Biomarker signatures of Early Cretaceous coals of Kutch Basin, western India

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The unique position of the Indian plate during the Late Mesozoic draws our attention to study the palaeofloral community from the Early Cretaceous coals of the Kutch Basin using organic geochemical proxies. The biomarkers were studied by GC–MS technique to reveal the botanical source of organic matter. The Rock-Eval pyrolysis data show that samples are thermally immature and organic matter is a mixture of type-II and type-III kerogen. Saturated hydrocarbons are characterized by $n\mathrm{C}_{14}$ to $n\mathrm{C}_{35}$ alkanes with odd over even preference (carbon preference index 1.4 to 3). The pristane/phytane ratios ranging from 0.8 to 2.9 indicate suboxic depositional environment. The occurrence of sesquiterpenoids and diterpenoids depicts that the organic matter was derived from conifers. The predominance of abietane/pimarane class diterpenoids and presence of phyllocladane suggest that Araucariaceae and Podocarpaceae-dominated conifer vegetation served as the source material for the formation of these Early Cretaceous coal beds of the Kutch Basin.

Keywords: Araucariaceae, coal, conifers, diterpenoids, Early Cretaceous.

Introduction

PALAEOGEOGRAPHIC model depicts that the Indian plate started moving towards the northern hemisphere during the Early Cretaceous after its separation from Gondwana and remained as an island continent during the entire Cretaceous until it collided with Asia in Early Eocene at ca. 50 Ma (ref. 1). Palaeobiologists suggest that such prolonged periods of physical isolation of the Indian plate from the rest of the world should have resulted in an endemic Early Cretaceous biota without close affinities to contemporary biota of other regions[2]. In this article, an effort has been made to reconstruct the nature of palaeovegetation of the island continent during the Early Cretaceous by investigating the Late Mesozoic coals from the Kutch Basin. These coal horizons preserve the signature of contemporary vegetation which helps examine the palaeofloral diversity on the Indian continent during the Early Cretaceous. Here, we report different types of biomarkers or chemical fossils which are stable under geological conditions and mostly originate from biological lipids. Terrestrial higher plant-derived biomarkers have been found to be useful as chemotaxonomic indicators and palaeobotanical proxies[3,4]. A detail organic–geochemical study has been undertaken to assess the botanical source and depositional environment of the Mesozoic coals of India.

Geological settings and sampling

The Kutch Basin, a pericratonic rift basin having good exposures of Mesozoic sedimentary rocks is ideal for investigation of contemporary vegetation. Biswas[5] classified the Mesozoic sequence into four lithostratigraphic units, viz. Jhurio, Jhumara, Jhuran and Bhuj Formation. Bhuj Formation represents the upper limit of Mesozoic succession. Thin beds of few centimetres, pockets and lenses of coal are reported from Jhuran and Bhuj formations, whereas Jhurio and Jhumara lack coal[6]. Seven samples were collected from 50 cm thick coal seam of Guneri mine section in Guneri village (23°47′6″N, 69°50′24″E) and four samples were taken from 35 cm thick coal seam of Trambau mine section in Trambau area (23°19′12″N, 69°43′42″E). One coaly shale was encountered from a 10 cm thick bed of Chawad river section (23°27′42″N, 69°13′36″E) in Dhamai Charakhara road crossing (Figure 1). Prakash[6] suggested that the samples of Guneri and Trambau areas belong to Bhuj Formation of Early Cretaceous age. Stable isotope study of fossil leaves reported that Chawad river sample is younger than Trambau samples (ca. 116 Ma) and is dated between Middle Aptian (ca. 116 Ma) and Early Albian (ca. 110 Ma)[7].

Sample preparation and methods

All 12 samples were taken for Rock-Eval pyrolysis. The powdered samples (60–100 mesh) were analysed in ‘Standard’ Rock-Eval 6. A full description of the method is given by Chattopadhyay and Dutta[8]. For biomarker study nine samples were selected. The analysis was performed on an Agilent 5975 mass spectrometer interfaced to a 7890 gas chromatograph. Saturate fractions were analysed on DB-1 (30 m × 0.25 mm

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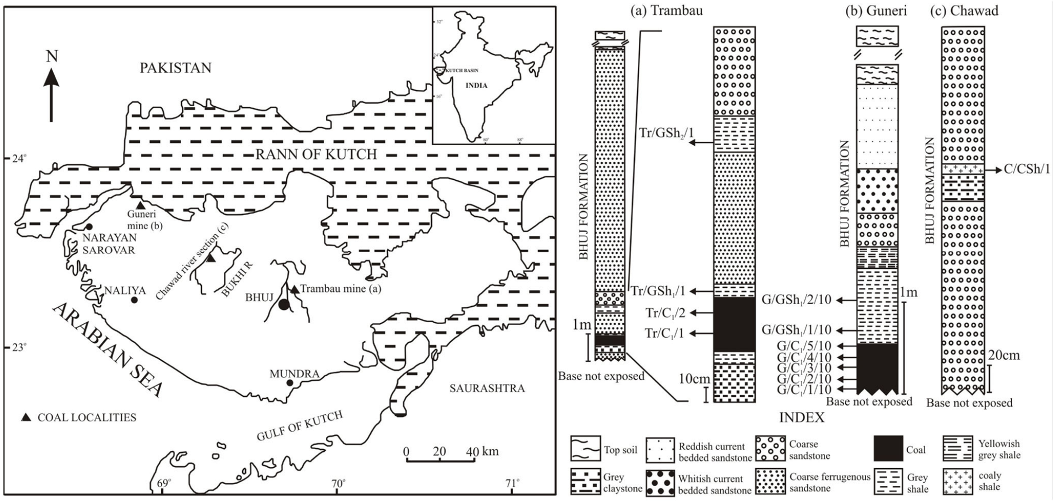

Figure 1. Regional map of Kutch (left) showing location of study areas (indicated by solid triangles) along with their lithologs on the right[6].

Table 1. Rock-Eval pyrolysis data and n-alkane parameters of Early Cretaceous coal and shale samples of Kutch Basin, western India

	Parameters									
Sample no.	S$_1$ (mg/g)	S$_2$ (mg/g)	PI	T$_{max}$ (°C)	S$_3$ (mg/g)	TOC (%)	HI	OI	CPI	Pristane/phytane
G/C$_1$/1/10	0.89	93.69	0.01	419	19.36	48.46	193	40	1.7	0.9
G/C$_1$/2/10	0.83	83.25	0.01	419	20.18	46.87	178	43	1.4	1.4
G/C$_1$/3/10	2.63	61.76	0.04	421	31.04	45.22	137	69	1.8	0.9
G/C$_1$/4/10	1.79	68.40	0.03	422	28.83	46.56	147	62	1.9	1.1
G/C$_1$/5/10	1.44	54.20	0.03	422	24.20	41.37	131	58	1.9	0.8
G/GSh$_1$/1/10	0.07	0.22	0.24	459	0.86	0.35	16	64	–	–
G/GSh$_1$/2/10	0.05	0.14	0.28	493	0.22	0.39	36	56	–	–
Tr/C$_1$/1	5.40	153.52	0.03	417	15.32	48.80	315	31	2.8	2.9
Tr/C$_1$/2	5.78	143.56	0.04	417	18.55	47.61	302	39	3.0	1.2
Tr/GSh$_1$/1	0.04	0.33	0.10	416	1.71	1.45	23	118	2.7	0.8
Tr/GSh$_2$/1	0.04	0.23	0.15	416	0.63	0.93	25	68	–	–
C/CSh/1	0.97	37.21	0.03	425	9.16	12.64	294	72	2.6	1.2

G, Guneri; Tr, Trambau; C, Chawad; C$_1$, Coal; CSh, Coaly shale; GSh, Grey shale.

i.d. × 0.25 μm film thickness) capillary column, whereas HP-5 MS fused silica (30 m × 0.25 mm i.d. × 0.25 μm film thickness) GC column was used for aromatic fraction. Detailed description on sample preparation and gas chromatography–mass spectrometry (GC–MS) is given elsewhere[9].

Results and discussion

Bulk organic matter type

The Rock-Eval data are given in the Table 1. The total organic compound (TOC) content of coal samples is high, ranging from 41.37% to 48.8% and the values for shale vary from 0.35% to 1.45%. The coaly shale of Chawad river section contains 12.64% TOC. Hydrogen indices (HI) of coal samples vary from 131 to 315 mg HC/g TOC and for shales from 16 to 36 mg HC/g TOC. Rock-Eval T$_{max}$ ranges from 416°C to 425°C, which clearly denotes that the studied samples are in thermally immature stage. The HI versus oxygen index (OI) and HI versus T$_{max}$ (Figure 2) cross plots for the coal samples show that the organic matter is a mixture of type-II and type-III kerogen; for the shale samples the plots are scattered in type-III and type-IV area because of low HI. It has been observed that minerals reduce the HI in shale samples[10].

n-Alkanes

The partial mass chromatograms at *m/z* 57 of Trambau and Chawad river section samples represent bimodal distribution pattern and are characterized by nC$_{14}$ to nC$_{33}$ with a high proportion of long chain n-alkanes maximizing at C$_{27}$ (Figure 3). Guneri samples exhibit unimodal pattern with considerable amount of medium chain

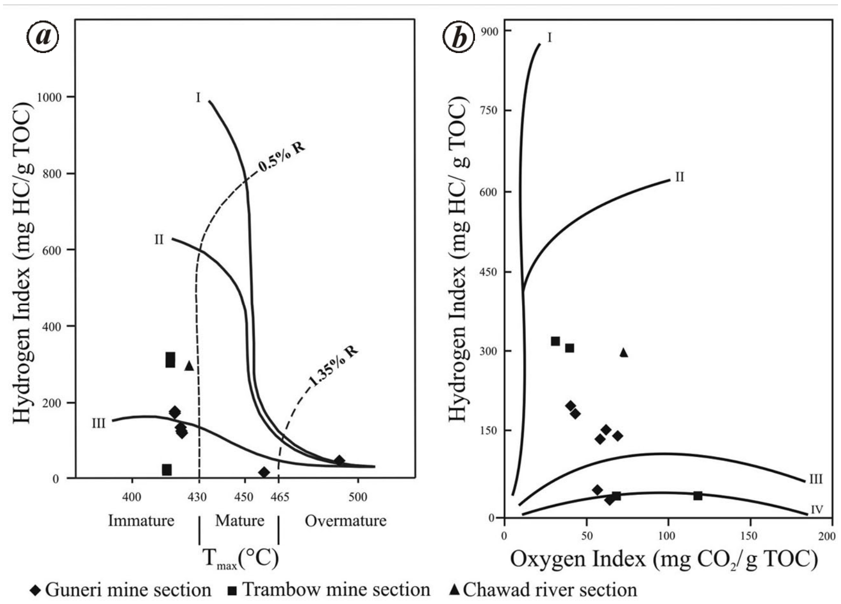

Figure 2. (***a***) Hydrogen index versus T_{max}; (***b***) Hydrogen index versus oxygen index plots for Early Cretaceous coal and shale samples of Kutch Basin, western India.

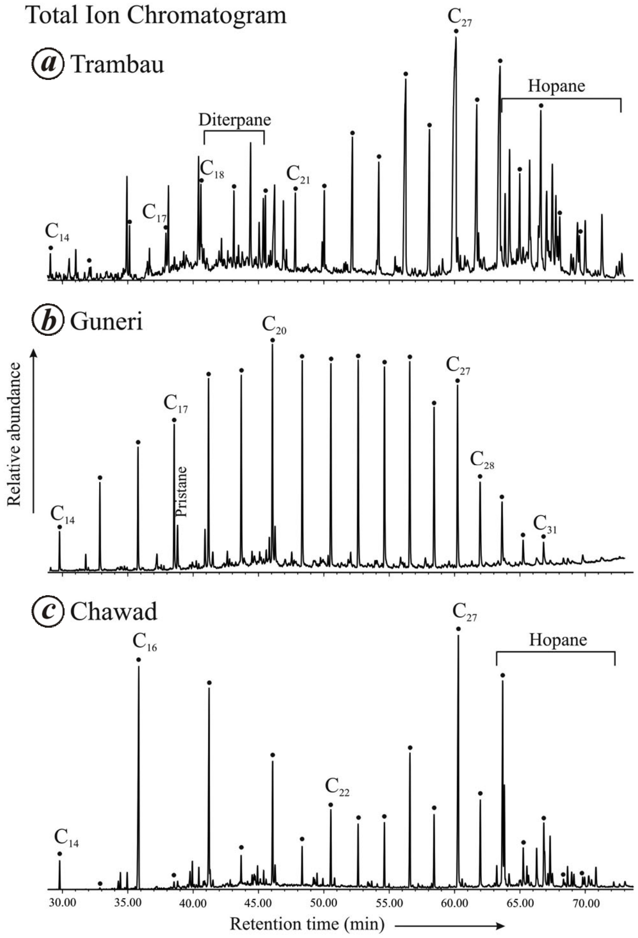

Figure 3. Total ion chromatograms (TIC) of the saturate fraction for representative coal samples from (***a***) Trambau mine section (Tr/C_1/l), (***b***) Guneri mine section (G/C_1/5/10) and (***c***) Chawad river section (C/CSh/1) of Kutch Basin, western India.

n-alkanes. The carbon preference index (CPI) (odd to even preference from nC_{23} to nC_{29})[11] ranges from 1.4 to 3 (Table 1). The isoprenoids pristane to phytane ratio varies from 0.8 to 2.9 (Table 1), which lies in the suboxic depositional environment[12]. In pristane/nC_{17} versus phytane/nC_{18} plot (Figure 4), the samples fall in the zone of early mature, terrigenous oxic depositional environment. The high abundance of long chain *n*-alkanes and odd predominance in higher molecular weight region along with high CPI value (>1) suggest the contribution from higher plants. Besides, the odd, long-chain *n*-alkanes nC_{27}, nC_{29} and nC_{31} are likely to be derived from higher plants[13].

Terpenoids

Sesquiterpenoids are represented by C_{15} drimane and C_{16} homodrimane in saturate fraction (Figure 5 and Table 2) and cadalene in aromatic fraction (Figure 6 and Table 3). Drimane and homodrimane are present in subordinate amount in Trambau and Chawad river sections and absent in Guneri samples. These two compounds are considered to have originated from hopanoid precursor bacteriohopantetrol (C_{35} tetrahydroxibacteriohopane) during diagenesis[14], whereas cadalene can be derived from both gymnosperm and angiosperm[15].

Saturated diterpenoids are characterized by the 8α(H) and 8β(H)-labdane, 4β(H)-19 and 4α(H)-18-norisopimarane, *ent*-beyerene, isopimarane, abietane, α-phyllocladane and unknown C_{18} diterpanes (Figure 5 and Table 2). Trambau and Chawad samples are characterized by high abundance of 4α(H)-18-norisopimarane and lack of abietane. But the Guneri sample shows moderate amount of abietane without labdane. The major aromatic diterpenoids such as dehydroabietane, 19-norabieta-4,8,11,13-tetraene, simonellite, retene, 2-methylretene (Figure 6 and Table 3) belong to regular abietane class and are derived from abietic acid[16]. Gymnosperm/conifer trees produce diterpenoid-based resins. Besides, some A-ring opened isohexyl alkylaromatic compounds like 2-methyl-1-(4-methylpentyl)naphthalene, 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene and its methylated counterpart 6-isopropyl-2,4-dimethyl-1-(4-methylpentyl)naphthalene are detected in the aromatic fraction. Laboratory experiments have shown that 2-methyl-1-(4-methylpentyl) naphthalene and 6-isopropyl-2-methyl-1-(4-methylpentyl) naphthalene can be derived from phyllocladane[17]. No angiosperm-related biomarker has been detected in the samples. Tricyclic isopimarane, bicyclic labdane and regular abietanes are found in all conifer families like Araucariaceae, Podocarpaceae, Cupressaceae and Pinaceae[15]. Isopimarane is considered to have originated from labdane-derived copalyl-pyrophosphate[18]. Decarboxylation to the acid of isopimarane class like isopimaric acid initially produces 4α(H)-18-norisopimarane, which is converted to stable equatorial isomer 19-norisopimarane[19,20] during later stage of diagenesis. Tetracyclic *ent*-beyerane and phyllocladane are reported from Cupressaceae, Podocarpaceae and Araucariaceae, but remain absent in Pinaceae[15,18]. Modern Pinaceae resins exclusively contain labdane and abietane-type diterpenoids[15,18], but lack in phenolic abietane and tetracyclic diterpane[18,21]. No such exclusive association of labdane and abietane is found in the studied samples. Therefore, the major contribution of Pinaceae the source vegetation is unlikely. Phenolic abietanes, especially found in Podocarpaceae and Cupressaceae[15,18], are absent in the studied samples. Besides, sesqiterpenoids like cedrane and cuparane are exclusively found in Cupressaceae[18]. Complete absence of the above-mentioned sesquiterpenoids rules out the contribution of Cupressaceae to the source vegetation. The predominance of abietane/primarane class compounds and presence of tetracyclic diterpenoids such as *ent*-beyerane and phyllocladane indicate a significant contribution of Araucariaceae to the organic matter. However, the contribution of Podocarpaceae to the source vegetation is also possible. The signature of Araucarian and Podocarpacean wood, cone and cycadalean ovule was reported from Deccan intertrappean sediments of Cretaceous period[22].

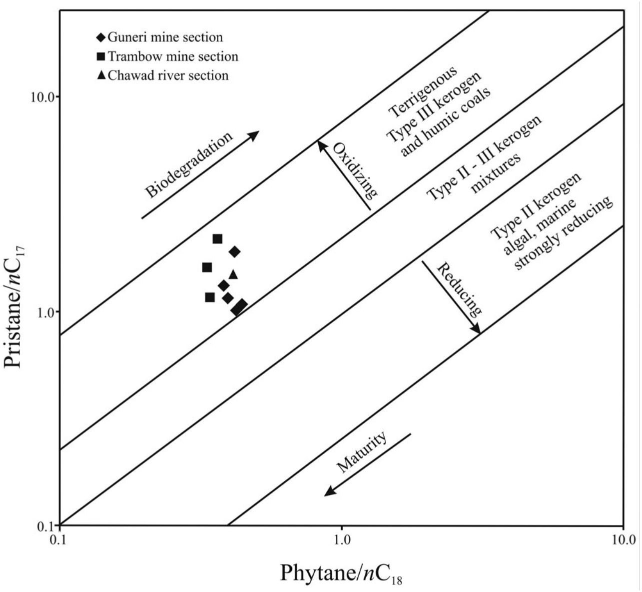

Figure 4. Pristane/nC_{17} versus phytane/nC_{18} plot of Early Cretaceous coal and shale samples from Kutch Basin, western India.

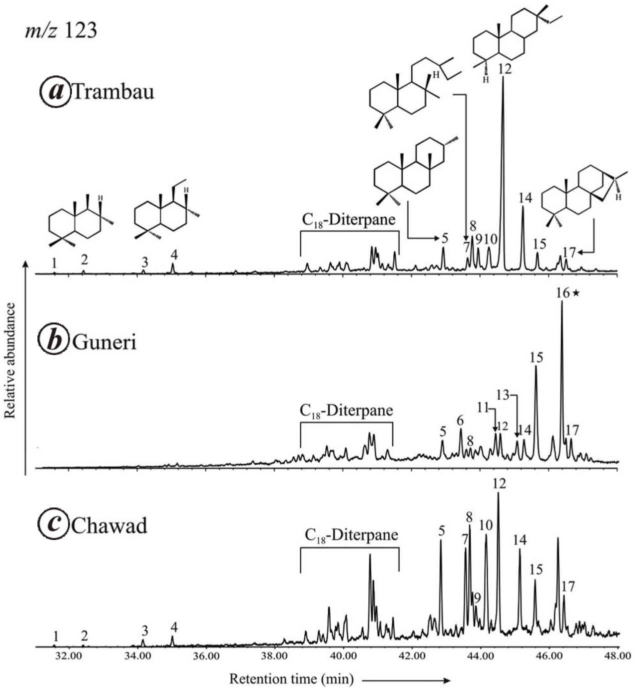

Figure 5. Distribution of sesquiterpenoids and diterpenoids of representative coal samples from (***a***) Trambau mine section (Tr/C_1/l), (***b***) Guneri mine section (G/C_1/2/10) and (***c***) Chawad river section (C/CSh/1) of Kutch Basin, western India. Solid star indicates sulphur.

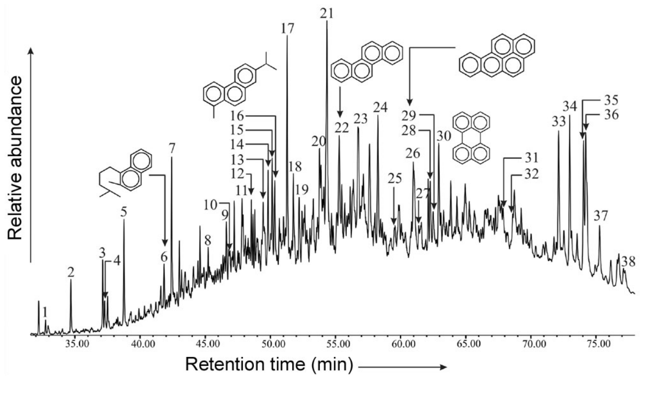

Figure 6. Total ion chromatograms of the aromatic fraction for a coal sample (G/C_1/3/10) from Guneri mine section, Kutch Basin, western India.

Table 2. Aliphatic sesquiterpenoids and diterpenoids detected in the Early Cretaceous coal samples, Kutch Basin, western India

Peak no.	Compound	Base peak	Molecular ion
1	8β (H)-Drimane	123	208
2	8β (H)-Drimane	123	208
3	8β (H)-Homodrimane	123	222
4	8β (H)-Homodrimane	123	222
5	C_{19} Tricyclic terpane	123	262
6	Possibly demethylated *ent*-beyerane?	109	260
7	8β (H)-Labdane	123	278
8	4β (H)-19-Norisopimarane	233	262
9	Isomer of C_{19} tricyclic terpane	123	262
10	8α (H)-Labdane	123	278
11	C_{20} Tricyclic terpane	191	276
12	4α (H)-18-Norisopimarane	233	262
13	C_{20} Tricyclic terpane	191	276
14	*ent*-Beyerane	123	274
15	Isopimarane	247	276
16	Abietane	163	276
17	α-Phyllocladane	123	274

Table 3. Aromatic compounds detected in the Early Cretaceous coal samples, Kutch Basin, western India

Peak no.	Compound	Base peak	Molecular ion
1	Naphthalene, 6-(1,1-dimethylethyl)-1,2,3,4-tetrahydro	173	188
2	Trimethyl naphthalene	155	170
3	Tetramethyl naphthalene	169	184
4	Cadalene	183	198
5	Tetramethyl naphthalene	169	184
6	2-Methyl-1-(4-methylpentyl)naphthalene	155	226
7	Trimethyl naphthalene + Tricyclic diaromatic terpane	155, 209	170, 224
8	19-Norabieta-4,8,11,13-tetraene	239	254
9	Dehydroabietane	255	270
10	Fluoranthene	202	202
11	6-Isopropyl-2-methyl-1-(4-methylpentyl)naphthalene	197	268
12	Simonellite	237	252
13	Methyl simonellite?	237	266
14	6-Isopropyl-2,4-dimethyl-1-(4-methylpentyl)naphthalene	211	282
15	Methyl pyrene	216	216
16	Retene	219	234
17	Unknown compound	251	266
18	Tetrahydrochrysene	232	232
19	C_2 Pyrene	230	230
20	2-Methylretene	233	248
21	Methyl-tetrahydrochrysene?	246	246
22	Chrysene/triphenylene	228	228
23	Dimethyl-tetrahydrochrysene?	260	260
24	Unknown compound	245	274
25	Trimethyl-tetrahydrochrysene?	274	274
26	Benzo[b]fluoranthenes	252	252
27	Benzo[k]fluoranthenes	252	252
28	Benzo[e]pyrene	252	252
29	Benzo[a]pyrene	252	252
30	Perylene	252	252
31	Indeno[1,2,3-*cd*]pyrene	276	276
32	Benzo[ghi]perylene	276	276
33	C_{31} Benzohopane	197	418
34	C_{32} Benzohopane	191	432
35	Unknown compound	448	448
36	C_{33} Benzohopane	191	446
37	C_{34} Benzohopane	191	460
38	C_{35} Benzohopane	191	474

The partial mass chromatogram at *m/z* 191 in saturate fraction represents the pentacyclic hopanoids associated with tetracyclic terpane, C_{24}–C_{26} 17,21-secohopanes (Figure 7). C_{32}–C_{34} benzohopanes are also abundantly present in the aromatic fraction (Figure 6 and Table 3). Saturated hopane series is characterized by C_{27}–C_{32} hopanoids, except C_{28}. C_{27} Hopane (17β(H)-22,29,30-trisnorhopane; peak 5; Figure 7) shows highest abundance in Trambau mine and Chawad river section samples, whereas in Guneri mine section coal C_{31} 17α(H),21β(H)-hopane (22R) (peak 14, Figure 7) exhibits its maximum abundance. $\beta\beta$-Hopanes of C_{29}–C_{31} carbon numbers are highly abundant in Trambau mine and moderate in Guneri mine and Chawad river section samples. Mono-unsaturated hopenes like 30-norneohop-13(18)-ene (peak 6; Figure 7), hop-17(21)-ene (peak 8; Figure 7), neohop-13(18)-ene (peak 11a; Figure 7) and homohop-17(21)-ene (peak 12c; Figure 7) are the precursors of hopane and indicate the immature nature of source rock. 17α,21β(H) and 17β,21α(H) configuration of hopanoids is thermodynamically more stable than their 17β,21β(H) isomer[23,24]. However, abundance of $\beta\beta$-hopanes and hopenes in the samples indicate low degree of thermal history. These monoene compounds are present in Trambau and Guneri mine samples and completely absent in Chawad river section. The presence of hopanoids along with drimane-based sesquiterpenoids suggests the input of bacterial biomass into the organic matter[3]. Homohopanes (C_{31} and C_{32}) are formed at the initial stage by the degradation of bacteriohopantetrol under slightly oxic environment, which are further transformed into C_{27}–C_{30} hopanes by demethylation process[14]. Demethylated hopane such as 30-norhopane is also derived from the same precursor as regular hopane during biodegradation of organic matter[25]. Sufficient amount of terrestrial input is associated with these hopanoids, which suggests that the microbial contribution is mainly related to the soil bacteria[3]. Tetracyclic C_{24}–C_{26} 17,21-secohopanes (peaks 1–3; Figure 7) are present in low concentration in all samples. Origin of these compounds is still debated. They are thought to be the products of thermal degradation during the maturation or microbial degradation of hopane precursors[13]. In this study, the presence of hopenes and $\beta\beta$-hopanes reflects the low thermal maturity of organic matter. The Rock-Eval T_{max} values also confirm low thermal maturity of the studied samples. Association of these C_{24}–C_{26} tetracyclic compounds with thermally immature compounds indicates that they are formed by the development of cleavage on *E*-ring of hopanoids due to microbial activity at early stage of diagenesis[13].

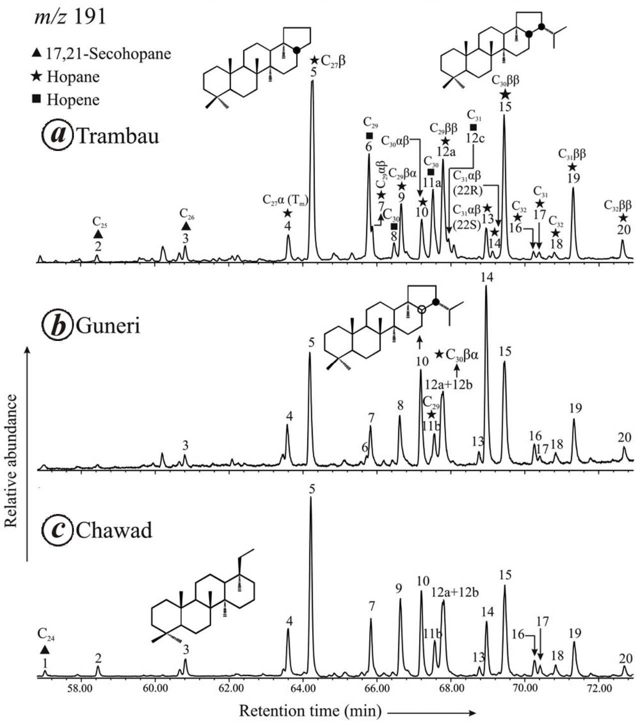

Figure 7. Partial mass chromatogram (*m/z* 191) of representative coal samples showing the distribution of hopanoids: ***a***, Trambau mine section (Tr/C_1/1); ***b***, Guneri mine section (G/C_1/2); ***c***, Chawad river section (C/CSh/1) of Kutch Basin, western India.

Polyaromatic hydrocarbons

The polycyclic aromatic hydrocarbons (PAHs) of 2–5 ring compounds such as naphthalene, fluoranthene, chrysene, benzofluoranthenes, benzopyrenes, perylene and alkylated homolouges such as naphthalene, 6-(1,1-dimethylethyl)-1,2,3,4-tetrahydro, dimethyl naphthalene, trimethyl naphthalene, tetramethyl naphthalene, 2-methyl-1-(4-methylpentyl)naphthalene, methyl pyrene, C_2-pyrene and 6-ring compounds benzo(*ghi*)perylene and indeno (1,2,3-*cd*)pyrene are found in the studied samples (Figure 6 and Table 3). PAHs like perylene and chrysene are considered to be derived from various biological precursors like wood-degrading fungi and algae respectively[26,27]. Besides, chrysene/triphenylene can also be produced by the thermal exposure of organic matter during combustion like other pyrolitic PAHs such as fluoranthene, methylated pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo(*ghi*)-perylene and indeno(1,2,3-*cd*)pyrene[28,29]. Therefore, the presence of such combustion-derived PAHs may reflect the burning of vegetation prior to deposition[28,30].

Conclusions

Rock-Eval pyrolysis results show that the organic matter of studied coal samples is thermally immature (Rock-Eval T_{max} varies from 416°C to 425°C) and is a mixture of type-II and type-III kerogen. The presence of hopenes and $\beta\beta$-hopanes confirms low thermal maturity of organic matter. The presence of C_{24}–C_{26} 17,21-secohopanes in the thermally immature coal samples does not support their thermal origin. The occurrence of diterpenoids suggests that conifers served as the source material for the formation of these coals. The predominance of abietane/primarane class diterpenoids and presence of tetracyclic diterpenoids (e.g. *ent*-beyerane, phyllocladane) indicate that Araucariaceae and Podocarpaceae conifers prevailed in western India during the Early Cretaceous.

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