

# Molecular fossils in Cretaceous condensate from western India

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The present study reports the biomarker distribution of condensate belonging to the early Cretaceous time frame using gas chromatography-mass spectrometry (GC-MS). The early Cretaceous palaeoenvironment was inscribed into these molecular fossils which reflected the source and conditions of deposition of the condensate. The saturate fraction of the condensate is characterized by normal alkanes ranging from  $n$ -C<sub>9</sub> to  $n$ -C<sub>29</sub> (CPI-1.13), cycloalkanes and C<sub>14</sub> and C<sub>15</sub> sesquiterpanes. The aromatic fraction comprises of naphthalene, phenanthrene, their methylated derivatives and cyclohexylbenzenes. Isohexylalkylnaphthalenes, a product of rearrangement process of terpenoids, is detected in the condensate. Several aromatic sesquiterpenoids and diterpenoids have been recorded. Dihydro-*ar*-curcumene, cadalene and ionene form the assemblage of sesquiterpenoids which are indicative of higher plant input. Aromatic diterpenoid fraction comprises of simonellite and retene. These compounds are also indicative of higher plants, particularly conifer source which had been a predominant flora during the Cretaceous time.

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## 1. Introduction

Condensate is liquid hydrocarbon of low density and high API gravity which remains in the gaseous state in the ground and condenses at lower depths (Hunt 1996). The condensation from gaseous to liquid phase is controlled by the temperature and pressure conditions in the reservoir. In condensates, liquid hydrocarbon remains dissolved in gaseous phase and fractionates out of the solution when the pressure drops below dew point. The separation into liquid hydrocarbons occurs through retrograde condensation. Previously, it was supposed that condensates are derived from resinates at low levels of maturity (Snowdon and Powell 1982). However, hydrous pyrolysis experiments resulted in pyrolyzates with entirely different composition than what is observed in natural condensates (Hwang and Teerman 1988). Condensates

may originate by several means – from kerogen as an intermediate product between oil and gas, conversion of oil to gas in a reservoir, and/or from gas phase migration of hydrocarbons out of an oil pool because of physical phenomena such as vaporization or gas stripping (Hunt 1996). Broadly, two types of gas-condensate systems can be distinguished. Firstly, condensates produced directly from source rock and secondly, those which are formed by transformation of petroleum (Botneva *et al.* 1990). Condensates may be enriched in paraffin compounds. Condensates rich in naphthenic and aromatic compounds may be formed by evaporative fractionation (Thompson 1987). The time frame of the present study, the early Cretaceous period, was crucial in the geological history of the Indian continent. During the bulk of the Jurassic period, India remained as a component of the southern supercontinent Gondwana.

**Keywords.** Cretaceous; condensate; Jaisalmer basin; biomarkers; conifer source.

Rifting plausibly began at the tail end of Jurassic (Briggs 2003). The Cretaceous period witnessed the voyage of India from the southern hemisphere towards north. There had been speculations that India persisted as an island continent during the Cretaceous, which were refuted on several occasions (Chatterjee and Hotton 1986; Briggs 2003). The Cretaceous period was warm and switched between arid and humid conditions (Föllmi 2012). The Jurassic–Cretaceous periods were dominated by gymnosperm flora, particularly conifers, which formed the most diverse group during that time. The huge reserves of terrigenous-source derived petroleum of the Jurassic–Cretaceous periods were fed by the coniferous plants to a large extent (Shanmugam 1985; Philp and Gilbert 1986). Biomarkers have been analyzed in order to understand the source organic matter. These are robust molecules, mostly lipids, which traverse a long journey from the biosphere to the geosphere after the demise of organisms and are recorded in rocks as chemical fossils (Brocks and Pearson 2005). The present work manifests the organic geochemical characteristics of the condensate recovered from the Pariwar Formation belonging to early Cretaceous age, Jaisalmer basin and sheds light on the precursor and palaeoenvironmental features.

## 2. Regional geology and stratigraphy

The Jaisalmer basin had developed as a pericratonic basin in the Rajasthan continental margin (Valdiya 2010). The most prominent and crucial sequence of this basin is the Mesozoic sequence commencing with Shumarwali Formation in the Triassic to the Parh Formation in the Cretaceous (Krishna 1987). Sedimentation in the Triassic began in a fluvial to deltaic environment. The early Jurassic environment was intertidal to neritic and the time window witnessed several cycles of carbonate depositions on stable shelf (Valdiya 2010). There were several phases of transgression and regression during the Cretaceous which induced the deposition of marine and deltaic sediments (Verma *et al.* 2012). The Mesozoic condensate in the present study has been recovered from the Lower Cretaceous Pariwar Formation. The Pariwar Formation represents regression with shallow marine and brackish conditions towards the lower part and complete regression with the setting in of continental condition towards the top (<http://www.dghindia.org/23.aspx>). Palynomorph and foraminifera studies indicate earlier part of early Cretaceous age for the Pariwar Formation (Valdiya 2010 and references therein). Further details of the geology and stratigraphy of the area cannot be provided due to proprietary reasons.

## 3. Samples and methods

### 3.1 Sample preparation

Condensate sample has been collected from a well in Jaisalmer basin, Rajasthan. The condensate sample, an assemblage of several compounds, is separated into saturate and aromatic fractions with the aid of column chromatography. The glassware used is sterilized with methanol and dichloromethane and fired at 300°C for 4 hours. Activated silica gel (100–200 mesh) is filled in a column and the condensate sample then added on it and allowed to dry overnight. The experiment commenced with the measurement of dead volume (DV) with *n*-hexane. Dead volume is the volume of solvent (*n*-hexane) added that completely soaked the silica gel. *n*-Hexane is added further (3/8 of dead volume) in order to elute the complete saturate fraction from the sample. A solution of *n*-hexane and dichloromethane is prepared in a proportion of 4:1 of 4DV. This is added to the sample in order to elute the aromatic fraction. The saturate and aromatic fractions are analyzed with gas chromatography–mass spectrometry.

### 3.2 Gas chromatography–mass spectrometry

The sample has been analyzed using an Agilent 5975 mass spectrometer interfaced to a 7890 gas chromatograph. The gas chromatograph is fitted with a DB-1 fused silica capillary column (30 m × 0.25 mm i.d., × 0.25 μm film thickness). Helium is used as carrier gas. The flow rate is 1 ml/min. The saturate and aromatic fractions are analyzed in full scan mode. Full scan analyses are conducted over a mass range of 50–600 Da. The sample is dissolved in *n*-hexane and injected by autosampler in pulsed splitless mode. The ion source operates in the electron ionization mode at 70 eV. The temperature of GC oven is held at 40°C (for 5 min) and then ramped to 310°C at 4°C/min and held for 5.5 min. Identification of compounds is based on comparison of elution pattern and mass spectra with those reported in the literature. Data have been processed using Chemstation software.

## 4. Results and discussions

### 4.1 Saturate hydrocarbons

The total ion chromatogram of the saturate fraction is presented in figure 1.

#### 4.1.1 Acyclic compounds

The saturate fraction is dominated by normal alkanes ranging from *n*-C<sub>9</sub> to *n*-C<sub>29</sub>. The distribution

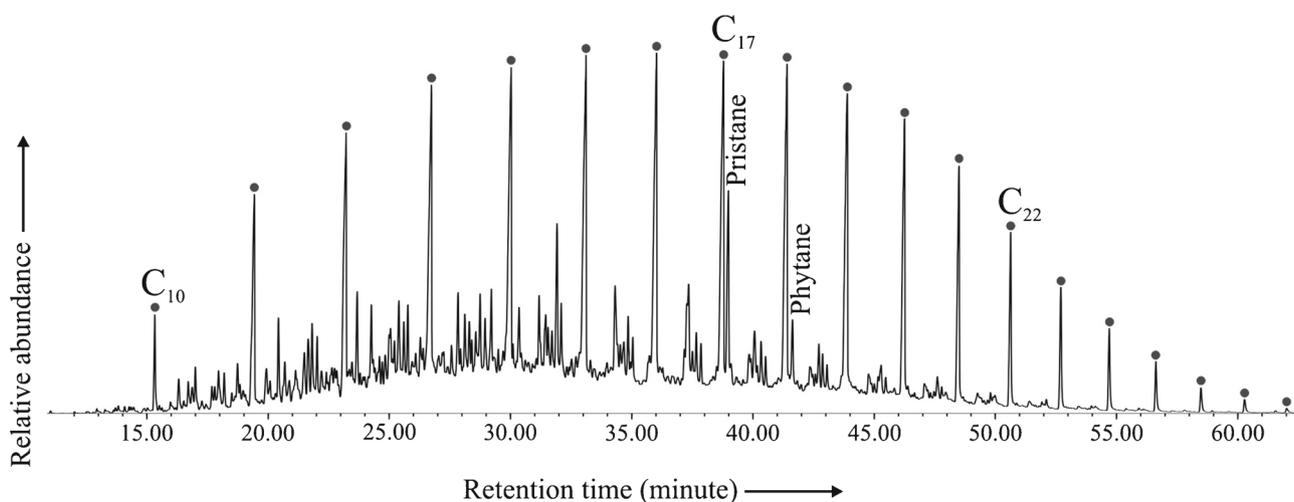


Figure 1. Total ion chromatogram of aliphatic fraction of the condensate of Cretaceous age from a well, Jaisalmer basin, western India. The solid circles indicate normal alkanes. Carbon numbers of *n*-alkanes are indicated.

of the normal alkanes is unimodal. A progressive rise from *n*-C<sub>10</sub> to *n*-C<sub>16</sub> and a gradual decrease thereafter up to *n*-C<sub>29</sub> is clearly observed in *m/z* 57. *n*-C<sub>12</sub> to *n*-C<sub>15</sub> are the dominant peaks in *m/z* 57. The normal alkane distribution displays odd carbon preference beyond *n*-C<sub>20</sub> and is consistent with the CPI value which is 1.13 (Marzi *et al.* 1993). The distribution of normal alkanes, particularly abundant in the C<sub>12</sub>–C<sub>15</sub> range, may suggest algal/bacterial input into the organic matter. Pristane and phytane are the major acyclic isoprenoids present in the condensate. There are several conjectures regarding the source of these acyclic compounds. The most usual source is believed to be the phytyl side chain of chlorophyll or bacteriochlorophyll (Brooks *et al.* 1969; Powell and McKirdy 1973). Archaea have also been supposed to be a source of pristane and phytane (Chappe *et al.* 1982). It has been postulated that catagenetic decomposition of methyltrimethyl-tridecylchromans might also produce pristane (Li *et al.* 1995). The pristane and phytane in the condensate is probably derived from higher plant chlorophyll or bacteriochlorophyll since signatures of archaea or tocopherols are not recorded. The pristane/phytane ratio is 3.86. The high pristane/phytane ratio is indicative of oxic to suboxic condition of deposition (Peters *et al.* 2005). The values of pristane/*n*-C<sub>17</sub> and phytane/*n*-C<sub>18</sub> are 0.37 and 0.09, respectively.

#### 4.1.2 Cycloalkanes

A homologous series of *n*-alkylcyclohexane (*m/z* 83) ranging from butyl cyclohexane to heptadecyl cyclohexane, maximizing at heptylcyclohexane, is observed. Another series of monocyclic alkanes identified as methyl-*n*-alkylcyclohexane (*m/z* 97) is detected in the condensate. The series

ranges from methyl-*n*-propyl-cyclohexane to methyl-*n*-hexadecyl-cyclohexane. Methyl-*n*-hexyl-cyclohexane is the most abundant among the other homologues. The homologous series of methyl-*n*-alkylcyclohexane can have three possible isomers – 1,2; 1,3; 1,4 (Fowler and Douglas 1984). In the present sample, probably all the three possible isomers are present since homologous triplets can be observed. However, at *m/z* 97, the homologous series display triplets very clearly in the range methyl-*n*-propyl-cyclohexane to methyl-*n*-heptyl-cyclohexane. The triplets beyond this range become obscure. The first member of the triplets is the most prominent and hence the most abundant isomer. *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes are possibly derived from the diagenetic alteration of algal fatty acids (Fowler *et al.* 1986). It has been proposed that *n*-alkylcyclohexanes might also be derived from bacterial lipid since their probable precursor is observed in thermo acidophilic bacterium (Fowler and Douglas 1984). Hence, both algal and bacterial origins of *n*-alkylcyclohexanes have been supposed. The reaction probably proceeds with the thermolysis of the heavy chained fatty acids into lighter chain *n*-alkanes and olefins. The reaction proceeds with the cyclization of olefinic radicals into the alkylcyclohexanes (Kissin 1990). However, the other confirmed signatures of algae such as steranes are not detected in the condensate. C<sub>29</sub> and C<sub>30</sub> hopanes are detected in considerably low abundance in an overloaded condensate sample.

#### 4.1.3 Sesquiterpenoids

The distribution of saturate sesquiterpenoids is presented in figure 2 and peak numbers are listed in table 1.

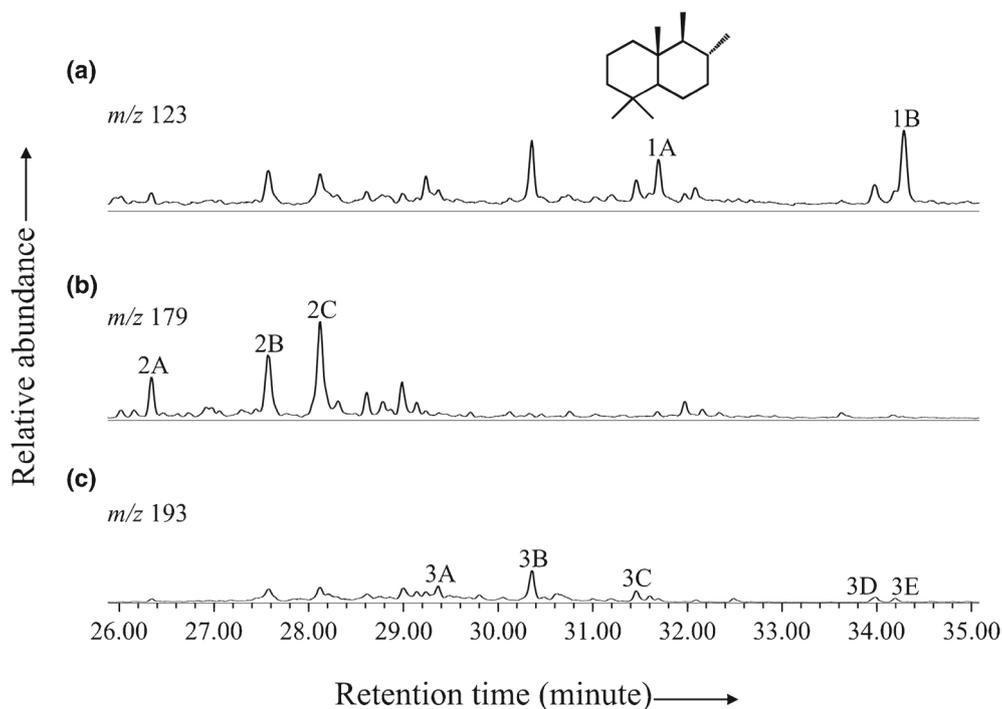


Figure 2. Partial mass chromatograms depicting the distributions of sesquiterpenoids (a) compounds bearing drimane-related skeletons ( $m/z$  123), (b)  $C_{14}$  rearranged bicyclic alkanes ( $m/z$  179) and (c)  $C_{15}$  rearranged bicyclic alkanes ( $m/z$  193) in the saturate fraction of condensate of Cretaceous age from a well, Jaisalmer basin, western India. Peak numbers are listed in table 1.

Table 1. Peak identifications, base peaks and molecular ions of saturate sesquiterpenoid compounds present in the Cretaceous condensate recovered from a well, Jaisalmer basin, western India.

Peak no.	Base peak	Molecular ion	Compound name
1A	123	208	Drimane
1B	123	222	Homodrimane
2A	179	194	$C_{14}$ rearranged bicyclic alkane
2B	179	194	$C_{14}$ rearranged bicyclic alkane
2C	179	194	$C_{14}$ rearranged bicyclic alkane
3A	193	208	$C_{15}$ rearranged bicyclic alkane
3B	193	208	$C_{15}$ rearranged bicyclic alkane
3C	193	208	$C_{15}$ rearranged bicyclic alkane
3D	193	208	$C_{15}$ rearranged bicyclic alkane
3E	193	208	$C_{15}$ rearranged bicyclic alkane

A homologous series of bicyclic alkanes with the drimane skeleton is identified from mass spectral data.  $C_{14}$  Nordrimane (mass fragments 109, 194) is observed which probably formed due to removal of a methyl group at the A ring of the drimane skeleton.  $C_{15}$  bicyclic sesquiterpane (drimane) is recorded in the sample which is further followed by an extended series of homodrimanes ranging from  $C_{16}$  to  $C_{20}$ . However,  $C_{17}$  homodrimane is not observed. They might be derived from sesquiterpenoid precursors present in higher plants (Alexander *et al.* 1984). It is also believed that these compounds might be derived by the

diagenesis of hopanoid precursors (Alexander *et al.* 1984; Wang *et al.* 1990). The possibility of tricyclic terpanes being the precursor of these bicyclic terpanes cannot be ruled out (Dimmler *et al.* 1984).

Apart from drimane and homodrimanes, other  $C_{14}$  sesquiterpanes are recorded in the sample. These compounds with base peaks 179 and 193 are  $C_{14}$  and  $C_{15}$  bicyclic sesquiterpanes, respectively (Alexander *et al.* 1984). These compounds are probably derived from drimane or drimane related precursors. There are three peaks with base peak 179 and molecular ion 194 which are probably isomers of A-nordrimane resulting from the loss of

methyl group from the A-ring (Weston *et al.* 1989). Two prominent peaks and three minor peaks with base peak 193 and molecular ion 208 have been observed which might be isomers of rearranged drimane where there has been a shift in methyl group from one location to another. The rearrangement process is plausibly acid catalyzed (Weston *et al.* 1989).

#### 4.1.4 Diamondoids

Diamondoids have been detected in the studied sample (figure 3; table 2). The isomers have been identified and listed based on the works of Fang *et al.* (2012). Diamondoids are cage-like rigid three dimensional molecules comprising fused ring alkanes whose structures are similar to diamonds. They may be conceived as truncated diamonds whose dangling bonds are terminated with hydrogen atom (Ali Mansoori 2007). Direct diamondoid precursors have not been observed in nature yet. However, these compounds are plausibly formed by the isomerization and rearrangement of polycyclic hydrocarbons, which in turn are generated by organisms, in the presence of a Lewis acid (Petrov *et al.* 1974). Artificial maturation of these sediments in the presence of mineral acids like montmorillonite, acidic aluminosilicate and calcium carbonate, was carried out. It was observed that along with other biomarkers, diamondoids were formed with the thermal maturity of the organic matter. It is worth mentioning that presence of montmorillonite facilitated the generation of diamondoids whereas calcium carbonate has an inhibition effect on it. In the present study, adamantane and its methylated as well as ethylated derivatives have been recorded whereas other diamondoids like diamantane, triamantane and higher polymantanes are not observed.

#### 4.2 Aromatic hydrocarbons

Apart from alkylated benzenes, naphthalenes, phenanthrenes and their methylated counterparts which are ubiquitous in all kinds of samples, several other aromatic compounds are recorded in the sample providing further insights to the organic matter input and depositional condition.

##### 4.2.1 Cyclohexylbenzenes

Cyclohexylbenzene and cyclohexylbenzene with one methyl substituent have been recorded in the sample. Structurally related biphenyls have also been observed. Two peaks are observed at  $m/z$  174. Based on the elution pattern presented in the chromatogram published by Alexander *et al.* (1994a),

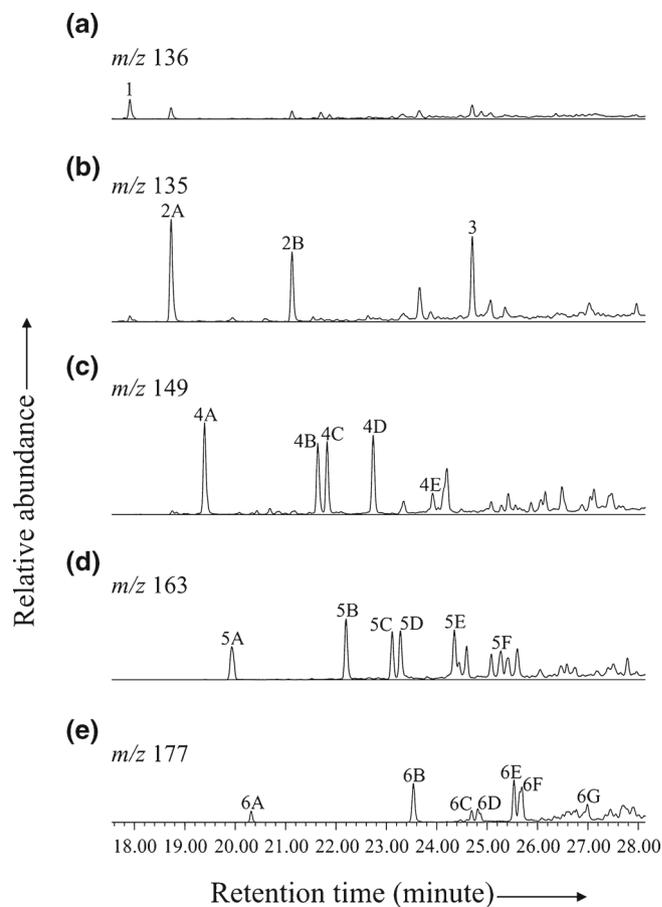


Figure 3. Partial mass chromatograms presenting the distributions of (a) adamantane ( $m/z$  136), (b) methyl- and ethyl-adamantane ( $m/z$  135), (c) dimethyl adamantane ( $m/z$  149), (d) trimethyl adamantane ( $m/z$  163) and (e) tetramethyl adamantane ( $m/z$  177) in the saturate fraction of condensate of Cretaceous age from a well, Jaisalmer basin, western India. Peak numbers are listed in table 2.

the first peak corresponds to an amalgamation of cyclohexyl-3-methyl benzene and cyclohexyl-2-methyl benzene. The second peak corresponds to cyclohexyl-4-methyl benzene. The origin of these compounds in petroleum is not very clear since they occur in crude oils from various types of source material and geological ages. The genesis of these bicyclic ring systems might occur through phenol coupling of precursor compound at oxidizing condition (Alexander *et al.* 1994a).

##### 4.2.2 Isohexylalkylnaphthalenes

A homologous series of isohexylalkylnaphthalenes ( $m/z$  155, 169, 183, 197, 211) is observed (figure 4) and the peaks are listed in table 3. Five isohexylalkylnaphthalene peaks have been identified by tallying the mass spectra of these peaks with those published by Ellis *et al.* (1996). These compounds are probably produced by aromatization

Table 2. Peak identifications, base peaks and molecular ions of diamodoid compounds (adamantane and methylated adamantanes) present in the saturate fraction of the Cretaceous condensate recovered from a well, Jaisalmer basin, western India.

Peak no.	Base peak	Molecular ion	Compound name
1	93	136	Adamantane
2A	135	150	1-Methyladamantane
2B	135	150	2-Methyladamantane
3	135	164	Ethyladamantane
4A	149	164	1,3-Dimethyladamantane
4B	149	164	1,4-Dimethyladamantane( <i>cis</i> )
4C	149	164	1,4-Dimethyladamantane( <i>trans</i> )
4D	149	164	1,2-Dimethyladamantane
4E	149	164	2,6- + 2,4-Dimethyladamantane
5A	163	178	1,3,5-Trimethyladamantane
5B	163	178	1,3,6-Trimethyladamantane
5C	163	178	1,3,4-Trimethyladamantane( <i>cis</i> )
5D	163	178	1,3,4-Trimethyladamantane( <i>trans</i> )
5E	163	178	1,2,3-Trimethyladamantane
5F	163	178	Unknown isomer of trimethyladamantane
6A	177	192	1,3,5,7-Tetramethyladamantane
6B	177	192	1,2,5,7-Tetramethyladamantane
6C	177	192	Unknown isomer of tetramethyladamantane
6D	177	192	1,3,5,6-Tetramethyladamantane
6E	177	192	1,2,3,5-Tetramethyladamantane
6F	177	192	1-Ethyl-3,5,7-trimethyladamantane
6G	177	192	Unknown isomer of tetramethyladamantane

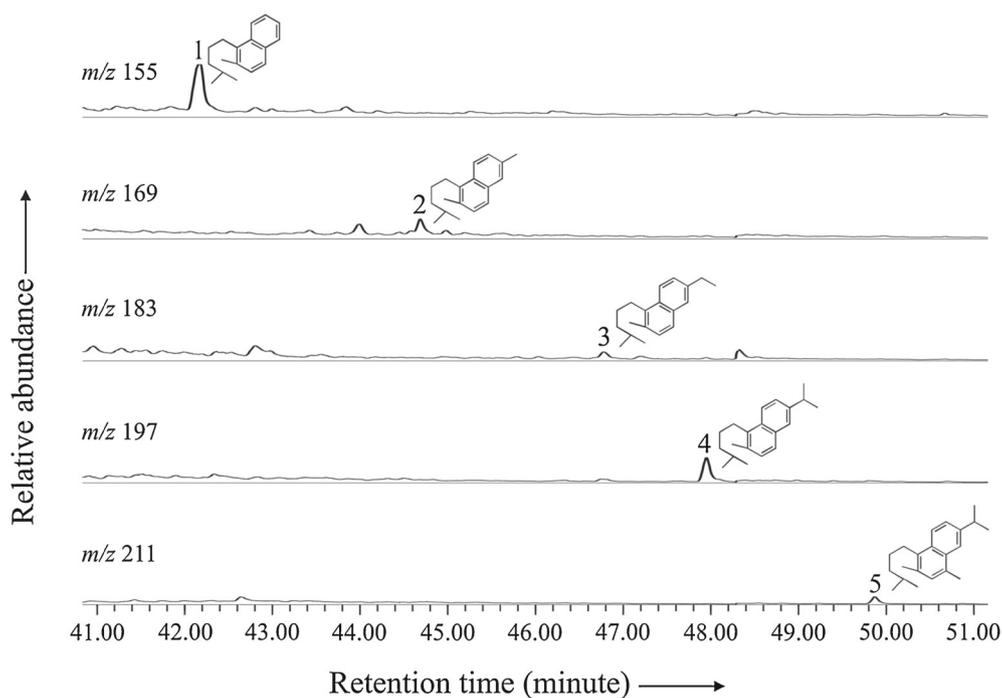


Figure 4. Partial mass chromatograms ( $m/z$  155, 169, 183, 197, 211) presenting the distributions of homologous series of isohexylalkylnaphthalenes (with molecular structures) in the aromatic fraction of condensate of Cretaceous age from a well, Jaisalmer basin, western India. Peak numbers are listed in table 3.

Table 3. Peak identifications, base peaks and molecular ions of isohexylalkylnaphthalene compounds present in the aromatic fraction of the Cretaceous condensate recovered from a well, Jaisalmer basin, western India.

Peak no.	Base peak	Molecular ion	Compound name
1	155	226	2-methyl-1-(4-methylpentyl)naphthalene
2	169	240	2,6-dimethyl-1-(4-methylpentyl)naphthalene
3	183	254	6-ethyl-2-methyl-1-(4-methylpentyl)naphthalene
4	197	268	6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene
5	211	282	6-isopropyl-2,4-dimethyl-1-(4-methylpentyl)naphthalene

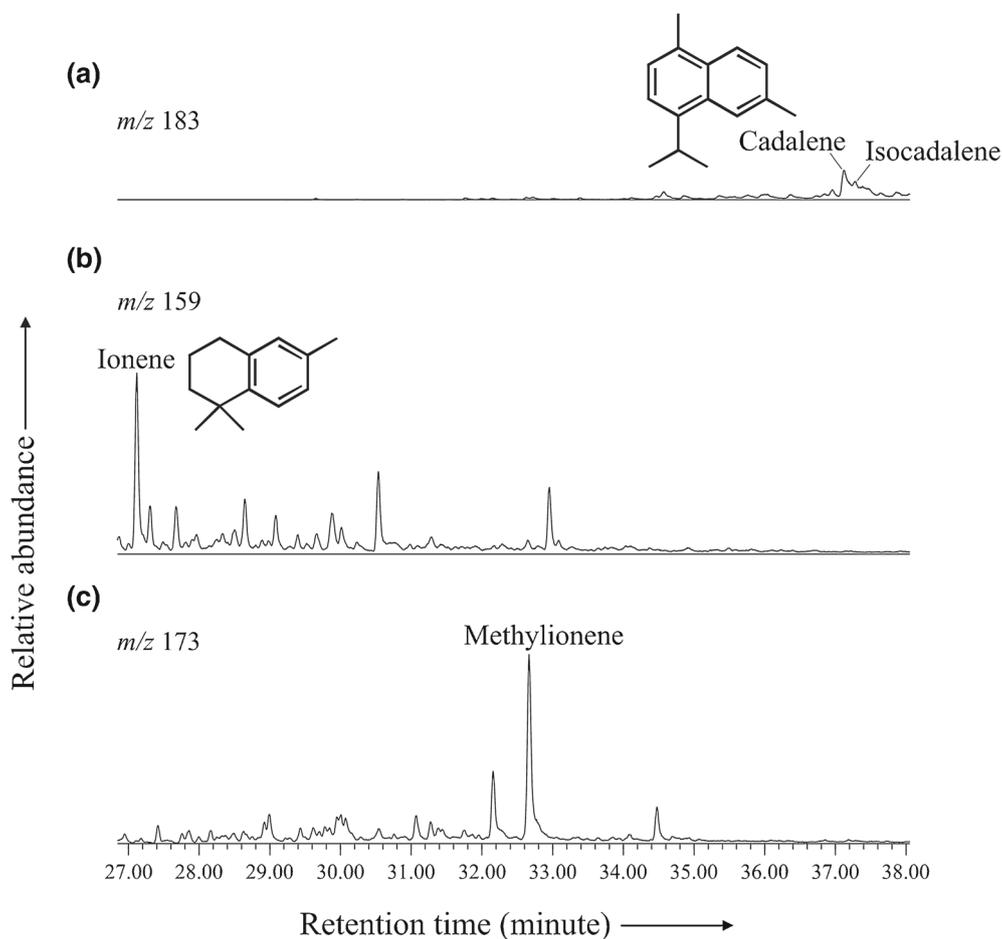


Figure 5. Partial mass chromatograms depicting the distributions of sesquiterpenoids (a) cadalene and isocadalene ( $m/z$  183), (b) ionene ( $m/z$  159) and (c) methyl-ionene ( $m/z$  173) in the aromatic fraction of condensate of Cretaceous age from a well, Jaisalmer basin, western India.

and rearrangement processes during diagenesis. The plausible reaction mechanism is described in Ellis *et al.* (1996). The fundamental conditions required for the reactions to proceed are the presence of an A/B ring system with a *gem*-dimethyl group in the A-ring at C-4, a methyl group at C-10 and an unsaturated B-ring. A shift of methyl group occurs from C-10 to C-5 along with opening of the A-ring thereby generating

an isohexyl chain. The B-ring gets aromatized. Laboratory experiments were conducted by Ellis *et al.* (1996) with non-aromatic diterpenoids and triterpenoids, which when heated under controlled conditions generated these compounds alongside other relevant compounds. The precursor compounds employed were labdan-8, 15-diol, phyllocladene and olean-18-ene. It is clearly evident that labdan-8, 15-diol and olean-18-ene produce

isohexylalkylbenzenes which are not observed in the present sample. Phyllocladene generates isohexylalkylnaphthalenes. However, higher plant diterpenoids and triterpenoids cannot always be colligated with isohexylalkylnaphthalenes since genesis of these compounds is fraught with uncertainties. For instance, the opening of ring A is not favoured in the presence of oxygenated functional groups in the A-ring. However, the process moves on with ease in the presence of a *gem*-dimethyl group in ring A. Considering the presence of other aromatic diterpenoids in the present sample like cadalene, simonellite and retene, it is credible that the isohexylalkylnaphthalenes might be modified products of higher plant diterpenoids.

#### 4.2.3 Sesquiterpenoids

The chromatograms of the following aromatic sesquiterpenoids are provided in figure 5.

Aromatic monocyclic sesquiterpenoid, dihydro-*ar*-curcumene is observed in the present sample. In spite of being an aromatic compound, it elutes in the saturate fraction plausibly because of low

polarity. A single peak of dihydro-*ar*-curcumene is observed from the chromatogram. However, the enantiomers (S, R) are not discernable. Previous studies (Ellis *et al.* 1995) have demonstrated the association of this compound with other higher plant markers, both gymnosperm and angiosperm. Ellis *et al.* (1995) opined that this compound might originate during diagenesis from natural product precursors like bisabolene or curcumene owing to the similarity in the structures. It might also be possible that cadinane-related structures go through a series of reactions which include aromatization, opening of ring and giving rise to dihydro-*ar*-curcumene.

Cadalene is reported in the present sample. This compound is probably the diagenetic alteration of cadinane-related compounds (Loureiro and Cardoso 1990). The presence of cadalene indicates higher plant source (Dutta *et al.* 2011a, b). Isocadalene is probably present which forms a shoulder to cadalene and cadalene is more predominant with respect to isocadalene. Isocadalene/cadalene ratio is useful for understanding maturity of sediments and crude oils. Natural

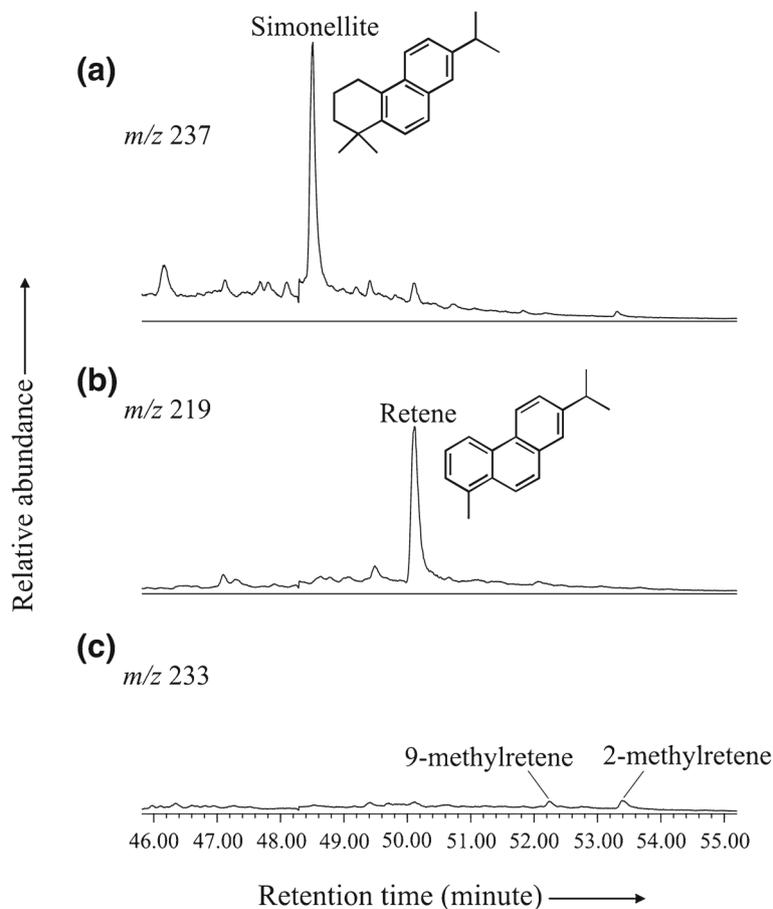


Figure 6. Partial mass chromatograms depicting the distributions of aromatic diterpenoids (a) simonellite ( $m/z$  237), (b) retene ( $m/z$  219) and (c) methylretene ( $m/z$  233) in the aromatic fraction of condensate of Cretaceous age from a well, Jaisalmer basin, western India.

products and laboratory experiments have shown that the abundance of isocadalene increases with depth/temperature (Alexander *et al.* 1994b).

Ionene ( $m/z$  159) and methyl-ionene ( $m/z$  173) have been recorded in the sample. They have been considered as degradation products of sesquiterpenoids or diterpenoids. These compounds are supposed to be alteration products of labdane-type diterpenoids (Yamamoto *et al.* 2006; Pereira *et al.* 2009; Menor-Salván *et al.* 2010).

#### 4.2.4 Diterpenoids

The chromatograms of the following aromatic diterpenoids are depicted in figure 6. Higher plant diterpenoid biomarkers are not recorded in the saturate fraction. This is probably because the saturate diterpenoids have been converted to their aromatic counterparts. This might be due to several factors. Firstly, thermal maturity might have played a role in the aromatization process. Also,

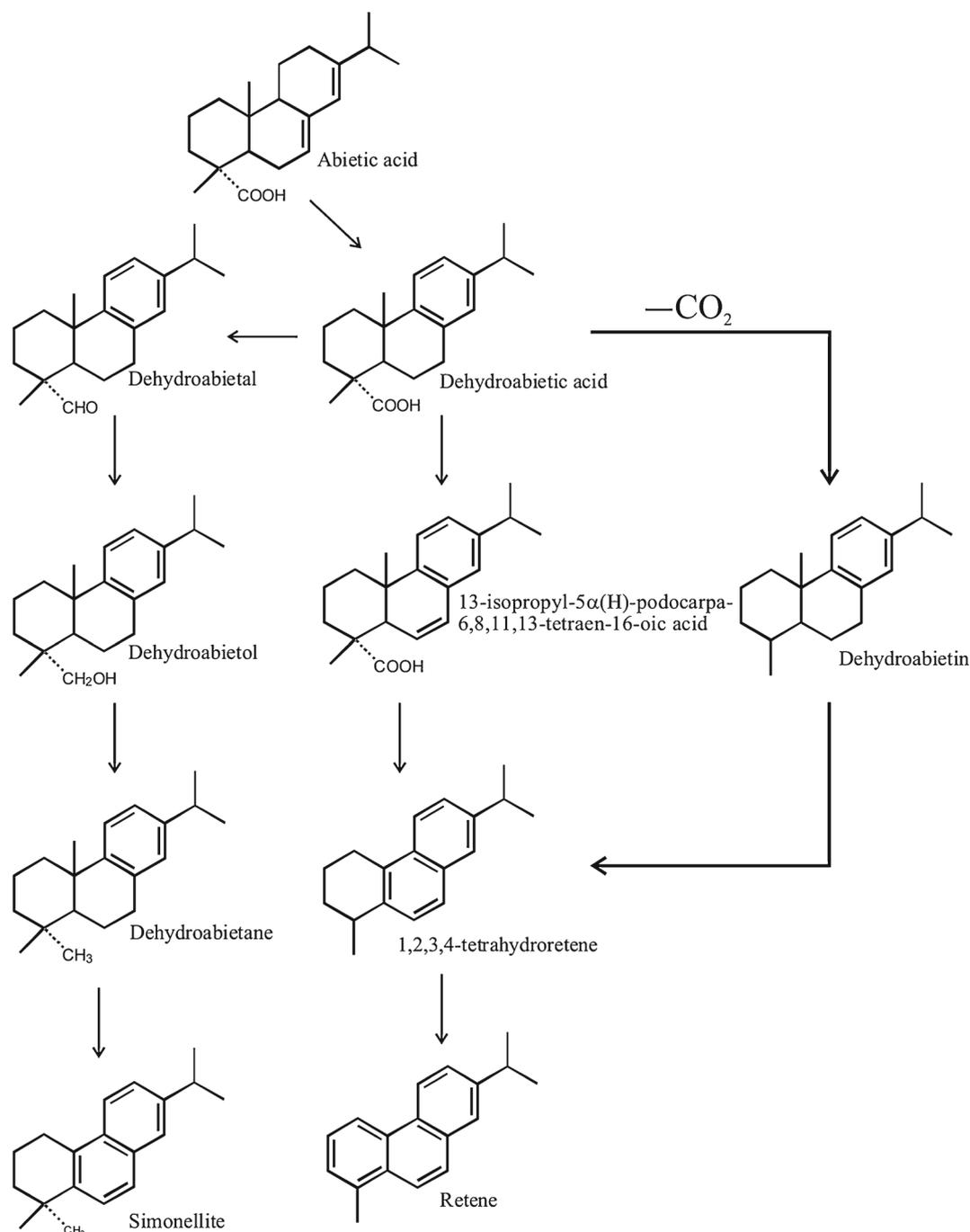


Figure 7. Possible mode of formation of simonellite and retene from abietic acid. Compounds enclosed in boxes are suggested intermediates (modified from Pereira and Rostad 1983).

clay is known to catalyze molecular rearrangement reactions and it favours the aromatization of terrestrial plant terpenoids (Romero-Sarmiento *et al.* 2010).

Simonellite is believed to be derived from higher plant precursors, particularly conifers (Otto and Simoneit 2001). This compound is a diagenetic product of abietic acid (Otto *et al.* 1997). However, it has been argued that generation of simonellite from abietic acid is not favourable since abietic acid does not possess any *gem*-dimethyl group. Simonellite may originate from precursors bearing *gem*-dimethyl group such as compounds possessing abietane-skeleton or phyllocladane (Bastow *et al.* 2001). Further advancement in the diagenetic process transforms simonellite to retene through aromatization of ring A and removal of a methyl group from the same (Pereira and Rostad 1983).

Retene is generally related to coniferous precursors and considered as a diagenetic product of abietane-type diterpenoids like abietic acid (Otto and Simoneit 2001, 2002; Marynowski *et al.* 2007). Bryophytes might bear precursor compound or compounds of retene. Although the supposed precursors like abietic acid or terrestrial plant diterpenoids like phyllocladane have not been reported in bryophytes but rearranged abietanes and compounds with kaurane skeleton have been observed (Romero-Sarmiento *et al.* 2010). There have been proposals of retene being derived from phyllocladane when subjected to thermal alteration. This involves aromatization of the rings in phyllocladane and the generation of an isopropyl group (Alexander *et al.* 1987). Although several propositions have been made regarding the genesis of retene and numerous precursors are inferred, the most widely accepted view is its derivation from gymnosperm coniferous precursors. The possible mode of formation of simonellite and retene is presented in figure 7. The assemblage of compounds that make up the condensate suggests that conifer has been the significant source into the organic matter.

Methylretene has also been observed although in very low abundance. Two peaks are discernable having the major fragments 233 and 248, signature of methylretene. The first peak corresponds to 9-methyl retene and the second peak corresponds to 2-methyl retene as compared with the data published by Bastow *et al.* (2001). Laboratory dehydrogenation experiments of simonellite have yielded retene as well as methylretene. It has been proposed that precursors having *gem*-dimethyl group may generate methylretene by the shift of a methyl group (Bastow *et al.* 2001).

Finally, the presence of these sesquiterpenoids and diterpenoids in the studied sample clearly

depicts that conifer-derived organic matter has contributed to the source biomass of the condensate. However, the predominance of normal alkanes ranging from C<sub>12</sub> to C<sub>15</sub> suggests that the organic matter was probably reworked by bacteria.

## 5. Conclusions

The present paper documents the organic geochemical characteristics of early Cretaceous condensate recovered from Jaisalmer basin, Rajasthan, India. The presence of aromatic sesquiterpenoids, for instance, dihydro-*ar*-curcumene, cadalene, ionene, are recorded which indicate higher plant precursors. Aromatic diterpenoids, simonellite, retene, and methylretene confirm the contribution of higher plants and also specify conifer source. The presence of normal alkanes dominant in the range of C<sub>12</sub>–C<sub>15</sub> plausibly suggests reworking by bacterial biomass. The absence of saturate diterpenoids indicates that the conditions were hugely favourable for the aromatization process. Also, the presence of some distinctive compounds like diamondoids, isohexylalkylnaphthalenes and methylretene hints to the fact that rearrangement reactions, either triggered by thermal factors or microbial activities, were significant processes that determined the geochemistry of the condensate.

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