



Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age

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ABSTRACT

Crocetane, an irregular C₂₀ isoprenoid, in sediments generally associated with gas hydrate settings, is a molecular indicator for the anaerobic oxidation of methane. Green sulfur bacteria (GSB) are the main source for specific aromatic carotenoids (e.g. isorenieratane) in sedimentary environments and are molecular indicators of photic zone euxinia (PZE). The present study comprises a detailed molecular and isotopic study of crocetane and GSB derived carotenoids in Devonian sediments of the Western Canada Sedimentary Basin (WCSB) covering a range of thermal maturities. In addition, a series of oils generated from Devonian source rocks of the basin have been analysed for crocetane. Crocetane was found in ten sediments from the WCSB and in seven Devonian WCSB crude oils. Its abundance was found to increase with thermal maturity, whereas the components derived from C₄₀ derived carotenoids decrease steadily. We were not able to identify 2, 6, 10, 15, 19-pentamethylcosane (PMI) neither in the Duvernay Formation sediments nor in the WCSB crude oils, consistent with previous findings. The preferred proposed natural product precursor for crocetane is thus GSB derived carotenoids. This is corroborated by their similar structural features and the $\delta^{13}\text{C}$ value of combined crocetane and phytane in these samples. However, contributions from other carotenoids cannot be fully excluded. Crocetane can provide evidence for PZE conditions in highly mature samples and crude oils of Devonian age.

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1. Introduction

Crocetane (**I**), an irregular tail-to-tail C₂₀ isoprenoid (2,6,11,15-tetramethylhexadecane) has been used as a molecular indicator for the anaerobic oxidation of methane in sediments derived from gas hydrate settings and methane rich mud volcanoes (e.g. Elvert et al., 1999, 2000; Thiel et al., 1999; Pancost et al., 2000). This compound has been detected in sediments comprising archaea mediating oxidation by reverse methanogenesis in co-operation with sulfate reducing bacteria (Hoehler et al., 1994; Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 2000; Pancost et al., 2000). In anoxic environments such as these, crocetane was found to be depleted in ¹³C (e.g. −120‰) suggesting that it derives from organisms mediating the anaerobic oxidation of ¹³C depleted methane (e.g. Thiel et al., 1999; Pancost et al., 2000). Moreover, crocetane has been reported in Western Australian crude oils from the Canning Basin of Devonian age (Barber et al., 2001; Greenwood and Sum-

mons, 2003). However, the discrete source of crocetane in the Devonian and especially in crude oils still remains ambiguous.

The biomarker isorenieratane (**II**) is generally derived from the carotenoid isorenieratene (**III**), which is synthesised by photosynthetic green sulfur bacteria (*Chlorobiaceae*) (e.g. Summons and Powell, 1986; Requejo et al., 1992; Grice et al., 1996; Koopmans et al., 1996). Another C₄₀ carotenoid, paleorenieratane (**IV**), also thought to be derived from GSB has been identified in Devonian aged sediments and crude oils (Hartgers et al., 1994; Requejo et al., 1992). GSB are strict anaerobes that require light and hydrogen sulfide in stratified water columns to carry out photosynthesis and are thus markers for photic zone euxinia (PZE) in depositional environments. Because carbon assimilation in GSB occurs via the reversed tricarboxylic acid cycle (TCA), their biomass and lipids are distinguished by ¹³C enriched values relative to organisms that use the C3 pathway for CO₂ fixation (Quandt et al., 1977; Sirevag et al., 1977). Sediments that contain crocetane and diaromatic carotenoids (**II** and **IV**), both representing euxinic conditions, are intriguing. One notable coincidence is the occurrence of crocetane in Devonian crude oils that have been sourced from a type II organic matter rich calcareous source rock deposited under PZE conditions.

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This paper comprises a detailed molecular and isotopic study of crocetane and GSB derived carotenoids (e.g. isorenieratane- **II** and paleorenieratane- **IV**) in calcareous sediments of the Western Canada Sedimentary Basin (WCSB, upper Devonian Duvernay Formation) that cover a range of thermal maturities. In addition, a series of oils generated from Devonian source rocks of the basin have been analysed for crocetane to establish its general occurrence in Devonian samples. Understanding the source of crocetane will certainly aid oil–source correlation studies of petroleum systems (especially of Devonian age).

2. Materials and methods

2.1. Western Canada Sedimentary Basin: Devonian source rock and crude oil samples

The Upper Devonian Duvernay Formation, part of the Late Devonian Woodbend Group in the central Alberta region of the Western Canada Sedimentary Basin (WCSB), has excellent hydrocarbon source potential (Stoakes and Creaney, 1984, 1985; Creaney and Allan, 1990; Chow et al., 1995) (Fig. 1). It is an organic matter rich basinal carbonate succession that was deposited in palaeo-water depths mostly greater than 100 m (Creaney and Allan, 1990). Total organic carbon (TOC) contents vary from 0.5% to 10.8% throughout the basin (Fowler et al., 2001). Hydrogen indices (HI) are reported to be between 500 and 600 mg HC/g TOC, indic-

ative of a type II kerogen. The Duvernay Formation exhibits a range of maturity levels from immature to over mature. Oils generated from the Duvernay Formation are mostly paraffinic-aromatic oils with low sulfur contents (less than 0.5%) (Grantham and Wakefield, 1988; Requejo et al., 1991).

Detailed geological descriptions and reports of geochemical characteristics of bitumens and kerogens from the Duvernay Formation have been provided by Creaney and Allan (1992) and Requejo et al. (1992). The stratigraphic succession of the Devonian in the WCSB is summarised in Fig. 2.

The sediments used in this study consist of 10 samples from the Duvernay Formation which are characterised by TOC values ranging from 1.5% to 5.4% and HI values ranging from 55 to 591 mg HC/g TOC (Table 1). The thermal maturity of the source rock samples increases with depth as shown by T_{max} values varying between 414 and 441 °C (Fig. 3). Seven crude oils reservoirised in various geological units in the WCSB, all Devonian in age, were also used in this study (Table 2).

2.2. Sample preparation

The sediment samples were surface extracted using a solution of dichloromethane and methanol (9:1), and dried before grinding. The samples were then ground to a particle size of approximately 150 µm using a ring mill.

2.3. Solvent extractions

The Duvernay Formation samples were extracted using an automated accelerated solvent extractor (ASE 200 Dionex, Sunnyvale, CA, USA). The ground sediments were weighed into pre-extracted stainless steel extraction cells containing pre-rinsed glass fibre filters. The cells were loaded into the turret of the ASE. The cells were preheated at 100 °C (2 min). A 9:1 mixture of dichloromethane and methanol was pumped into the cells using a pressure of 1000 psi for 5 min. The entire procedure was repeated until the solvent in the collection vial became colourless. Finally, the extracts were combined and the solvent was removed under a nitrogen purge.

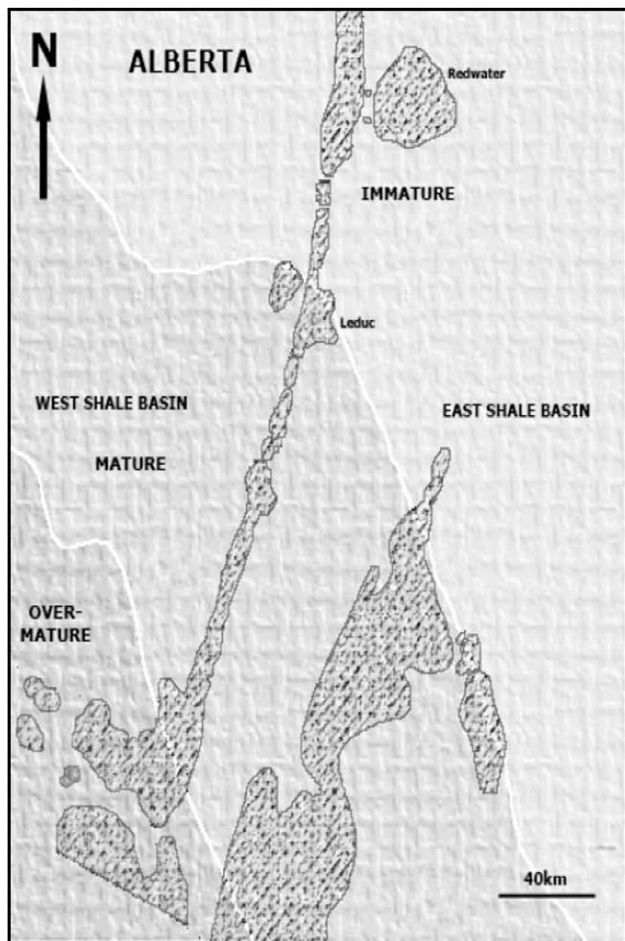


Fig. 1. A map of east central Alberta Basin, showing the location of the wells from which the sediment samples penetrating the Devonian Duvernay Formation were used for this study (modified after Stoakes and Creaney, 1985).

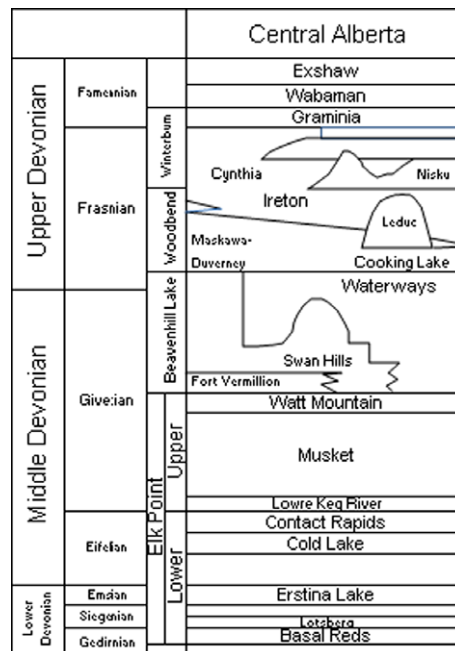


Fig. 2. Generalized stratigraphic column of the Alberta Basin in the Western Canada Sedimentary Basin, showing the Devonian subsurface (modified after Wendte, 1992).

Table 1

Sample description, organic carbon (TOC) and Rock-Eval pyrolysis parameters of source rocks studied from the Duvernay Formation, WCSB. Samples are listed in order of increasing maturity.

Locality	Depth (m)	TOC (wt.%) ^a	T _{max} (°C)	HI (mg HC/g TOC) ^a
Redwater	1147.3	5.4	419	591
Redwater	1157.2	4.7	414	494
Imperial Kingman	1402.7	2.7	426	410
Imperial Kingman	1404.5	3.2	426	432
Leduc	1766.9	3.6	434	465
Leduc	1773	4.5	436	576
Ferrybank	2239.5	4.0	437	273
Ferrybank	2248.7	3.3	437	247
Imperial Cynthia	2971.5	1.5	440	55
Imperial Cynthia	2973.7	4.2	441	303

^a TOC, total organic carbon; HI, hydrogen index.

2.4. Fractionation of crude oils and sediment extracts using column chromatography

The Duvernay Formation sediment extracts were fractionated using a large scale liquid chromatography method. The sediment extract was applied to the top of a large column (20 cm × 0.9 cm i.d.) containing activated silica gel (120 °C, 8 h), which was pre-washed with *n*-hexane. The saturated fraction was eluted with *n*-hexane (35 ml), the aromatic hydrocarbon fraction with a solution of dichloromethane in *n*-hexane (40 ml, 30%), and the polar fraction with dichloromethane and methanol (40 ml, 50%).

Devonian sourced crude oils were fractionated using a small scale column liquid chromatography method (Bastow et al., 2007). The sample was applied to the top of a small column (5.5 cm × 0.5 cm i.d.) containing activated silica gel (120 °C, 8 h). The saturated fraction was eluted with *n*-hexane (2 ml), the aromatic hydrocarbon fraction with a solution of dichloromethane in *n*-hexane (2 ml, 30%), and the polar fraction with dichloromethane and methanol (2 ml, 50%).

2.5. 5A molecular sieving

Straight chain hydrocarbons were separated from branched and cyclic hydrocarbons by treating the saturated fractions with activated (250 °C, 8 h) 5A molecular sieves (Murphy, 1969; Dawson et al., 2005; Grice et al., 2008) in cyclohexane. In a typical 5A

Table 2

Devonian crude oil samples containing crocetane (Western Canada Sedimentary Basin and Canning Basin).

Sample	Depth (m)	Age-source	Cr/Ph SIM <i>m/z</i> 169 [*]
2204 Woodriver	1856	Nisku Fm	0.07
2221 Big Valley	1569.7	Duvernay Fm	0.04
2158 Clive	1868	Duvernay Fm	0.45
2177 Lone Pine	2362.8	Duvernay Fm	0.36
1634 Rich	2231	Winnipegosis Fm	0.08
207 Aquitane	1805.6	Keg River Fm	0.16
807 Zama	1516.5	Keg River Fm	0.31
Blina-1	–	Late Devonian	0.63 ^{**}
Janpam North-1	–	Late Devonian	0.40 ^{***}

^{*} Ratios of crocetane to phytane (Cr/Ph) refer to measurements of the peak heights in *m/z* 169 ion chromatogram.

^{**} The Cr/Ph ratio is from Barber et al. (2001).

^{***} The Cr/Ph ratio is from Greenwood and Summons (2003).

molecular sieving separation, a portion of the saturate fraction in cyclohexane was added to a 2 ml vial, ¼ of it filled with activated 5A molecular sieves. The vial was capped and placed into a pre-heated aluminium block (85 °C, overnight). The resulting solution was then cooled and filtered through a small column of silica plugged with cotton wool (pre-rinsed with cyclohexane) and the sieves were rinsed thoroughly with cyclohexane yielding the branched/cyclic fraction (5A excluded).

2.6. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analyses were performed on a Hewlett Packard (HP) 5973 mass spectrometer interfaced to a HP 6890 gas chromatograph fitted with a 60 m × 0.25 mm i.d. WCOT fused silica capillary column coated with 0.25 µm thick film (DB-5, J&W Scientific). In a typical analysis, the GC oven was programmed from 40 °C to 310 °C at 3 °C/min with initial and final hold times of 1 and 30 min, respectively. Samples (in *n*-hexane) were injected in split-less mode using a HP 6890 series autosampler. The carrier gas used was ultra high purity helium with a constant flow rate of 1 ml/min.

For crocetane identification, the analyses were performed on the same instrument but fitted with a 60 m × 0.25 mm i.d. DB-1701 column coated with 0.25 µm thick film (J&W Scientific). The mass spectrometer was operated in selected ion monitoring (SIM) mode to monitor *m/z* 113, 169, 183, 197 and 282. An internal

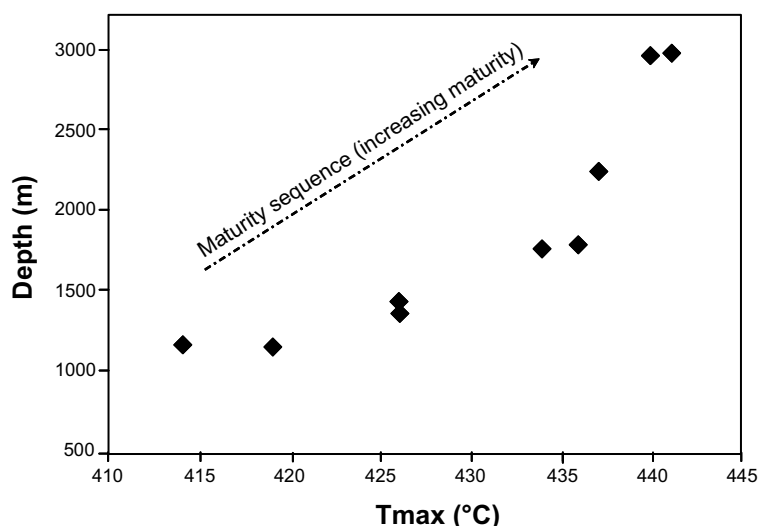


Fig. 3. Depth profile showing maturities (*T*_{max}) of studied sediment samples from the Duvernay Formation.

perdeuterated aromatic standard was added to the aromatic fraction for quantification purposes (see below also).

For alkylbenzene and alkylnaphthalene quantifications, weighed aliquots of crude oils were spiked with internal standards before the small scale silica column fractionation was performed. Aromatic fractions were purified as described by Bastow et al. (2007). Tri- and tetramethylbenzenes and tetramethylnaphthalenes were analysed in selected ion monitoring mode (SIM) scanning for the following ions: m/z 119 (trimethylbenzenes), m/z 133 (tetramethylbenzenes) and m/z 184 (tetramethylnaphthalenes). Compounds were quantified relative to d_8 -naphthalene. No corrections for individual response factors were made.

2.7. Compound specific isotope analyses (CSIA)

CSIA were performed on a Micromass IsoPrime instrument. Methods are described in Grice et al. (2008). The average values of three runs for each compound is reported and only results with a standard deviation of less than 0.4‰ were used.

2.8. Quantum mechanical calculations

Ab initio quantum mechanical calculations have been performed for selected cases in order to examine the relative energy of the systems. Given the size of the molecules to be studied, the hybrid functional B3LYP (Becke, 1993; Stephens et al., 1994) was selected as an appropriate Hamiltonian and calculations have been performed with both the 3-21G** and 6-31G** basis sets in order to evaluate the influence of this numerical factor on the results. B3LYP represents a hybrid density functional, based on the adiabatic connection method of Becke, where the Becke gradient corrected exchange functional is mixed with Hartree–Fock exchange and the Lee–Yang–Parr gradient-corrected correlation functional in a parameterized expression. 6-31G** represents a basis set where core orbitals are presented by a linear contraction of 6 Gaussians and the valence orbitals are represented by a double-zeta combination of a 3 Gaussian contraction and a single further Gaussian. In addition, polarization functions are added for all atoms including hydrogen (Hehre et al., 1972).

All calculations have been performed using NWChem version 4.7 (Apra et al., 2005), with a fine grid for integration of the exchange correlation potential, implying a target accuracy for the total energy of 10^{-7} with respect to the quadrature. Full geometry optimisation was applied to all configurations to obtain the local minimum with an energy converged to better than 0.01 kJ/mol with respect to structural parameters. No correction has been made for zero point energy or finite temperature effects.

3. Results and discussion

3.1. Crocetane (I) in sediments and crude oils of WCSB

The branched/cyclic hydrocarbon fractions of a suite of Devonian aged sediments and crude oils from WCSB were analysed by GC–MS. Since both the suite of Duvernay oils and sediment samples examined represent a range of maturity levels, they present an opportunity to examine the formation of crocetane, through maturity from individual aromatic biomarker compounds isorenieratane (II) and paleorenieratane (IV) of GSB.

Studies concerning the GC elution behaviour of phytane (V) and crocetane (I) have been reported previously (e.g. Robson and Rowland, 1993; Thiel et al., 1999; Barber et al., 2001). Robson and Rowland (1993) achieved partial GC separation of these two compounds using an OV-1 stationary phase. Thiel et al. (1999) also achieved partial resolution of phytane (V) and crocetane (I) on a

squalane column using hydrogen as a carrier gas. Barber et al. (2001) developed a method for analyses of these diastereomeric isoprenoids in sediments and crude oils using a β -cyclodextrin column using helium as a carrier gas. In this study, we utilised a DB-1701 column (60 m, 0.25 mm i.d., J&W Scientific) of relatively greater polarity, which is more readily available commercially and can be routinely used in organic geochemical studies to achieve a similar separation of phytane (V) and crocetane (I). Single ion monitoring of m/z 169 and m/z 183 were used to determine the peak areas and thus the ratio of crocetane (I) relative to phytane (V) in sediments and crude oils (Table 2 and Fig. 4). A calibration with artificial standards of crocetane (I) and phytane (V) was used in the analyses as described by Barber et al. (2001) and Greenwood and Summons (2003).

Crocetane was found to be present throughout the Duvernay Formation sequence and in all the Devonian crude oils (Table 2 and Fig. 4). The relative abundance of crocetane (I) to phytane (V) i.e. Cr/Ph in the Duvernay Formation sediment samples gradually increases with thermal maturity represented by T_{\max} values ranging between 414 and 441 °C (Fig. 4). However, the Cr/Ph in the crude oils varies between samples (Table 2). Clive, Lone Pine and Zama crude oils show the highest relative abundances of crocetane having Cr/Ph of 0.45, 0.36, and 0.31, respectively. The remaining samples show much lower relative abundances of crocetane having Cr/Ph ranging between 0.16 and 0.04. The occurrence of crocetane (I) in various crude oil samples has been shown previously by Barber et al. (2001) and Greenwood and Summons (2003). It is apparent that crocetane (I) appears to be generally higher in Devonian aged oils (e.g. the Canning Basin, Western Australia) and Devonian oils from WCSB (this study).

3.2. Diaromatic carotenoids in sediments of WCSB

Aromatic carotenoids (such as isorenieratane- II and paleorenieratane- IV) contain one or more trimethyl substituted aromatic rings connected by an isoprenoid chain. The structural similarity of crocetane (I), the irregular tail-to-tail linked C_{20} isoprenoid 2,6,11,15-tetramethylhexadecane, with these carotenoids and their co-occurrence in Devonian source rocks and crude oils in WCSB is interesting since it could imply a common origin.

The diaromatic carotenoids (II and IV) as well as aryl isoprenoids are important constituents of the aromatic hydrocarbon fractions of the Devonian Duvernay Formation (WCSB) and related oils (Summons and Powell, 1986; Requejo et al., 1991; Hartgers et al., 1994). Molecular and isotopic studies of these particular compounds show that two C_{40} diaromatic carotenoids (II and IV) have a significant contribution from carotenoids of photosynthetic GSB.

Abundances ($\mu\text{g/g}$ TOC) of the extractable aromatic hydrocarbons were determined for the Devonian Duvernay Formation source rock samples. The depth abundance profiles for isorenieratane (II) and paleorenieratane (IV) show a decrease in concentration from 236 to 8 $\mu\text{g/g}$ TOC and from 1874 to 22 $\mu\text{g/g}$ TOC, respectively, with depth (Fig. 4). Both reach a minimum concentration at 1773 m, corresponding to a maturity of 436 °C T_{\max} . At a T_{\max} of 437–441 °C, concentrations of both compounds are below detection limit (Fig. 4). These data show that the change in concentration of diaromatic carotenoids is proportional to thermal maturation of the organic matter present in the sediments.

Another comparison of change in concentration of diaromatic carotenoids with a traditional maturity parameter, (C_{32}) homohopane 22S/22(S+R), was made to further assess whether the change in abundance of diaromatic carotenoid composition is directly related to maturity. The quantitative abundance of isorenieratane

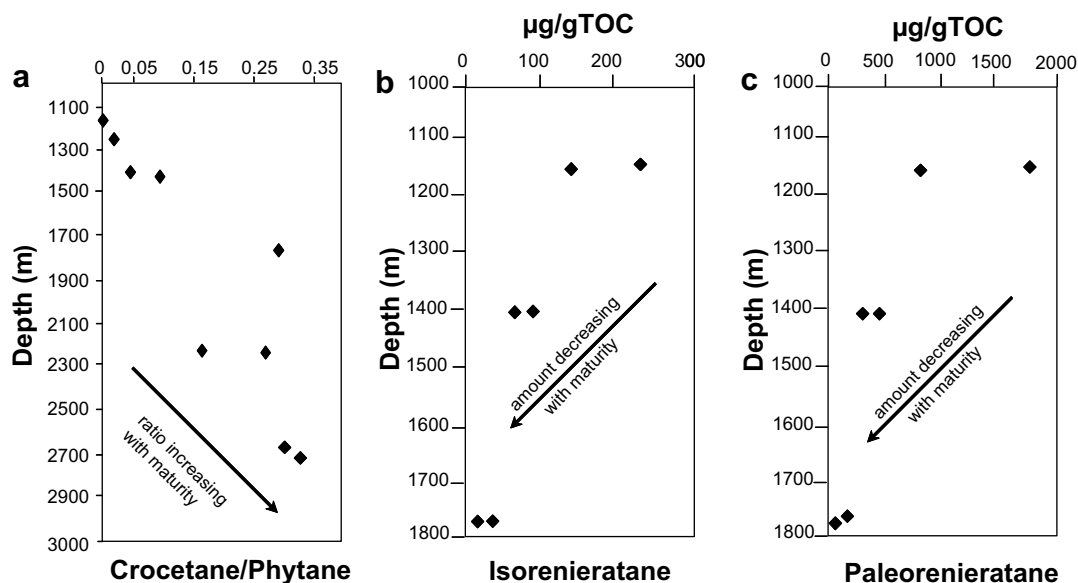


Fig. 4. Plots of (a) Cr/Ph ratio versus depth (b) abundance of (II) versus depth and (c) abundance of (IV) versus depth from Duvernay Formation sediment extracts. The direction of the arrows indicates increasing and decreasing maturity.

(II) shows that there is a similar decrease in concentration of isorenieratane (II) with an increase in C_{32} 22S/22(S+R) and thus rising thermal maturity (Fig. 5). The concentration of isorenieratane (II) decreases from 236 to 0 $\mu\text{g/g}$ TOC parallel to an increase in the ratio of C_{32} 22S/22(S+R) from 0.26 to 0.68. These data also support that the variation in abundance of isorenieratane (II) is proportional to maturation.

With increasing maturation, the abundance of Cr/Ph in Duvernay source rock bitumens increases to a point, whereas diaromatic carotenoids decrease steadily. The Cr/Ph appear to correlate

strongly with maturity, as shown by its correlation with T_{max} values ($R^2 = 0.84$). Similarly, the diaromatic carotenoid isorenieratane shows a strong correlation with depth ($R^2 = 0.79$).

3.3. Potential sources for crocetane (I) based on structure

Several potential sources for crocetane have been proposed previously and these include: (i) a diagenetic product of the C_{25} irregular isoprenoid, 2,6,10,15,19-pentamethylcosane (PMI, VI see Barber et al., 2001) reported in cultured organisms, microbial communities and sediments consisting of methanogenic (e.g. Koga et al., 1993; Schouten et al., 1997, 2001a,b) and methanotrophic archaea (Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 1999, 2000; Pancost et al., 2000) and (ii) a direct biological precursor from microbial consortia consisting of methanotrophic archaea and sulfate reducing bacteria that are typically depleted in ^{13}C (e.g. Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 2000; Pancost et al., 2000; Orphan et al., 2001), due to carbon assimilation from an isotopically depleted carbon source (i.e. biogenic methane). However, in the Duvernay Formation sediments and the WCSB crude oils, we were not able to identify any PMI (VI). Only small amounts of a C_{25} regular isoprenoid were observed, consistent with the findings of Greenwood and Summons (2003). These data are also consistent with the notion that PMI (VI) has not yet been reported in samples predating the Cretaceous.

Based on structural grounds and the findings above, other potential sources for crocetane (I) include a variety of carotenoid derived biomarkers (e.g. lycopene (VII), β -carotene (VIII), β -isorenieratene (IX), isorenieratene (III), renieratene (X) and paleorenieratene (XI), okenone (XII) via β -cleavage. Interestingly, sedimentary bitumens and oils of Palaeozoic age have been reported to contain high concentrations of carotenoid derivatives including a large array of carotenoid cyclisation and degradation products (Grice et al., 1996, 2005; Koopmans et al., 1996, 1997; Clifford et al., 1998; Sinninghe Damsté et al., 2001). These products also include aryl isoprenoids (e.g. Pedentchouk et al., 2004). In certain instances, β -carotene (VIII) can yield β -isorenieratene by aromatisation (Koopmans et al., 1998). Isorenieratene (II)

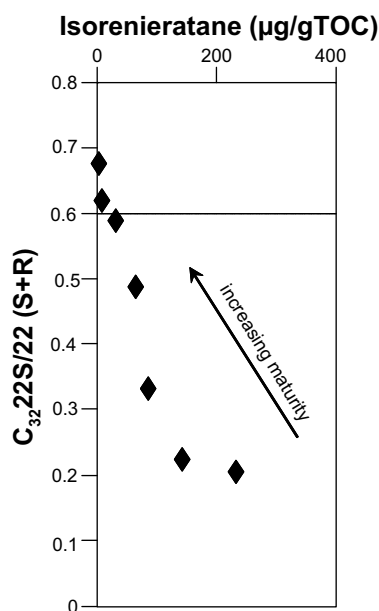


Fig. 5. Plot of abundance of (II) versus the variation of a hopane maturity parameter (C_{32} homohopane 22S/22(S+R)) in Duvernay Formation sediment extracts. The direction of the arrow indicates increasing maturity.

can also be formed from β -carotene (**VIII**) by aromatisation of both cyclohexenyl moieties. The aryl isoprenoids, which can be formed by carbon-carbon bond cleavage of both isorenieratane (**II**) and β -isorenieratane, thus can have a mixed $\delta^{13}\text{C}$ signature (Grice et al., 1997; Koopmans et al., 1998; Pedentchouk et al., 2004). $\delta^{13}\text{C}$ analyses reported for isorenieratane (**II**) and paleorenieratane (**IV**) in the Duvernay Formation sediments (e.g. Hartgers et al., 1994) are consistent with a GSB source being significantly enriched in ^{13}C relative to algal biomarkers, in keeping with the use of the reversed TCA cycle in *Chlorobiaceae* (Evans et al., 1966), which can lead to biomass enriched in ^{13}C (Quandt et al., 1977; Sirevag et al., 1977). Given that no β -carotene, okenane, or lycopane components are evident in the Duvernay Formation sediments, it is likely that carotenoids such as isorenieratane (**II**), paleorenieratane (**IV**) and renieratane, derived from *Chlorobiaceae*, are the most likely sources for crocetane. However, contributions from other carotenoids cannot be fully excluded for reasons described above.

3.4. Potential sources of crocetane (**I**) based on $\delta^{13}\text{C}$

Crocetane (**I**) has been previously identified by its light isotopic signature confirming a source associated with anaerobic methane oxidation (Thiel et al., 1999; Peckmann et al., 2002; Birgel et al., 2006). The combined $\delta^{13}\text{C}$ data of Cr and Ph reported by Barber et al. (2001) does not show any evidence for a ^{13}C depleted source. However, a slight ^{13}C enrichment was observed (Barber et al., 2001). The $\delta^{13}\text{C}$ values of pristane and combined crocetane (**I**) with phytane (**V**) in samples from this study are shown in Table 3. Given that the preferred precursor(s) for crocetane (**I**) are the carotenoids of GSB, phytane should be slightly less depleted in ^{13}C relative to pristane, assuming that pristane and phytane are predominantly sourced from the phytyl side chain of chlorophyll *a*. Contributions from halophilic archaea cannot be entirely excluded given that a C_{25} regular isoprenoid has been identified in these samples (Grice et al., 1998). Even so, $\delta^{13}\text{C}$ of the combined crocetane (**I**) and phytane (**V**) with increasing thermal maturity shows a greater $\Delta\delta$ difference to pristane, especially in the two deepest samples where the Cr/Ph is the highest. Taking into account the approximate percentage of crocetane (**I**) relative to phytane (**V**) in these samples, an estimated $\delta^{13}\text{C}$ value for crocetane (**I**) varies between -11 and -6‰ , consistent with a GSB source.

In addition to the source effects mentioned above, the $\delta^{13}\text{C}$ data of pristane and phytane (**V**) show a maturity effect throughout the section. The $\Delta\delta$ difference of pristane from the least mature sample to most mature sample is 3.9‰ , and for phytane (**V**) it is 5.4‰ . The larger $\Delta\delta$ difference with regards to rising maturity for phytane (**V**) can be attributed to a greater contribution of ^{13}C enriched crocetane (**I**) from a GSB source.

Table 3
 $\delta^{13}\text{C}$ values of pristane (Pr) and phytane (Ph) for the Western Canada Sedimentary Basin sediment extracts.

Sample, depth (m)	T_{max} ($^{\circ}\text{C}$)	$\delta^{13}\text{C}$ Pr (‰) ^a	$\delta^{13}\text{C}$ Ph (‰) ^a
G000542, 1147.3	419	-32.5 (0.39) ³	-31.6 (0.28) ³
G000584, 1402.7	426	-32.9 (0.18) ³	-32.4 (0.08) ²
G000553, 1766.9	434	-29.9 (0.09) ³	-29.6 (0.08) ²
G000557, 1773	436	-30.2 (0.07) ³	-29.4 (0.35) ³
G000595, 2239.5	437	-27.8 (0.38) ³	-28.3 (0.42) ³
G000601, 2971.5	440	-27.7 (0.12) ³	-26.1 (0.14) ³
G000603, 2973.7	441	-28.5 (0.14) ²	-26.2 (0.24) ²

^a Numbers in parentheses are standard deviations, superscript numbers are number of replicate analyses.

3.5. Formation of crocetane (**I**) from *Chlorobiaceae* carotenoids

Crocetane (**I**) can arise from isorenieratene through β -cleavage. With increasing maturation, the ratio of Cr/Ph in Duvernay source rock bitumens increases, whereas the C_{40} derived carotenoid components decrease steadily. β -Cleavage of long chain alkylthiophenes and alkylbenzenes has also been demonstrated by MSSV pyrolysis (at $300\text{ }^{\circ}\text{C}$ for 72 h) leading to generation of lower molecular weight alkylated thiophenes and benzenes (Sinninghe Damsté et al., 1998).

Additional diagenetic products of carotenoids include tetramethylbenzenes (TeMBs) (van Aarssen et al., 2007). An investigation on the relationship of 1,2,3,4-TeMB and 1,2,3,5-TeMB with Cr/Ph was carried out on the oils for this purpose. No TeMBs were present in the sediments, probably due to loss through evaporation. The occurrence of 1,2,3,4-TeMB and 1,2,3,5-TeMB both in kerogen pyrolysates of Duvernay Formation sediment samples and in crude oils from the WCSB has previously been reported (Requejo et al., 1992; Hartgers et al., 1994). The abundance of crocetane (**I**) and the high concentration of 1,2,3,5-TeMB ($\mu\text{g/g}$ oil) are evident in the Devonian oils studied herein (Fig. 6). The strong relationship demonstrated for the concentration of 1,2,3,5-TeMB and Cr/Ph points to a common source i.e. Devonian aged GSB carotenoid (palaerenieratene, **XI**) for 1,2,3,5-TeMB and crocetane (**I**). On the other hand the 1,2,3,4-TeMB is low in concentration when crocetane (**I**) is relatively higher. The lack of a trend is probably related to multiple sources for the 1,2,3,4-TeMB (Hoefs et al., 1995; Pedentchouk et al., 2004) and a predominant GSB source for crocetane (**I**). In order to demonstrate any difference in thermal stability of isorenieratene (**II**) and paleorenieratene (**IV**), or in their unsaturated forms of isorenieratene (**III**) and palaerenieratene (**XI**), respectively, *ab initio* quantum mechanical calculations were undertaken at the B3LYP/3-21** and B3LYP/6-31G** levels. For the unsaturated case, the conformation of the hydrocarbon backbone connecting the two benzene rings is unambiguous. However, for the saturated case there are four chiral centres and many possible local minima to be explored. In order to reduce the computational demands it has been assumed that the particular stereochemistry of the connecting hydrogen chain is unlikely to influence the preferential substitution pattern for benzene rings. Hence, in the present study the same conformation of the saturated hydrocarbon backbone is used for both isorenieratene (**II**) and paleorenieratene (**IV**) to ensure that any energy difference is solely related to the isomerism of the methyl substituents on the aromatic rings. Investigation of whether the methyl substitution pattern might induce a change of conformation is left for future work. Furthermore, it is assumed the molecule adopts an extended conformation and that the influence of solvent is negligible. In aqueous environments the saturated species may undergo some degree of folding in order to lower the effective surface area. Again, this remains the subject of future research.

For the unsaturated species, the energy differences are 5.8 and 7.0 kJ/mol at the B3LYP/3-21G** and B3LYP/6-31G** levels, respectively, with palaerenieratene (**XI**) being the thermodynamically favoured molecule in both cases. The small change as a function of basis set suggests that the result is likely to be robust with respect to this factor. Furthermore, the preference for palaerenieratene (**XI**) can be understood in terms of competition between the desire to avoid steric hindrance between the hydrocarbon backbone and the methyl substituents of the terminal benzene rings and the preference to maintain conjugation; palaerenieratene (**XI**) has one less methyl group adjacent to the unsaturated backbone than isorenieratene (**III**).

Considering the case of isorenieratene (**II**) and paleorenieratene (**IV**), the energy difference is 0.4 kJ/mol in favour of isorenieratene (**II**) at the B3LYP/3-21G** level, which switches to a preference of

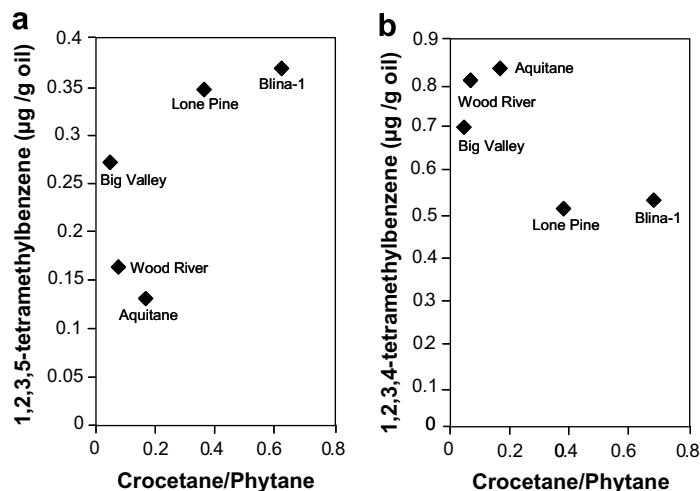


Fig. 6. Plot of abundances of (a) 1,2,3,5-TeMB and (b) 1,2,3,4-TeMB versus Cr/Ph ratio in Devonian crude oils from WCSB and Canning Basin.

0.8 kJ/mol for paleorenieratane (**IV**), with the improvement in the basis set. Given the small energy difference and sensitivity to numerical parameters, the two molecules should be considered as indistinguishable in terms of energy within the limitations of the uncertainties of present day hybrid density functional theory. Again, this is consistent with physical intuition. Once the driver of trying to maintain conjugation between the benzene rings and the hydrocarbon backbone is removed, both molecules are equally able to adopt a conformation that minimises steric hindrance.

3.6. Geological significance of crocetane (**I**) in sediments and oils

The biomarker isorenieratane (**II**) and its diagenetic products are commonly reported in sediments and certain oils throughout the Phanerozoic and Paleozoic. Crocetane (**I**) which does not share an anaerobic methane oxidation source is only abundant in crude oils and sediments of Devonian age. There is one report of a low abundance of crocetane (**I**) in sediments of Triassic age from the Kockatea shale (Greenwood and Summons, 2003). Grice et al. (2005) reported isorenieratane and aryl isoprenoids across the Permian/Triassic boundary in several sections, but no crocetane (**I**) was evident in these samples (Grice, unpublished). Interestingly, the chemical controls on the generation and destruction of diverse diagenetic products of carotenoids are as yet unsolved (see Sinninghe Damsté et al., 2001). As suggested by Brocks and Schaeffer (2008) the array of diagenetic products of carotenoids in Palaeoproterozoic sediments appear rather different to those reported in Phanerozoic sediments. Brocks and Schaeffer (2008) suggest that clues to this discrepancy may lie in the differences in water chemistry and ecology. Based on the abundance of crocetane in Devonian samples it is suggested that the array of diagenetic products of carotenoids in Paleozoic sediments are also rather different to those reported in post-Paleozoic sediments. Crocetane's occurrence in Palaeoproterozoic sediments has not yet been fully explored. Further work is necessary to understand the formation and controls on the diagenetic products of carotenoids in geological samples. In addition, pyrolysis experiments should be carried out in order to investigate the diagenetic source relationship between the diaromatic carotenoids and crocetane (**I**). Unfortunately there was not enough immature sedimentary sample available to carry out additional pyrolysis experiments in the present study.

4. Conclusions

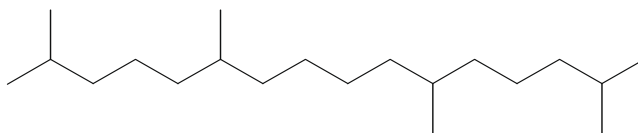
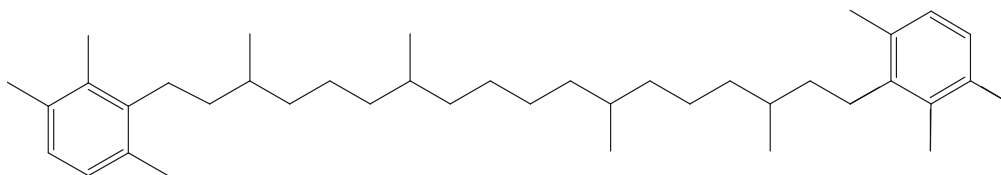
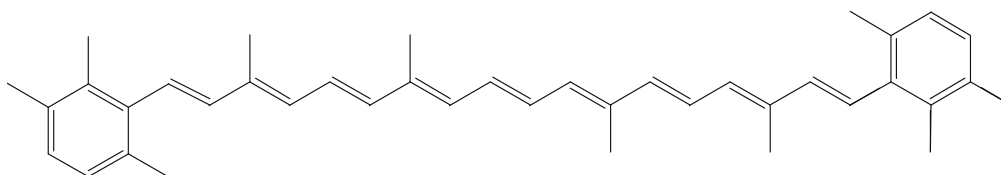
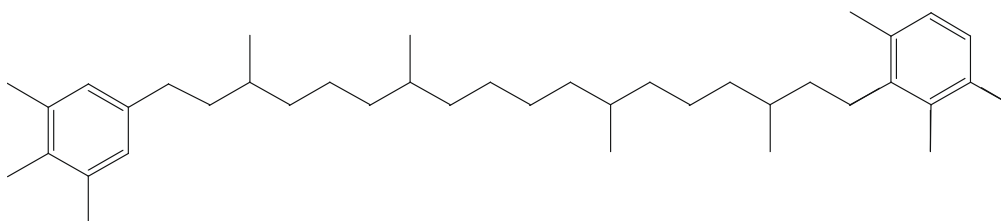
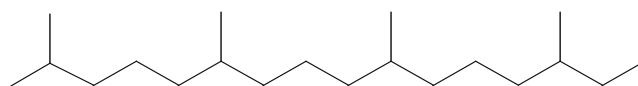
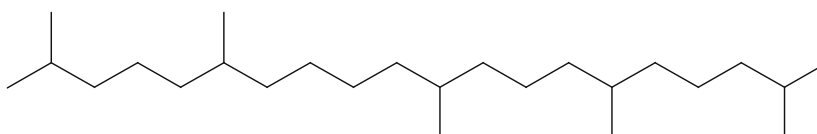
A detailed molecular and isotopic study of crocetane (**I**) and GSB derived carotenoids in sediments of the WCSB (upper Devonian Duvernay Formation) covering a range of thermal maturities showed that the Cr/Ph steadily increases in the maturity sequence. The depth abundance profiles for GSB derived carotenoids show a decrease in concentration with depth and concomitant increase in the relative abundance of crocetane (**I**). Crocetane (**I**) was also found to be present in all seven WCSB crude oils analysed.

In the Duvernay Formation sediments and the WCSB crude oils, we were not able to identify PMI (**VI**), which is consistent with previous findings. Thus, the preferred proposed natural product precursor for crocetane (**I**) is GSB derived isorenieratene (**III**) and palaerernieratene (**XI**). This is based on their similar structural features and the $\delta^{13}\text{C}$ of combined crocetane (**I**) and phytane (**V**) in these samples. However, contributions from other carotenoids cannot be fully excluded. It is proposed that crocetane (**I**) arises from the β -cleavage of diaromatic carotenoid moieties of GSB that have been incorporated into the kerogen structure. Crocetane (**I**) can provide evidence for PZE conditions in highly matured samples and crude oils of Devonian age.

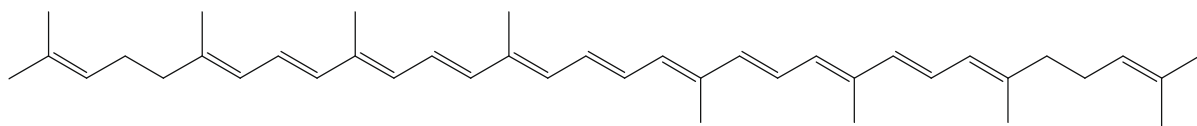
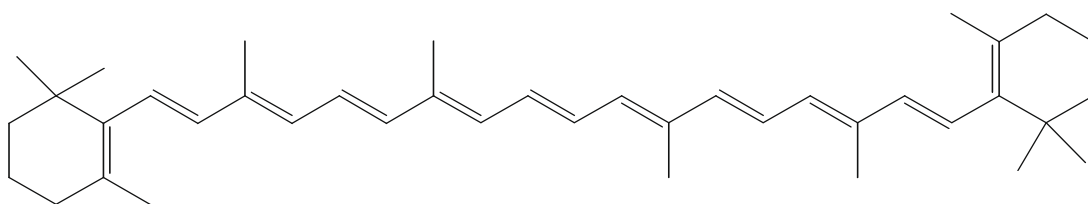
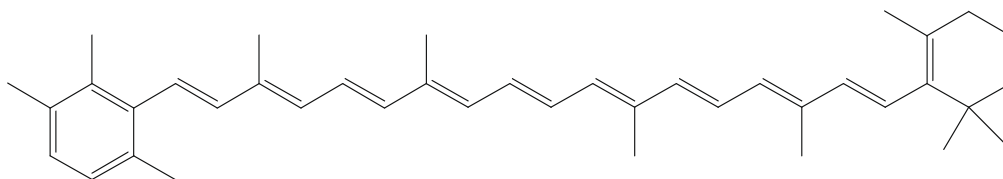
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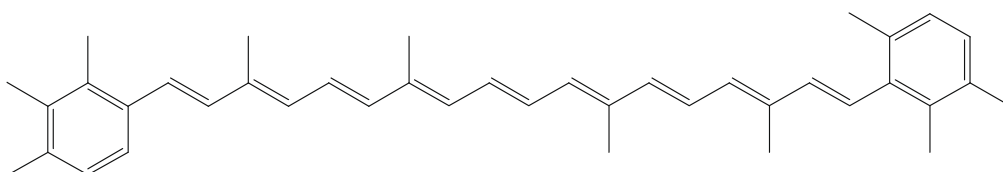
Associate Editor—L. Schwark

Appendix A**Crocetane (I)****Isorenieratane (II)****Isorenieratene (III)****Paleorenieratane (IV)****Phytane (V)****PMI (VI)**

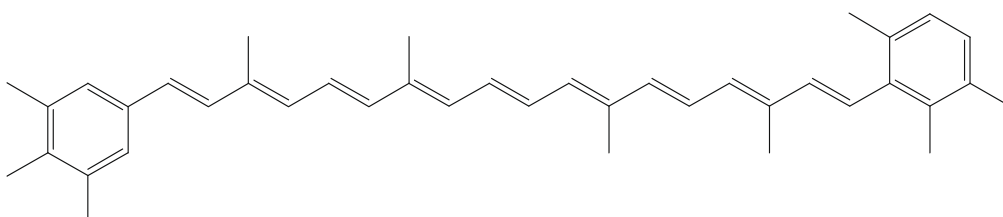
Lycopene (VII)

 β -Carotene (VIII) β -Isorenieratene (IX)

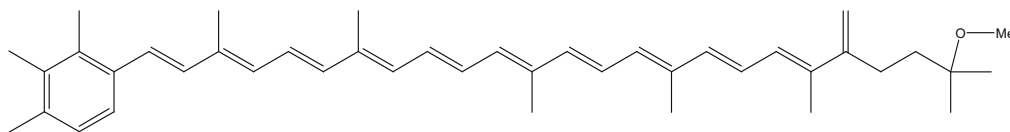
Renieratene (X)



Palaerenieretene (XI)



Okenone (XII)



References

- Apra, E., Windus, T.L., Straatsma, T.P., Bylaska, E.J., de Jong, W., Hirata, S., Valiev, M., Hackler, M.T., Pollack, L., Kowalski, K., Harrison, R.J., Dupuis, M., Smith, D.M.A., Nieplocha, J., Tipparaju, V., Krishnan, M., Auer, A.A., Brown, E., Cisneros, G., Fann, G.L., Fruchtl, H., Garza, J., Hirao, K., Kendall, R., Nichols, J.A., Tsemekhman, K., Wolinski, K., Anchell, J., Bernholdt, D., Borowski, P., Clark, T., Clerc, D., Dachsel, H., Deegan, M., Dyall, K., Elwood, D., Glendening, E., Gutowski, M., Hess, A., Jaffe, J., Johnson, B., Ju, J., Kobayashi, R., Kutteh, R., Lin, Z., Littlefield, R., Long, X., Meng, B., Nakajima, T., Niu, S., Rosing, M., Sandrone, G., Stave, M., Taylor, H., Thomas, G., van Lenthe, J., Wong, A., Zhang, Z., 2005. NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.7 Pacific Northwest National Laboratory, Richland, WA 99352-0999, USA.
- Barber, C.J., Grice, K., Bastow, T.P., Alexander, R., Kagi, R.L., 2001. The identification of crocetane in Australian crude oils. *Organic Geochemistry* 32, 943–947.
- Bastow, T.P., van Aarssen, B.K.G., Lang, D., 2007. Rapid small scale separation of saturate, aromatic and polar components in petroleum. *Organic Geochemistry* 38, 1235–1250.
- Becke, A.D., 1993. Density-functional thermochemistry III. The role of exact exchange. *Journal of Chemical Physics* 98, 5648–5652.
- Birgel, D., Thiel, V., Hinrichs, K., Elvert, M., Campbell, K.A., Reitner, J., Farmer, J.D., Peckmann, J., 2006. Lipid biomarker patterns of methane seep microbialites from the Mesozoic convergent margin of California. *Organic Geochemistry* 38, 1289–1302.
- Brooks, J.J., Schaeffer, P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. *Geochimica et Cosmochimica Acta* 72, 1396–1414.
- Clifford, D.J., Clayton, J.L., Sinninghe Damsté, J.S., 1998. 2,3,6-/3,4,5-Trimethyl substituted diaryl carotenoid derivatives (Chlorobiaceae) in petroleum of the Belarussian Pripyat River Basin. *Organic Geochemistry* 29, 1253–1267.
- Creaney, S., Allan, J., 1990. Hydrocarbon generation and migration in the Western Canada sedimentary basin. In: Brooks, J. (Ed.), *Classic Petroleum Provinces*. Geological Society of London Special Publication, vol. 50, pp. 189–202.
- Creaney, S., Allan, J., 1992. Petroleum systems in the foreland basin of Western Canada. In: Macqueen, R.W., Leckie, D.A. (Eds.), *Foreland Basins and Fold Belts*. American Association Petroleum Geologist Memoir, 55, pp. 279–308.
- Chow, N., Wendte, J., Stasiuk, L.D., 1995. Productivity versus preservation controls on two organic-rich carbonate facies in the Devonian of Alberta: sedimentological and organic petrological evidence. *Bulletin of Canadian Petroleum Geology* 43, 433–460.
- Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry* 36, 95–104.
- Elvert, M., Suess, E., Whiticar, M.J., 1999. Anaerobic methane oxidation associated with marine gas hydrates: superlight C isotopes from saturated and unsaturated C₂₀ and C₂₅ irregular isoprenoids. *Naturwissenschaften* 86, 295–300.
- Elvert, M., Suess, E., Greinert, J., Whiticar, M.J., 2000. Archaea mediating anaerobic methane oxidation in deep-sea sediments at cold seeps of the eastern Aleutian subduction zone. *Organic Geochemistry* 31, 1175–1187.
- Evans, M.C.W., Buchanan, B.B., Arnon, D.I., 1966. A new ferredoxin-dependent carbon reduction cycle in a photosynthetic bacterium. *Biochemistry* 55, 928–934.
- Fowler, M.G., Stasiuk, L.D., Hearn, M., Obermajer, M., 2001. Devonian hydrocarbon source rocks and their derived oils in the Western Canada Sedimentary Basin. *Bulletin of Canadian Petroleum Geology* 49, 117–148.
- Graham, P.J., Wakefield, L.L., 1988. Variations in the sterane carbon number distributions of marine source rock derived crude oils through geological time. *Organic Geochemistry* 12, 61–73.
- Greenwood, P.F., Summons, R.E., 2003. GC-MS detection and significance of crocetane and pentametylicosane in sediments and crude oils. *Organic Geochemistry* 34, 1211–1222.
- Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1996. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Organic Geochemistry* 25, 131–147.
- Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, N.W. Germany) inferred from molecular and isotopic compositions of biomarker components. *Organic Geochemistry* 26, 677–690.
- Grice, K., Cao, C., Love, G.D., Böttcher, M.E., Twitchett, R.J., Grosjean, E., Summons, R.E., Turgeon, S.C., Dunning, W., Jin, Y., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. *Science* 307, 706–709.
- Grice, K., de Mesmay, R., Glucina, A., Wang, S., 2008. An improved and rapid 5A molecular sieve method for gas chromatography isotope ratio mass spectrometry of *n*-alkanes (C₈–C₃₀). *Organic Geochemistry* 39, 284–288.
- Hartgers, W.A., Sinninghe Damsté, J.S., Requejo, A.G., Allan, J., Hayes, J.M., Ling, Y., Xie, T., Primack, J., de Leeuw, J.W., 1994. Molecular and carbon isotopic study towards the origin and diagenetic fate of diaromatic carotenoids. *Organic Geochemistry* 22, 703–725.
- Hehre, W.J., Ditchfield, R., Pople, J.A., 1972. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *Journal of Chemical Physics* 56, 2257.
- Hinrichs, K.U., Summons, R.E., Orphan, V., Sylva, S.P., Hayes, J.M., 2000. Molecular and isotopic analysis of anaerobic methane-oxidizing communities in marine sediments. *Organic Geochemistry* 31, 1685–1701.
- Hoehler, T., Alperin, M.J., Albert, D.B., Martens, C., 1994. Field and laboratory studies of methane oxidation in an anoxic marine sediment: evidence for a methanogen-sulfate reducer consortium. *Global Biogeochemistry Cycles* 8, 451–463.
- Koga, Y., Nishihara, M., Morij, H., Akagawa-Matsushita, M., 1993. Ether lipids of methanogenic bacteria: structures, comparative aspects, and biosynthesis. *Microbiology Reviews* 57, 164–182.
- Koopmans, M.P., Carson, F.C., Sinninghe Damsté, J.S., Lewan, M.D., 1998. Biomarker generation from Type II-S kerogens in claystone and limestone during hydrous and anhydrous pyrolysis. *Organic Geochemistry* 29, 1395–1402.
- Koopmans, M.P., Schaeffer-Reiss, C., de Leeuw, J.W., Lewan, M.D., Maxwell, J.R., Schaeffer, P., Sinninghe Damsté, J.S., 1997. Sulphur and oxygen sequestration of *n*-C37 and *n*-C38 unsaturated ketones in an immature kerogen and the release of their carbon skeletons during early stages of thermal maturation. *Geochimica et Cosmochimica Acta* 61, 2397–2408.
- Koopmans, M.P., Köster, J., Van Kaam-Peters, H.M.E., Kenig, F., Schouten, S., Hartgers, W.A., de Leeuw, J.W., Sinninghe Damsté, J.S., 1996. Diagenetic and catagenetic products of isorenieratene: molecular indicators for photic zone anoxia. *Geochimica et Cosmochimica Acta* 60, 4467–4496.
- Murphy, M.T.J., 1969. Analytical methods. In: Eglinton, G., Murphy, M.T.J. (Eds.), *Organic Geochemistry: Methods and Results*. Springer-Verlag, New York, pp. 576–598.
- Orphan, V.J., Hinrichs, K.U., Ussler III, W., Paull, C.K., Taylor, L.T., Sylva, S.P., Hayes, J.M., Delong, E.F., 2001. Comparative analysis of methane-oxidising Archaea and sulfate reducing bacteria in anoxic marine sediments. *Applied and Environmental Microbiology* 67, 1922–1934.
- Pancost, J.S., Sinninghe Damsté, J.S., de Lint, S., van der Maarel, M.J.E.C., Gottschal, J.C., 2000. Biomarker evidence for widespread anaerobic methane oxidation in Mediterranean sediments by a consortium of methanogenic archaea and bacteria. *Applied and Environmental Microbiology* 67, 1126–1132.
- Peckmann, J., Goedert, J.L., Thiel, V., Michaelis, W., Reitners, J., 2002. A comprehensive approach to the study of methane-seep deposits from the Lincoln Creek Formation, western Washington State, USA. *Sedimentology* 49, 855–873.
- Pedentchouk, N., Freeman, K.H., Harris, N.B., Clifford, D.J., Grice, K., 2004. Sources of alkylbenzenes in Lower Cretaceous lacustrine source rocks, West African rift basins. *Organic Geochemistry* 35, 33–45.
- Quandt, I., Gottschalk, G., Ziegler, H., Stichler, W., 1977. Isotope discrimination by photosynthetic bacteria. *FEMS Microbiological Newsletters* 1, 125–128.
- Requejo, A.G., Gray, N.R., Freund, H., Thomann, H., Melchior, M.T., Gebhard, L.A., Bernardo, M., Pictroski, C.F., Hsu, C.S., 1992. Maturation of petroleum source rocks-1. Changes in kerogen structure and composition associated with hydrocarbon generation. *Energy Fuels* 6, 203–214.
- Requejo, A.G., Allan, J., Creaney, S., Gray, N.R., Cole, K.S., 1991. Aryl isoprenoids and diaromatic carotenoids in Paleozoic source rocks and oils from the Western Canada and Williston Basins. *Organic Geochemistry* 19, 245–264.
- Robson, J.N., Rowland, S.J., 1993. Synthesis, chromatographic and spectral characterisation of 2,6,11,15-tetramethylhexadecane (crocetane) and 2,6,9,13-tetramethyltetramethylhexadecane. *Organic Geochemistry* 20, 1093–1098.

- Schouten, S., Wakeham, S.G., Sinninghe Damsté, J.S., 2001a. Evidence for anaerobic methane oxidation by archaea in euxinic waters of the Black Sea. *Organic Geochemistry* 32, 1277–1281.
- Schouten, S., Hartgers, W.A., Lopez, J.F., Grimalt, J.O., Sinninghe Damsté, J.S., 2001b. A molecular isotopic study of ^{13}C -enriched organic matter in evaporitic deposits: recognition of CO_2 -limited ecosystems. *Organic Geochemistry* 32, 277–286.
- Schouten, S., Schoell, M., Rijpstra, W.I.C., Sinninghe Damsté, J.S., de Leeuw, J.W., 1997. A molecular stable carbon isotope study of organic matter in immature Miocene Monterey sediments, Pismo basin. *Geochimica et Cosmochimica Acta* 61, 2065–2082.
- Sinninghe Damsté, J.S., Kohnen, M.E.L., Horsfield, B., 1998. Origin of low-molecular-weight alkylthiophenes in pyrolysates of sulfur-rich kerogens as revealed by micro-scale sealed vessel pyrolysis. *Organic Geochemistry* 29, 1891–1903.
- Sinninghe Damsté, J.S., Schouten, S., van Duin, A.C.T., 2001. Isorenieratene derivatives in sediments: possible controls on their distribution. *Geochimica et Cosmochimica Acta* 65, 1557–1571.
- Sirevag, R., Buchanan, B.B., Berry, J.A., Troughton, J.H., 1977. Mechanisms of CO_2 fixation in bacterial photosynthesis studied by the carbon isotope technique. *Archaeological Microbiology* 112, 35–38.
- Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J., 1994. Ab initio calculation of vibrational adsorption and circular dichroism spectra using density functional force fields. *Journal of Physical Chemistry* 98, 11623–11627.
- Stoakes, F.A., Creaney, S., 1984. Sedimentology of a carbonate source rock: the Duvernay Formation of central Alberta. In: Eliuk, L. (Ed.), *Carbonates in Subsurface and Outcrop CSPG Core Conference*. Calgary, Alberta, pp. 132–147.
- Stoakes, F.A., Creaney, S., 1985. Sedimentology of a carbonate source rock: the Duvernay Formation of central Alberta. In: Longman, M.W., Shanley, K.W., Lindsay R.F., Eby, D.E., Eliuk, L. (Eds.), *Rocky Mountain Carbonate Reservoirs – A Core Workshop*. SEPM Core Workshop No. 7, Golden, Colorado, August 10–11, 1985, pp. 343–375.
- Summons, R.E., Powell, T.G., 1986. Chlorobiaceae in Paleozoic seas revealed by biological markers, isotopes and geology. *Nature* 319, 763–765.
- Thiel, V., Peckmann, J., Seifert, R., Wehrung, P., Reitner, J., Michaelis, W., 1999. Highly isotopically depleted isoprenoids: molecular markers for ancient methane venting. *Geochimica et Cosmochimica Acta* 63, 3959–3966.
- van Aarssen, B.K.G., Bastow, T.P., Hill, R., Murray, A., 2007. Separating source and maturity influences on the origin of petroleum liquids. 23rd IMOG Book of Abstracts, Torquay, England.
- Wendt, J.C., 1992. Overview of the Devonian of the Western Canada Sedimentary Basin, Devonian-early Mississippian carbonates of the Western Canada Sedimentary Basin: a sequence stratigraphic framework. *Society of Sedimentary Geology* 28, 1–24.