting the Single-Scan method, using oil immersion objective (50 x).

Sikorová et al. (2005), Taylor et al. (1998) and ICCP (2001) were followed in the description and terminology for huminite, liptinite and inertinite groups of macerals respectively as provided by the ICCP. Automatic computerized point counter utilizing Petroglite software (2.35 versions) was used for quantitative estimations of macerals. The estimation was obtained based on 500 counts per sample. Sapphire (0.594) was used as a standard in huminite reflectance measurements and is performed using immersion oil (refractive index: 1.518), photometry system (PMT III), and software MSP 200.

RESULTS AND DISCUSSION

Source of the Organic Matter

The identification of organic source can be made based on biomarker studies (eg. Bianchi et al., 1993; Prahel et al., 1994; Canuel et al., 1997; Canuel and Zimmerman, 1999; Goñi and Thomas, 2000; Jaffé et al., 2001; Wakeham et al., 2002; Mead et al., 2005), organic petrography and palynofacies (Suarez-Ruiz et al., 2012 and the references therein). Nevertheless, multidisciplinary approaches can provide more refined results.

The selected ion chromatograms representing *n*-alkanes (*m/z* 57) and triterpenoids (*m/z* 191) in the saturated fraction of the studied samples are given in Figs. 3 and 4 respectively. The identified biomarker compounds are listed in Table 1. The distribution patterns are characterized by the homologues series of *n*-C₁₂ to *n*-C₃₃ molecular range. A bimodal distribution is evident in most of the samples. Substantial amounts of hopanes are also identified in the selected ion chromatogram of the sediment extracts representing triterpenoids. The non-hopanoid pentacyclic triterpenoids; olean-12-ene and olean-18-ene are also identified. The palynofacies analysis shows the dominance of phytoclast group in all the samples (63-87%; Table 2, Fig.5). The striate and striped phytoclasts with more irregular outlines are dominant in all the samples. The cuticles with visible stomatas are also present. AOM sub dominates (4-35%) the particulate organic matter content with minor palynomorphs (2-11%). The representative microphotographs of various palynofacies components are shown in Fig.6. The organic petrographical compositions of the samples in terms of maceral and mineral matter contents are listed in Table 3. Representative microphotographs of various macerals and minerals are shown in Fig.7. The study shows that the major content is the mineral matter in the studied samples (range: 68-77%) with a dominance of clay minerals, which appears fluorescence (Fig.7a). The

Table 1. Biomarker compounds identified in the saturate fraction of Warkalli samples

Peak no.	Compound	Base peak	Molecular ion
1	De-A-triterpanoid	313	328
2	De-A-Lupane	123	330
3	De-A-triterpanoid	109	330
4	De-A-triterpanoid	95	330
5	17,21-secohopane (C25)	191	344
6	22,29,30-Trisnorneohop-13(18)-ene	191	368
7	Unknown compound	190	408
8	17 \pm (H)-22,29,30-Trisnorhopane	191	370
9	17 ² (H)-22,29,30-Trisnorhopane	149	370
10	Neohop-13 (18)-ene	191	410
11	30-norhopane	191	398
12	Olean-12-ene	218	410
13	Olean-18-ene	204	410
14	Hop-17(21)-ene	367	410
15	17 ² (H),21 \pm (H)-30-Norhopane	177	398
16	\pm^2 -hopane	191	412
17	17 ² (H),21 \pm (H)-30-Norhopane	177	398
18	17 \pm (H),21 ² (H)-Homohopane (22 S)	191	426
19	17 \pm (H),21 ² (H)-Homohopane (22 R)	191	426
20	²² -hopane	191	412
21	17 ² (H),21 ² (H)-Homohopane	205	426

fluorescence of the clay-mineral groundmass is an indication of the presence of microscopically invisible organic matter (Jasper et al., 2009). Siderite (Fig.7b) and pyrite (Fig.7c) minerals are also present in small amounts. The huminite group dominates which is typical in peat, lignite or bituminous coal (Taylor et al., 1998; Sýkorová et al., 2005). The detrohuminite (detritus: attrinite + densinite) forms the major constituent of the huminite group varying from 4 to 28 vol. %. Although the subgroup telohuminite (structured macerals: ulminite + textinite) are present (Fig.7d), their representation is fairly low. Few corpohuminite grains are also recorded in the samples (Fig.7e). The liptinite group of macerals varies from 1 to 5 vol. %, and is mainly represented by the sporinite (pollen-spores), cutinite (cuticles), resinite (resins/wax/latex), suberinite (suberins), and liptodetrinite (detritus). Sporinites with ornamentation is the most common form (Fig.7f) Cutinites are relatively thin and occur as fragments (Fig.7h). The inertinite group macerals are sporadic and is represented mainly by the funginite (0.5-2 vol. %, Fig.7l).

The distribution pattern of *n*-alkanes is generally based on contributions from terrestrial/emergent plants, floating/submerged

Table 2. Result of palynofacies analysis of the Warkalli samples

Sample no.	AOM (%)	Phytoclasts (%)	Palynomorphs (%)
W-16	10	83	7
W-15	9	85	5
W-14	17	76	7
W-13	8	83	9
W-12	16	78	6
W-11	35	63	2
W-10	15	75	11
W-9	17	78	5
W-8	10	86	3
W-7	13	82	5
W-6	23	72	6
W-5	4	87	9
W-4	11	81	8
W-3	30	65	5
W-2	12	80	8
W-1	17	79	5
Average	16	78	6

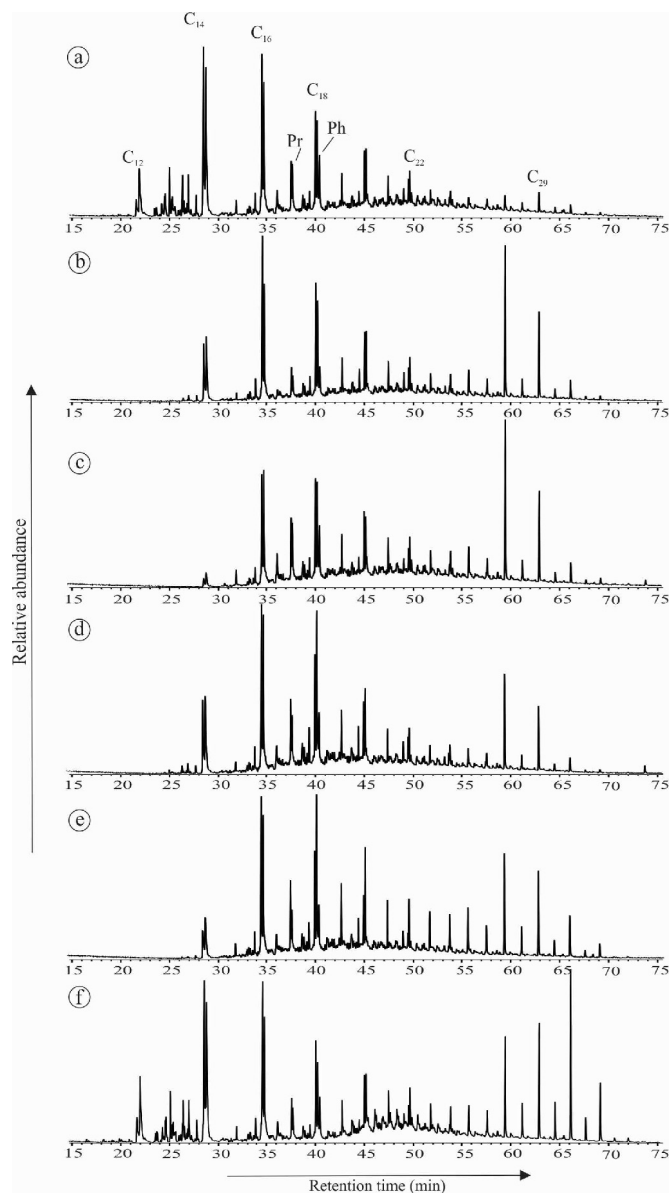


Fig.3. Partial mass chromatograms (m/z 57) of samples (a) W-16, (b) W-13, (c) W-11, (d) W-10, (e) W-3, (f) W-1.

vegetation and aquatic algae and bacteria (Regnery et al., 2013). However, it can vary depending on the degree of maturity of the organic matters, redox conditions and the mineral matter contents (Eglinton and Hamilton, 1967; Shimoyama and Johns, 1972; Cranwell et al., 1987; Püttmann and Bracke, 1995). A bimodal distribution is evident in most of the samples with the dominance of short chain n -alkanes (maximizing at n -C₁₆) and long chain n -alkanes (maximizing at n -C₂₇); suggesting diverse organic matter source. The high abundance of short-chain n -alkanes ($< n$ -C₂₀) with the predominance of even C-number is evident in some of the samples (Fig. 3a, d, e). Three possible sources for these n -alkanes are microbial alteration of algal detritus, reductive process acting on alkanolic acids or lipid compounds, and direct microbial input (Welte and Ehardt, 1968; Welte and Waples, 1973; Dembicki et al., 1976; Simoneit, 1977a, b; Grimalt et al., 1986; Nishimura and Baker, 1986). Microorganisms of various species (e.g., bacteria, fungi, yeast) are also known to produce even C-numbered n -alkanes in the range of n -C₁₂ to n -C₂₂. However, a predominant origin of organic matter from algae and microorganisms is indicated by the occurrence of short-chain n -alkanes in high amounts (Cranwell, 1977). The triterpenoid distribution shows a high relative abundance of by Neohop-13(18)-ene, 30-norhopane and 17 α (H) and 21 β (H)-

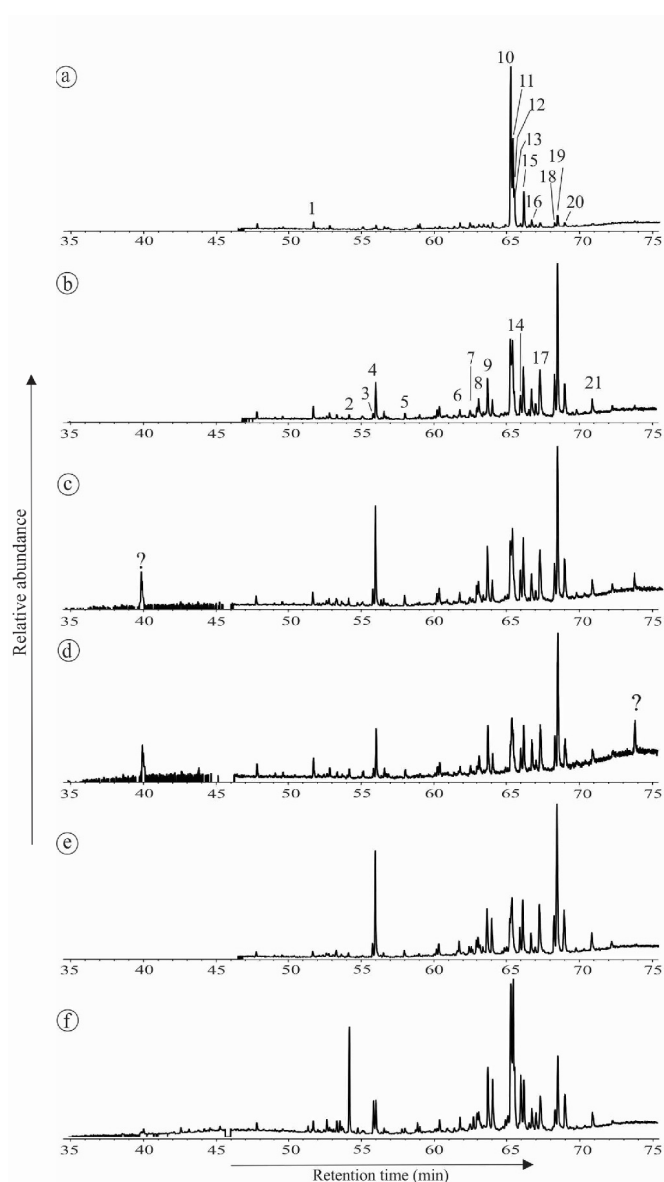


Fig.4. Partial mass chromatograms (m/z 191) of samples (a) W-16, (b) W-13, (c) W-11, (d) W-10, (e) W-3, (f) W-1.

homohopane. These pentacyclic compounds are mainly derived from bacterio-hopantetrol and to some extent 3-desoxyhopanes (Ourisson et al., 1979; Rohmer et al., 1992). The extended hopanes, 22R and 22S epimer of 17 α (H), 21 β (H)-homohopanes and 17 β (H), 21 β (H)-homohopane, are present in the samples, which are considered to be formed from the bacterio-polyhopanol present in the prokaryotic cell membrane (Roushdy et al., 2010). The AOM which lacks a distinct and recognizable outline indicates microbial degradation of organic matter (Tyson, 1995; Kumar et al., 2012). Together with hopanoid distribution, the copious presence of AOM in most of the samples (4-35%; Table 2, Fig.5) further suggests prominent microbial activity on the peat biomass.

The co-dominance of odd C-numbered long chain n -alkanes in the range between n -C₂₇ to n -C₃₁ and triterpenoids suggests typical higher plants source, in which they occur as the major constituent in plant waxes (Eglinton and Hamilton, 1963, 1967; Pant and Rastogi, 1979; Halloway, 1982; Wolff et al., 1989; Trendel et al., 1989; ten Haven et al., 1992) indicates the input from terrestrially derived plant material. This is further supported by the predominance of macerals of the huminite group and dominance of phytoclasts in the particulate organic matter. In addition, the calculated carbon preference index

Table 3. Macerals contents (Vol. %), mineral matter content (Vol. %) and huminite reflectance (Rr %) of the studied Warkalli samples.

Sample No.	W-1	W-3	W-7	W-16	Average
Macerals					
Huminite(H)	17	5	5	30	14
Telohuminite	2	0	1	2	1
Textinite	1	0	0	1	
Ulminite	2	0	1	1	
Detrohuminite	15	5	4	28	13
Attrinite	7	3	2	4	
Densinite	8	2	2	24	
Gelohuminite	0	0	0	0	0
Corpohuminite	0	0	0	0	
Gelinite	0	0	0	0	
Liptinite (L)	5	3	1	1	2
Sporinite	1	0	1	1	
Cutinite	2	1	1	0	
Suberinite	0	0	0	0	
Resinite	1	1	0	0	
Alginite	0	0	0	0	
Bituminite	0	0	0	0	
Fluorinite	0	0	0	0	
Exsudatinitite	0	0	0	0	
Liptodetrinite	2	2	0	0	
Inertinite (I)	2	1	0	0	1
Semifusinite	0	0	0	0	
Fusinite	0	0	0	0	
Funginite	2	1	0	0	
Secretinite	0	0	0	0	
Micrinite	0	0	0	0	
Macrinite	0	0	0	0	
Inertodetrinite	0	0	0	0	
Mineral Matter (Total)	77	92	94	68	83
Other	76	92	94	68	
Pyrite	1	0	0	1	
Fluorescing H	6	3	4	8	
Non-fluorescing (H)	11	2	1	22	
Total Fluorescing (H+L)	11	6	5	9	
Non-fluorescing (H+I+M)	89	95	95	90	
H (mmf)	72	56	83	98	
L (mmf)	21	38	17	2	
I (mmf)	6	6	0	0	
Rr mean %	0.26	0.28	0.27	0.24	0.26

(CPI) values are greater than 1 in all the studied samples (Table 4). The CPI values >1 indicate a predominant higher-plant input, whereas values >5 suggest significant input of the vascular plant (Peters et al., 2005). However, a significant bacterial activity can also lead to low CPI values (Chaffee et al., 1986; Stefanova et al., 1995). Higher terrigenous aquatic ratio (TAR) values (>1) are attributed to terrestrial sources, whereas lower values (<1) indicates aquatic input. However, higher proportions of *n*-alkanes are typically found in the land-derived

Table 4. *n*-Alkane parameters calculated for the Warkalli samples

Sample	CPI	TAR	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈
W-16	1.43	0.59	0.61	0.69	0.35
W-13	3.62	4.58	0.73	0.93	0.76
W-11	2.57	4.74	1.01	1.06	0.68
W-10	3.37	1.85	0.79	0.70	0.37
W-3	2.29	2.25	0.85	0.58	0.29
W-1	1.58	4.48	0.63	0.73	0.72

CPI = $2(n-C_{23} + n-C_{25} + n-C_{27} + n-C_{29}) / (n-C_{22} + 2(n-C_{24} + n-C_{26} + n-C_{28}) + n-C_{30})$ (Peters and Moldowan, 1995)

TAR = $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{15} + n-C_{17} + n-C_{19})$ (Bourbonniere and Meyers, 1996)

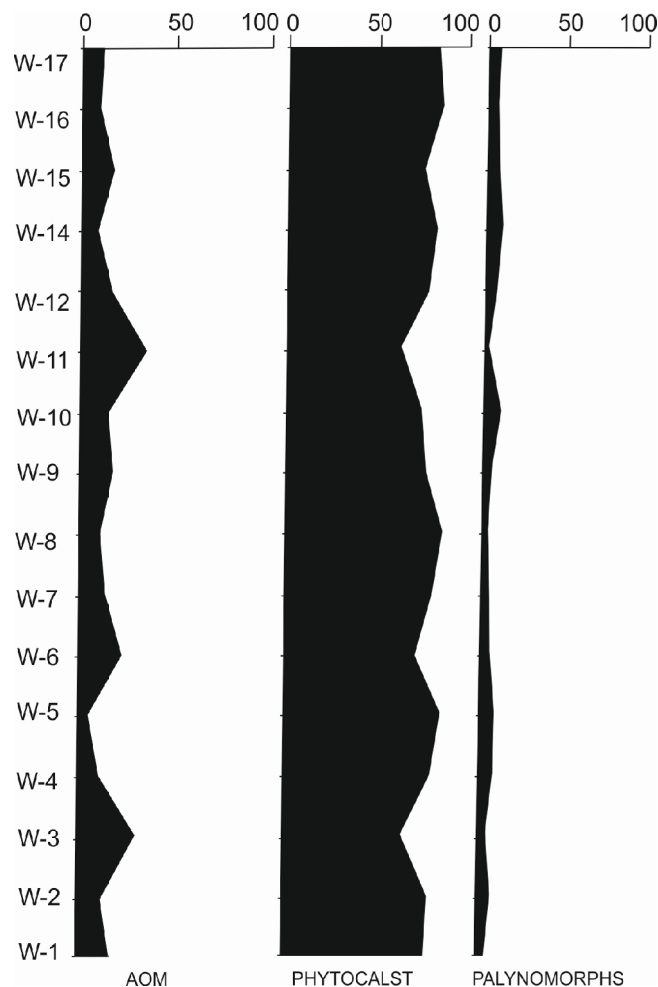


Fig.5. Frequency distribution of the various palynofacies components in the studied samples.

organic matter than those from aquatic algae, and therefore TAR may over-represent the total amounts from terrigenous sources (Cranwell et al., 1987; Goossens et al., 1989; Meyers and Ishiwatari, 1993). Nevertheless, this ratio is significant in ascertaining the relative input from terrigenous and aquatic sources (Meyers, 1997). In Warkalli sediments, the TAR values are high (Table 4) in most of the samples which are consistent with the prominent higher plant input. However, the topmost sample (below the sandy clay horizon) showed low value suggesting more aquatic input.

Earlier studies on Warkalli sediments based on palynomorphs (Ramanujam, 1987; Singh and Rao, 1990; Rao and Rajendran, 1996), megafossils (Awasti and Ahuja, 1982; Awasti and Panjwani, 1984; Awasti and Srivastava, 1989, 1990, 1992, 2005) and resin chemistry (Dutta et al., 2010) indicated the presence of the angiosperm vegetation in Warkalli sediments. The present study shows the occurrence of non-hopanoid pentacyclic triterpenoids with oleanane type of carbon skeletal structure which are considered to be derived from β -amyryn in higher plants during diagenesis (Philp, 1985; Simoneit, 1986; Trendel et al., 1989, ten Haven et al., 1992). Angiosperm wood, root, and bark form the source of these compounds in which they are a major constituent (Karrer et al., 1977). Therefore, the occurrence of these triterpenoids also supports significant angiosperm source input in Warkalli sediments.

Hydrocarbon Source Characteristics

Rock-Eval pyrolysis technique is the most widely used method to characterize the hydrocarbon source rock (Hunt, 1979; Peters, 1986; Dahl et al., 2004). Palynofacies analysis also serves as an efficient

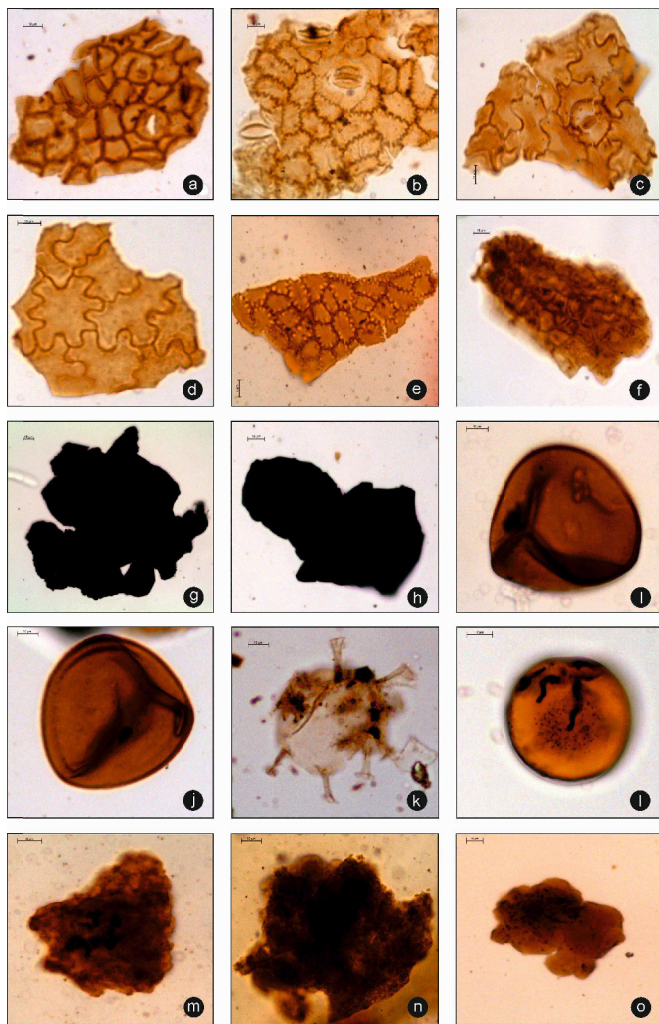


Fig.6. Representative palynofacies components in studied Warkalli samples (a-f) non-opaque phytoclast, (g-h) opaque phytoclast, (i-k) palynomorphs, (l) resin and (m-o) amorphous organic matter.

tool to know the hydrocarbon potential of source rocks (Batten, 1981, 1996; Tyson, 1995). In addition, organic petrography is also being convincingly applied to evaluate source rock potential (Taylor et al., 1998). Source rock characterization includes the determination of three main factors viz., the amount of organic matter, the type of kerogen, and the thermal maturity attained by the organic matter.

Amount of Organic Matter

The two useful measurements related to the quantity of organic matter are the total organic carbon (TOC), and the hydrocarbons generated during pyrolysis (S2). In Rock-Eval pyrolysis method, the TOC is determined by the sum of the carbon in the pyrolyzate with that obtained by oxidizing the residual OM (Peters, 1986). Based on TOC, Peters (1986) defined the source rocks as poor (0-0.5 wt. %), fair (0.5-1 wt. %), good (1-2 wt. %) and very good (>2 wt. %). The TOC content of Warkalli samples ranges from 0.8 to 6.72 wt. % with an average of 3.45 wt. % (Table 5). The majority of the studied samples show TOC values >2 wt%; suggesting that these sediments are of fair to the excellent source potential. However, most of the samples analyzed have S2 yields less than 2.0 mg HC/g rock, and only 2 samples (W1 and W11) showed higher values (Table 5).

Pyrolysis S2 yields <2.0 mg HC/g rock are generally considered to be source rocks with poor generative potential; yields greater than 2.0 mg HC/g rock are of fair to excellent potential (Ryu, 2008). Thus, although having enough TOC, the S2 yields indicate that most samples

are having poor generative potential, but high TOC and S2 yields of samples W-1 and W-11 indicate that these samples (sediments) can generate hydrocarbons.

Type of Kerogen

A van Krevelen plot of whole rock hydrogen index (HI) and oxygen index (OI) can be used to classify the dominant type of kerogen (i.e., gas or oil prone) in potential source rocks (Tissot and Welte, 1978; Bordenave et al., 1993). The HI in the studied samples varies from 16 to 106 mg HC/g TOC, and the OI varies from 113 to 344 mg CO₂/g TOC (Table 5). HI values are high from middle to lower part of the sequence, and the bottom most sample showed the highest HI value. The HI vs. OI plot (Fig. 8) indicates that the studied sequence contains type III kerogen (gas prone).

A cross plot between S2 and TOC provides the kerogen type as well as the potential to generate hydrocarbons. Espitalié et al. (1985) pointed out that during pyrolysis, type I kerogen can yield up to 80 wt.% hydrocarbons (H₂~HI of 800 mg/g TOC), type II kerogen up to 50-60 wt.% hydrocarbon (H₂~HI of 500-600 mg/g TOC), and type III kerogen can yield at most 15-30 wt.% hydrocarbons. The line marked at 700 mg HC/g TOC (organic material with 70 wt.% hydrocarbon) is proposed as a boundary to separate type I from type II kerogens in the S2 vs. TOC diagram (Erik et al., 2006). According to Langford and Blanc-Valleron (1990) an HI = 200 (H₂~20 wt. % hydrocarbons) is the boundary between type II and III kerogens. These lines made on the S2 vs. TOC diagram based on the HI values separate various kerogen types (Langford and Blanc-Valleron, 1990).

The S2 vs. TOC plot for the studied Warkalli samples is shown in Fig.9. It also shows that the associated kerogen is of type III. The palynofacies analysis showed the predominance of phytoclasts (terrestrial woody material) in these samples. This also suggests the input of dominantly type III kerogen/organic matter (Tyson, 1995). Petrographically, the dominance of huminite macerals is also pointing towards the gas prone kerogen. The presence of type III kerogen clearly indicates that the carbonaceous-rich Warkalli samples can generate gaseous hydrocarbon.

Thermal Maturity

Thermal maturity data are a key component of basin analysis and hydrocarbon assessment. Although source rocks have adequate organic material contents and kerogen types suitable for oil and/or gas production, it takes a long time for them to produce hydrocarbons unless they are buried to a sufficient depth (Sari and Aliyev, 2006).

Table 5. Rock-Eval parameters measured for the Warkalli samples

Sample	S1	S2	S3	T _{max}	HI	OI	TOC
W-16	0.07	0.34	2.42	381	16	113	2.14
W-15	0.21	1.11	7.67	390	17	114	6.72
W-14	0.05	0.2	1.5	397	25	188	0.8
W-13	0.07	0.23	2.41	367	18	188	1.28
W-12	0.25	1.78	11.37	406	28	180	6.31
W-11	0.19	2.64	9.97	410	41	156	6.41
W-10	0.06	0.52	2.76	415	40	212	1.3
W-9	0.2	1.51	11.9	406	44	344	3.46
W-8	0.13	1.23	5.34	411	43	185	2.88
W-7	0.14	1.39	4.46	413	55	175	2.55
W-6	0.13	1.37	5.05	408	48	176	2.87
W-3	0.15	1.05	4.46	399	43	183	2.44
W-1	0.66	6.1	6.3	416	106	139	5.78
Average	0.17	1.49	5.81	401	40	181	3.4

S1= free hydrocarbons (mg HC/g), S2= amount of hydrocarbons (mg HC/g), S3= released carbon dioxide (mg CO₂/g), T_{max}= temperature maximum (°C), OI= oxygen index= (S3/TOC) × 100; (mg HC/g TOC), HI= hydrogen index= (S2/TOC) × 100; (mg HC/g TOC), TOC= total organic carbon (%)

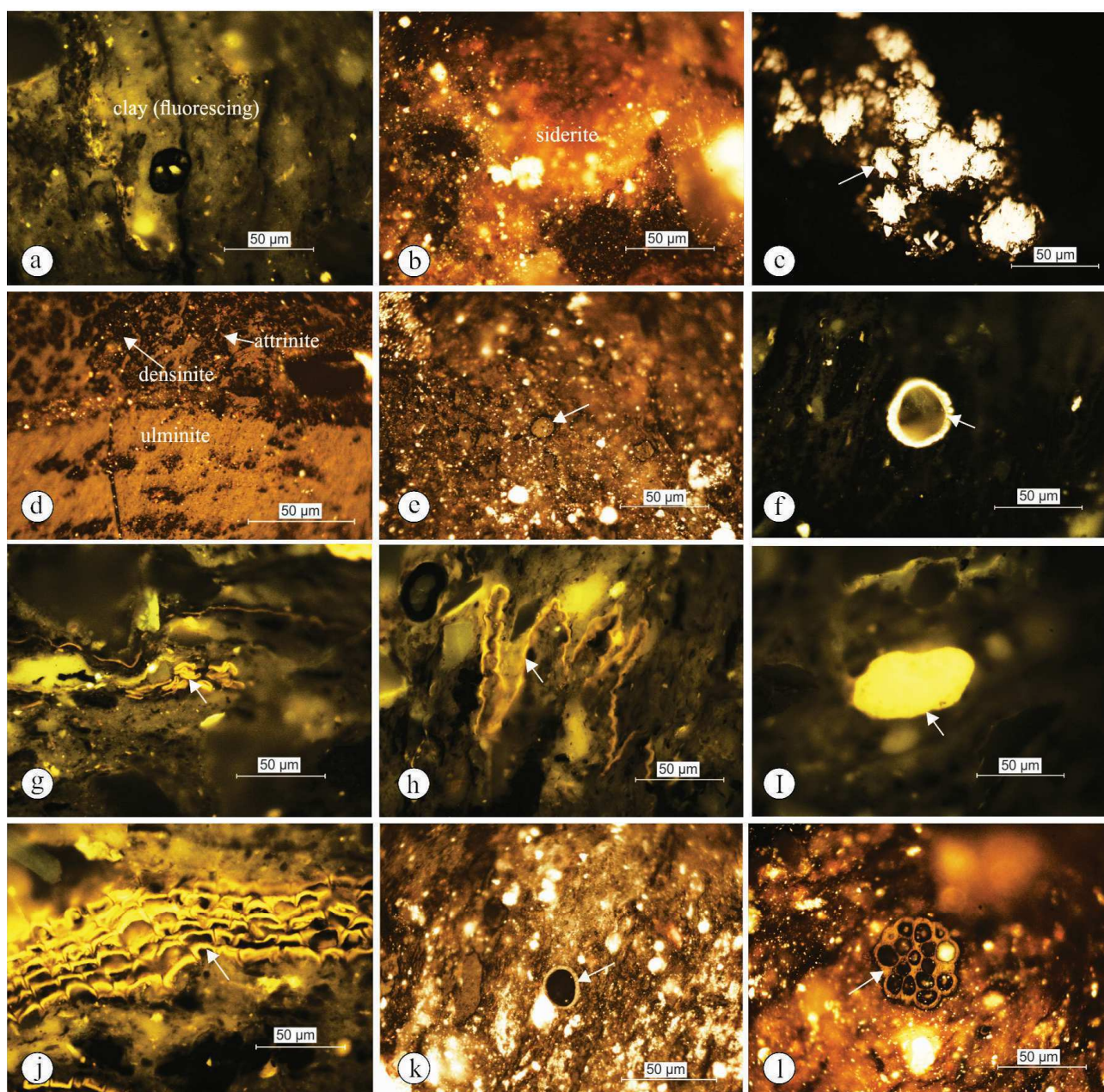


Fig.7. Photomicrographs of representative minerals and macerals (a) clay, (b) siderite, (c) pyrite, (d) ulminite, attrinite, densinite, (e) corphominite, (f-g) sporinite, (h) cutintie, (i) resinite, (j) suberinite, (k-l) funginite. Photomicrographs taken under reflected white light (b-e and k-l) and in fluorescence mode (a, f-j).

The T_{max} data provide constraints on the maximum depth of burial and paleogeothermal gradient (Dewing and Sanei, 2009). The Rock Eval T_{max} ($^{\circ}C$) defines the level of thermal maturity attained by the organic matter. T_{max} is an index of maturity because, the temperature at which the maximum rate of pyrolysis increases with the increase in maturity of kerogen. For type III kerogen, the oil window will start at the T_{max} in the range 430-435 $^{\circ}C$ (Espitalié, 1986). The cross plot between HI and T_{max} (Fig.10) also shows the kerogen type and the maturity attained by the organic matter. The T_{max} values of the studied samples range from 367 $^{\circ}C$ to 416 $^{\circ}C$ with an average of 401 $^{\circ}C$ (Table 5) indicates that the samples are having type III kerogen, and constituted by immature organic matter. The mean random huminite reflectance (R_r) values of the studied samples also range from 0.24 to 0.29% R_r (av. 0.26% R_r ; Table 3) suggesting that the organic matter is in the immature stage, which is consistent with the T_{max} values. The maturity values (R_r) falls under the early diagenetic zone of methane generation (Taylor et al., 1998). A general increase in the T_{max} is also observed

from middle to bottom parts of the section which is consistent with the increase in HI values.

Thermal maturity of the sediments can also be identified from the biomarker composition. In Warkalli samples, mono-unsaturated hopenes like hop-17(21)-ene and neohop-13(18)-ene are identified (Table 1). These compounds have been reported from many immature sediments (e.g. Bechtel et al., 2003; Sinninghe Damste et al., 2014). Hopanes with the $17\alpha,21\beta(H)$ and $17b,21\alpha(H)$ are also identified which are thermodynamically more stable compounds (Ensminger et al., 1974; Rohmer et al., 1980). However, the predominance of $17\beta(H)$ over the $17\alpha(H)$ suggests that these sediments have experienced only a mild thermal maturation (Ensminger et al., 1977). The mild thermal maturation is also indicated by the presence of least stable $\beta\beta$ -hopanes (Paul and Dutta, 2015). As the Warkalli sedimentary sequence is extending towards the continental shelf and encountered at greater depths (Prabhakar Rao, 1968), chances to attain the required thermal maturity to produce thermogenic hydrocarbons cannot be ruled out. It

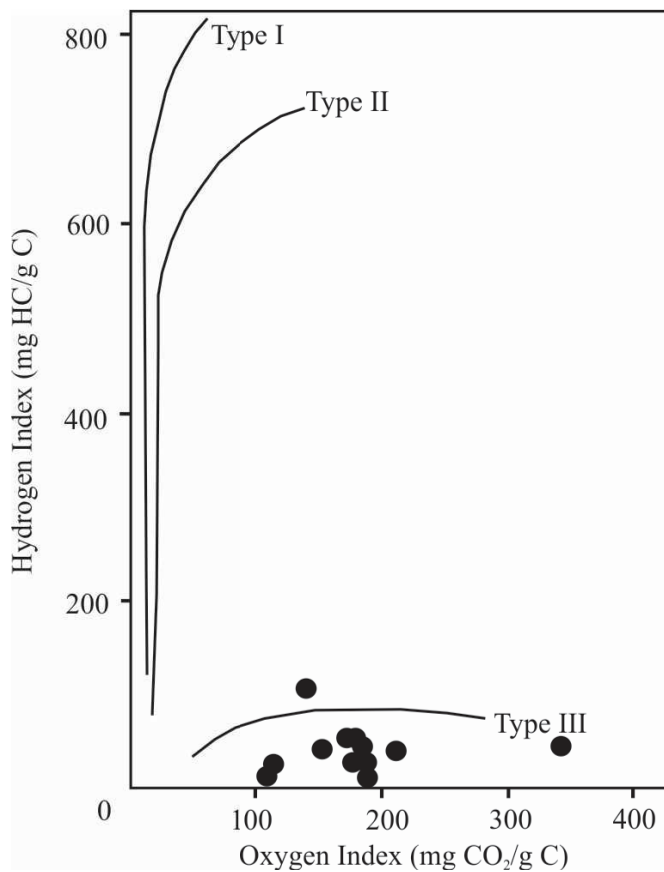


Fig.8. The HI vs. OI plot of Warkalli samples.

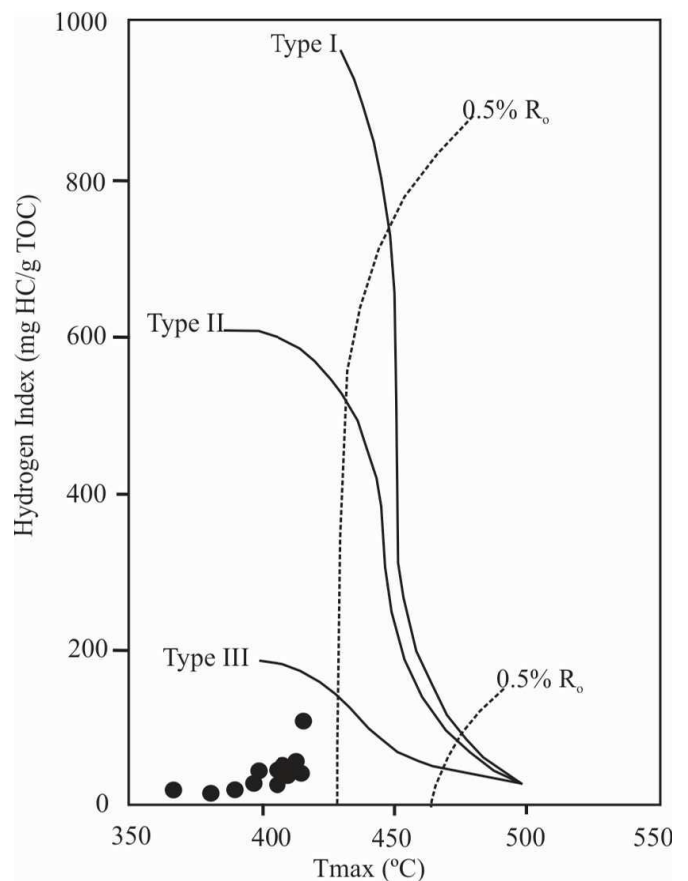


Fig.10. The plot between HI and T_{max} of Warkalli samples.

is also noted that the immature organic matter can produce biogenic gas from the bacterially mediated anaerobic mineralization. These gaseous hydrocarbons mostly contain methane, up to 2% of ethane, propane butane and pentane can also occur (Rice and Claypoole, 1981). However, the distribution of gas and its trapping mechanisms along with the structural and hydrodynamic history of the study area should be taken into account. Looking into the increasing demand of natural gas worldwide, these shallow organic-rich deposits need more attention to meet the future energy requirements.

Depositional Environment

The organic-rich sediments contain incorporated and preserved

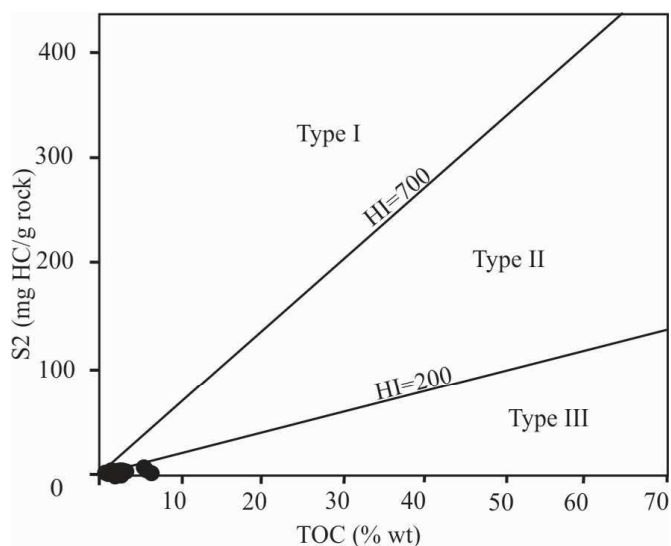


Fig.9. The S2 vs. TOC plot of Warkalli samples.

organic matters that can provide important information on the biological input (e.g. aquatic vs. terrestrial), bioproductivity or eutrophication levels, redox potential, and other palaeoenvironmental attributes (Lüniger, L. Schwark, 2002). These organic matter reflect the facies, and can record the changes occurred on the palaeo-environment (Carvalho et al., 2006). The study of biomarker compositions can provide the most detailed information on palaeoenvironmental conditions. The ratio of isoprenoids, pristane (Pr) and phytane (Ph) is one of the most commonly used geochemical parameters as the indicator of the redox conditions in the depositional environment and source of organic matters (Powell and McKirdy, 1973; Didyk et al., 1978). In an oxidizing environment, the phytol side-chain of chlorophyll is believed to lead to the formation of pristane and under reducing condition, result to the formation of phytane. Therefore, high Pr/Ph ratios generally indicate the oxidation of organic matter, and low values suggest reducing conditions. However, this ratio can be modified by various factors such as maturation (Tissot and Welte, 1984), and differences in the precursor source inputs (Volkman and Maxwell, 1986; ten Haven et al., 1987; Peters et al., 2005). The Pr/Ph ratio >3 reflects a strong input from the terrigenous oxidized environmental conditions, whereas the ratio <0.8 suggests anoxic conditions (Peters et al., 2005). In the studied Warkalli samples, the ratio ranges from 0.61 to 1.01 (Table 4); suggesting a suboxic condition of the basin during the peat deposition. The oxic environments are characterized by the strong fungal degradation. Fungal attack on structured organic matters in the oxidizing environment leads to the formation of AOM by bacterial action (Ercegovic and Kostia, 2006). The high relative or absolute abundances of AOM-usually associated with sediments beneath upwelling water masses was taken to indicate bottom water of low (dysoxic) oxygen concentrations (Davey and Rogers, 1975; Tissot and Pelet, 1981; Summerhayes, 1983; Paction et al., 2011). AOM has been

found to decrease in shallow shelf sediments and increase in a basinward direction, in darker-coloured, organic-rich facies with dysoxic-anoxic conditions (Dow and Pearson, 1975; Bujak et al., 1977; Pacton et al., 2011). AOM is present in low-moderate content further suggests the suboxic nature of the basin. The extrapolation of the frequency of AOM, phytoclasts, and palynomorphs in the APP ternary diagram of Tyson (1995) is given in Fig.11. The cluster over field-II indicates a dysoxic-anoxic basin conditions. It also suggests that the deposition of these sediments occurred mainly in a shoreline and brackish/freshwater (marginal marine) conditions.

The low $Pr/n-C_{17}$ and $Ph/n-C_{18}$ values (Table 4) compared to oils, and immature kerogen indicates a low extent of diagenetic transformation of phytol in the depositional setting (Bechtel et al., 2002; Zdravkov et al., 2011). Padmalal et al. (1995) suggested that the Warkalli carbonaceous sediments are deposited in continental conditions. In the present study, the plot of $Pr/n-C_{17}$ vs. $Ph/n-C_{18}$ suggests that the encountered organic matters were deposited in a transitional environment (Fig.12). Earlier studies on Warkalli sediments based on palynomorph and ostracod assemblages suggest marginal marine, brackish lagoons and brackish and freshwater swamps (Rao and Ramanujam, 1975; Ramanujam, 1987; Rao, 1995). Recently, Kern et al. (2013) suggest a coastal environment, from the intertidal zone to the back swamps.

Sediment Characteristics

The Warkalli Formation in the onshore part of the Kerala-Konkan Basin is dominated by siliciclastic sediments with interbedded lignite seams (Poulose and Narayanaswamy, 1968; Rao and Rajendran, 1996; Kumaran et al., 2008). Macroscopically, the carbonaceous-rich samples collected from the Warkalli beach cliff section are black in colour. However, they are sticky in contact with water; indicating its rich clay content. Typically, lignite/coal is characterized based on the maceral and mineral matter content, rank/thermal maturity, ash yield or mineral content (grade), and the sulphur content. It can be distinguished from other organic-rich rocks either macroscopically or comparison of petrographic composition (macerals) with the TOC content. Coal can be defined as an organic-rich sedimentary rock with TOC content in excess of 50 wt. % (Jasper et al., 2009). Generally, Indian lignites are characterized by the TOC content greater than 30 wt. % (Raju and Mathur, 2013).

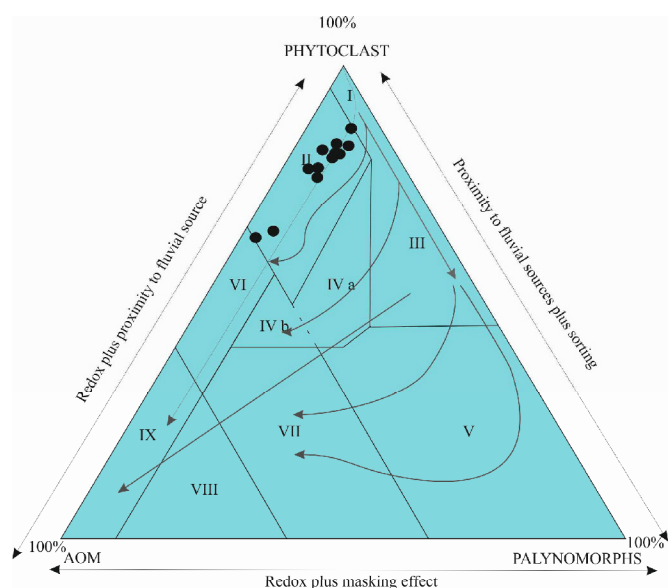


Fig.11. Amorphous organic matter–Palynomorphs–Phytoclast (APP) diagram (Tyson, 1995), showing representation of organic matter groups and depositional fields for the studied section.

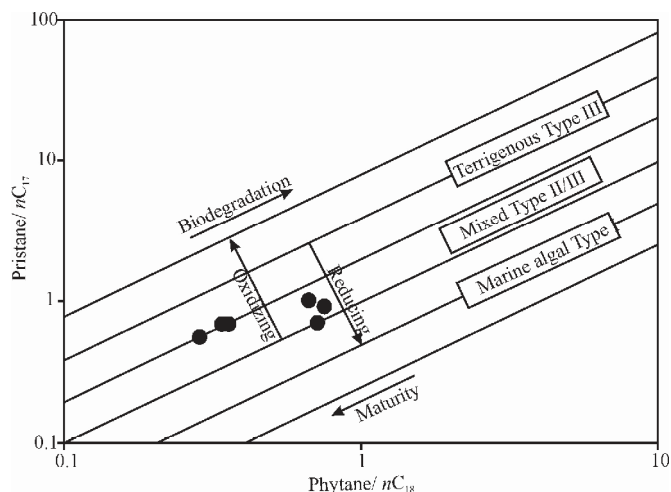


Fig.12. The plot of $Pr/n-C_{17}$ vs. $Ph/n-C_{18}$ reflecting the depositional environment.

In organic matter-rich sediments such as carbonaceous shales, the maceral contents range between 10 and 40 vol.%, and TOC between 5 and 20 wt.%. In other clastic rocks, the maceral composition is typically less than 5 vol. %, and the TOC is rarely higher than 2 wt. % (Jasper et al., 2009). However, the TOC and maceral composition are always not comparable because of the presence of submicroscopic organic matter. In clay-rich rocks like mudstone often has a high amount of microscopically invisible organic matter, embedded in the groundmass (Scheidt and Littke, 1989). In Indian lignites, the average mineral matter content varies from 7 to 20 vol. % (Singh, A. et al., 2012, 2013, Singh, P.K. et al., 2015; Singh, V.P. et al., 2017). According to Wüst et al. (2001), the organic-rich soil or sediment with 65-80 % mineral matter (ash, dry basis) can be classified as 'carbonaceous-rich soil/sediment'. Hence, with the major dominance of clay minerals, the studied samples of Warkalli Formation exposed on the beach cliff sections can be considered as carbonaceous clay. This is well supported by the TOC content which is less than 5 wt. % (Table 5).

CONCLUSIONS

The Mio-Pliocene carbonaceous clays of the Warkalli cliff section in the southern Indian State of Kerala has been studied to understand the characteristics of organic matter, thermal maturity, and their hydrocarbon source potential and depositional conditions. The organic composition and bulk geochemical characterization of these sediments reveal that they are essentially carbonaceous clays. High influx from terrestrial higher plants to the peat biomass is inferred from high CPI, TAR values, and the predominance of phytoclasts particulate organic matter. The presence of non-hopanoid triterpenoids and abundant hopanoids in the organic matter extracts suggest that the main sources of organic matter were angiosperm vegetation and microbial biomass. Abundant hopanoids and the predominance of $17\alpha(H), 21\beta(H)$ -homohopane(R) indicate that the diagenesis of organic matter was mainly governed by the bacterial activity.

The overall characteristics suggest that the studied carbonaceous clay deposits were formed in a marine influenced marginal depositional setting under suboxic conditions. High TOC content and the presence of type III kerogen indicate the ability of these deposits to generate gaseous hydrocarbon. However, the sediments being immature (as indicated by T_{max} , huminite reflectance, and biomarkers) the chances of thermogenic gaseous hydrocarbon generation could prevail only at the deeper levels of the basin. Further studies need to be done on these sediments to identify its potential as a source of biogenic gas.

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