

Geochemical Evolution of Occluded Hydrocarbons inside Geomacromolecules: A Review

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ABSTRACT: Within geomacromolecules, such as kerogen, asphaltene, and solid bitumen, other compounds can be adsorbed and even occluded as free molecules. The occluded components have been well preserved by the macromolecular structure, and retain some of the primary geochemical information. In this work we try to probe the geochemical evolution of occluded hydrocarbons inside geomacromolecules associated with the geomacromolecule evolution from kerogen → asphaltene → solid bitumen. The results show that occluded hydrocarbons can be transferred steadily from kerogen → asphaltene → solid bitumen. Later-evolved geomacromolecules not only inherit the occluded hydrocarbons from the former ones, but can also occlude some new free molecules. Occluded hydrocarbons are subject to a relatively independent thermal evolution, whereas the evolution of adsorbed molecules is constrained by other factors besides thermal stress. Elucidation of the geochemical evolution of occluded hydrocarbons inside geomacromolecules will be helpful in oil (bitumen)–source correlation, identification of mixed-source reservoirs, and characterization of hydrocarbon accumulation and evolution.

1. INTRODUCTION

During geological history, dead organisms successively undergo the geological processes of sedimentation, diagenesis, catagenesis, and metagenesis, accompanied by the occurrence of a variety of biochemical or chemical reactions and the formation of geomacromolecules. Fulvic acid, humic acid, and humin usually form during the deposition of organic matter through the processes of microbial degradation, polymerization, and condensation; kerogen is generated through sediment diagenesis, and then asphaltene is derived from the kerogen cracking (Figure 1).¹ Solid bitumen can also be formed during the degradation of kerogen,² although it is mainly derived from crude oil evolution processes, including thermal alteration, deasphalting, or biodegradation.³ Thus, such geomacromolecules are the products of sedimentary organic matter in different evolution stages and contain a significant amount of geochemical information, making them some of the most studied objects in many fields, such as biogeochemistry, environmental geochemistry, and oil/gas geochemistry.

Geomacromolecules generally have high molecular weights and complex chemical structures (but no regular molecular formula), and are actually admixtures. Some conceptual structure models representing the largest possible set of physicochemical analytical data for geomacromolecules have previously been used to represent the structures of humic matter,^{4–6} kerogen,^{7,8} and asphaltene.^{9–11} Specific acids or alkalis are usually used to isolate humic matter¹² and kerogen,⁸ whereas asphaltene¹³ and solid bitumen^{14,15} are obtained by treatment with appropriate organic solvents.

As representative geomacromolecules from source rock or oil reservoirs, kerogen, asphaltene, and solid bitumen are important study objects for the geochemical information encoded with them. Their macromolecular structures can adsorb and even occlude other small molecules (e.g.,

biomarkers).^{16–19} The occluded molecules can be well preserved by the macromolecular structure and thus prevented from contact with extraneous reagents, catalysts, microbes, or surface-derived formation waters flowing through the deposit.^{20–22} Therefore, the occluded fraction can retain primary organic geochemical information over the geological time.^{20–22} Besides the free molecules occluded inside the geomacromolecular structure, some biomarkers are covalently bonded to the geomacromolecular structure so that they retain earlier geochemical characterization.^{23–25}

In studies on the adsorbed and occluded components of geomacromolecules, researchers have detected many biomarkers among the occluded compounds. These biomarkers have proved to be useful in studies of organic matter with depleted soluble fractions,¹⁷ oil (bitumen)–source correlation,^{16,26} identification of mixed-source reservoirs,^{27–29} and characterization of hydrocarbon accumulation and evolution.¹⁹

2. ADSORPTION–OCCLUSION IN GEOMACROMOLECULES

2.1. Adsorption–Occlusion Phenomena Inside the Structure of Geomacromolecules. In the extraction of kerogen using different solvents, such as chloroform, a mixture of methanol/acetone/chloroform, or a mixture of CS₂ and *N*-methyl-2-pyrrolidinone, extraction yields typically increase with increasing polarity of the organic solvents, indicating an abundance of noncovalent bond interactions between the organic matter and the kerogen structure.^{30,31} Asphaltene, from the oils suffered from serious biodegradation and depleted in *n*-alkanes, has been dissolved in toluene and reprecipitated from

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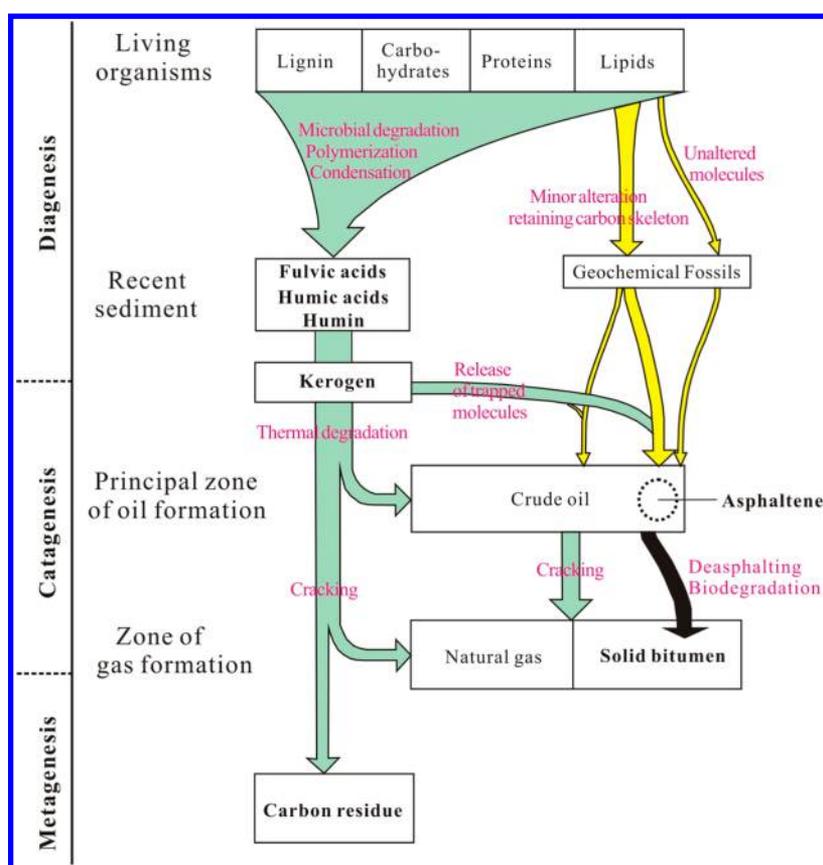


Figure 1. Formation and evolution of geomacromolecules in geological situations. Figure adapted with permission from ref 1. Copyright 1984 Springer-Verlag.

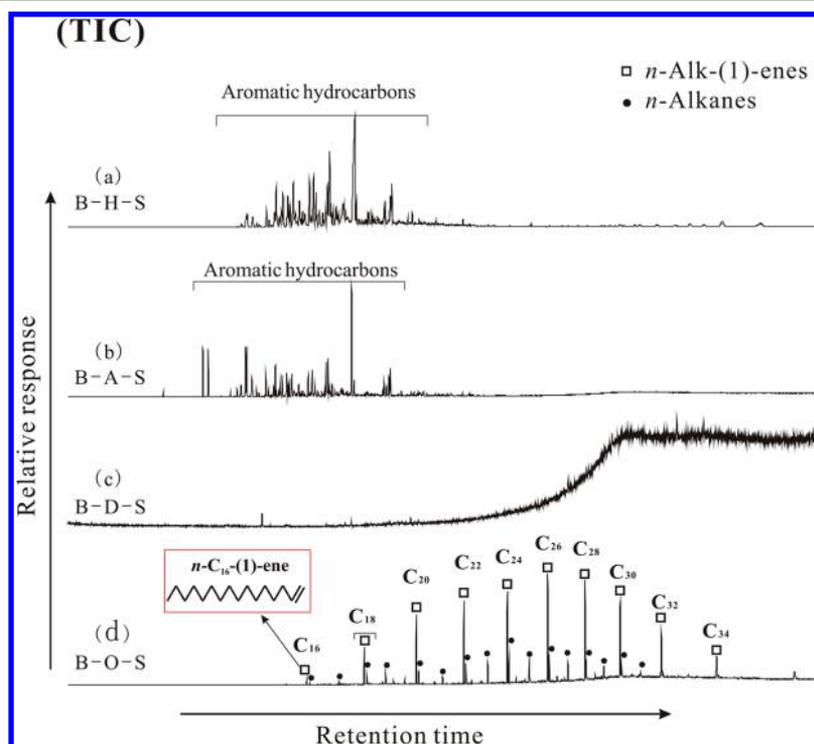


Figure 2. Total ion chromatograms of the *n*-hexane eluents from the extracts and oxidative degradation products of solid bitumen in Jurassic Shaximiao Formation of northwestern Sichuan basin, China. (a) the *n*-hexane extract of solid bitumen; (b) the acetone extract of solid bitumen; (c) the dichloromethane extract of solid bitumen; (d) the mixture obtained following oxidative degradation treatment of solid bitumen. Figure adapted with permission from ref 17. Copyright 2012 Science Press. The biomarker assignments are listed in Table 1.

n-heptane, and then a series of *n*-alkanes are detected in the organic phase after the reprecipitation of asphaltene, indicating that some primary components were trapped within the asphaltenes.^{32,33} The components present as noncovalently bonded moieties inside the geomacromolecular structure are regarded as adsorbed or occluded molecules. To test and verify the adsorption–occlusion process within the asphaltene structure, Zhao et al.³⁴ carried out simulation experiments under high-pressure/high-temperature conditions, using asphaltenes from a low-matured crude oil and *n*-C₂₀D₄₂ as the target compound; they detected *n*-C₂₀D₄₂ in the occluded fraction from the pyrolyzed residue. Cheng et al.¹⁷ detected a series of even-carbon-numbered *n*-alk-1-enes, *n*-alkanes, some isoparaffins, and biomarker compounds from the occluded fraction of solid bitumen (Figure 2).

Table 1. Biomarker Assignments for the Peaks in Figures 2, 4, and 7

peak	compound
C ₁₆ –C ₃₄	C ₁₆ –C ₃₄ <i>n</i> -alk-1-ene or <i>n</i> -alkane
C ₂₁ T, C ₂₃ T	C ₂₁ , C ₂₃ tricyclic terpanes
Ts	22,29,30-trisnorneohopane-II
Tm	22,29,30-trisnorneohopane
C ₂₉ H	C ₂₉ 17 α ,21 β (H)-30-norhopane
C ₃₀ H	C ₃₀ 17 α ,21 β (H)-hopane
C ₃₁ H	C ₃₁ 17 α ,21 β (H) 22S- and 22R- homohopane
C ₂₁ P	pregnane
C ₂₇ S–C ₂₉ S	C ₂₇ –C ₂₉ regular sterane

2.2. Occluded Components in Geomacromolecules and Their Release. There is no clear-cut boundary between adsorbed and occluded fractions within the structures of geomacromolecules. Generally, components that are easily

extracted from the periphery of the macromolecules by conventional organic solvents are referred to as the adsorbed fraction, while components in the core region of the macromolecular structure that are difficult to extract by conventional organic solvents are considered as the occluded fraction.³⁵ Therefore, the occluded components can only be effectively released if the network structure of the macromolecule is destroyed.

Many methods have been used to release occluded components from geomacromolecules, such as pyrolysis,^{36–40} hydrolysis,^{23–25,41–43} chemical reduction,^{21,22} and oxidative degradation.^{44–48} However, not all of these methods are suitable for releasing occluded hydrocarbons from geomacromolecules. When the former three methods are applied to treat geomacromolecules, covalently bonded aliphatic chains in the macromolecule structure may be cleaved, and the fragments would be indistinguishable from the occluded hydrocarbons.^{16,49} Prior study showed some differences in biomarkers from the extract and the hydrolysis products of asphaltenes, resins, kerogen from the same source rock,⁴¹ which may be partly attributed to the admixture of bonded and occluded biomarkers from geomacromolecules. Mild oxidative degradation of geomacromolecules can avoid these problems, allowing for reliable isolation of the occluded hydrocarbons, because the oxidative cracking of any aliphatic components directly chemically bonded to the macromolecule structure will bear distinct hallmarks (for example, cleaved as aliphatic acids). Therefore, the hydrocarbons obtained after the oxidation of geomacromolecules are not generated by bond cleavage, but are the occluded components.^{16,45} Reagents such as H₂O₂, NaIO₄, RuO₄, and so on can be used for mild oxidative degradation of geomacromolecules.^{16,49,50}

By using the method of mild oxidative degradation with H₂O₂/CH₃COOH to treat geomacromolecules, many bio-

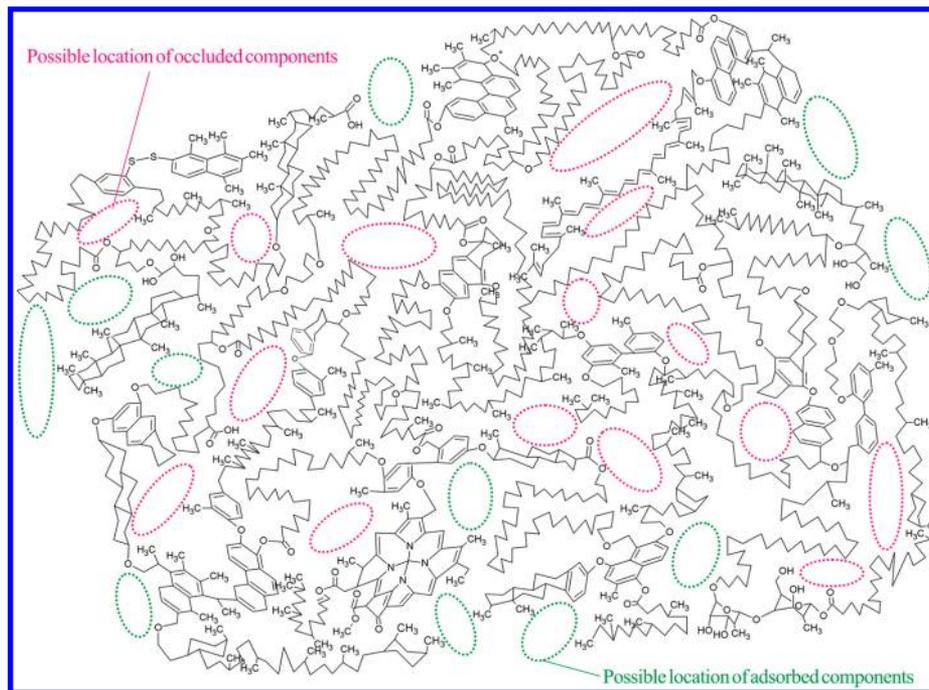


Figure 3. Possible location of adsorbed and occluded components inside low-maturity Type I-a kerogen from the Green River shale. The chemical structure of kerogen (H/C = 1.64, O/C = 0.06, MW = 21187) was modeled according to Behar and Vandembroucke,⁶⁵ with minor modifications. Figure adapted with permission. Copyright 1987 Elsevier.

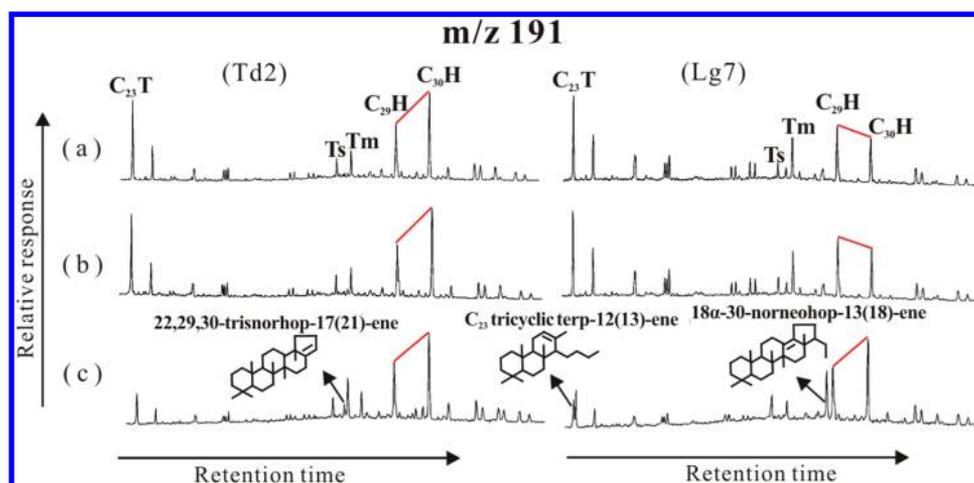


Figure 4. Partial m/z 191 mass chromatograms of the n -hexane eluents of different fractions from Well Td2 and Lg7: (a) crude oil; (b) acetone extract of asphaltene; (c) mixture obtained following oxidative degradation treatment of asphaltene. Figure adapted from ref 66. Copyright 2009 American Chemical Society. The biomarker assignments are listed in Table 1.

markers associated with their parent biomass are detected among the occluded components of the geomacromolecules, such as terpanes, steranes, and series of even-carbon-numbered n -alk-1-enes and n -alkanes.^{17–19,26–29,46–48}

3. EVOLUTION PROPERTY OF OCCLUDED HYDROCARBONS WITHIN THE STRUCTURE OF GEOMACROMOLECULES

During the general processes of oil and gas generation and evolution, kerogens are degraded to produce oils (including asphaltenes), and asphaltenes can be degraded to form solid bitumen (Figure 1). In this section, the evolution of occluded hydrocarbons is investigated within geomacromolecules during the evolution process of kerogen \rightarrow asphaltene \rightarrow solid bitumen.

3.1. Evidence for Occluded Hydrocarbon Transfer with Geomacromolecule Evolution. **3.1.1. Geomacromolecule Structure and Its Adsorption/Occlusion Capabilities.** Asphaltene is derived from kerogen, and can be viewed as the soluble fragment of kerogen in crude oils.¹ They have a similar macromolecular structure²⁰ which basically contains an interconnected network formed by polycyclic aromatic rings, with some aliphatic chains and heteroatoms covalently bonded to the aromatic rings as branch chains.^{51–57} The branch chains can curl or fold in three-dimensional (3D) space,^{58,59} and form a complex 3D structure. Some spaces or cracks, such as the mobile-phase portion of kerogen^{60,61} and the microporous structural units of asphaltene,^{45,62,63} can be found inside this 3D structure, which can accommodate small molecules. Snowdon et al.⁶⁴ suggests that occluded molecules inside asphaltene are located in minor cyclic structures connected by different groups, whereas the adsorbed ones are present on the surfaces of the asphaltene macromolecules (their Figure 1). Similarly, there are many minor cyclic structures capable of accommodating occluded molecules within kerogens, such as those from Green River shale (Figure 3).⁶⁵

The solid bitumen derived from crude oils (containing asphaltene) comprises enriched asphaltene components, so its macromolecular structure should also have microporous structural units similar to asphaltenes. So kerogen, asphaltene, and solid bitumen can accommodate small free molecules within their macromolecular skeletons, because the micro-

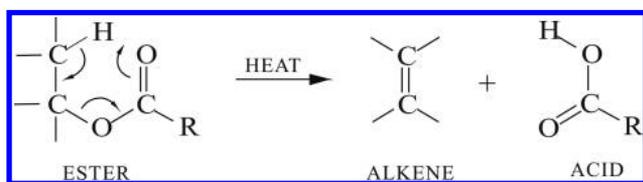
porous structural units have been preserved through the geomacromolecule evolution processes.

3.1.2. Biomarkers Trapped Inside Geomacromolecules. A lot of biomarkers, such as n -alkanes, terpanes, and steranes, have been detected within the structures of geomacromolecules. The occluded n -alkanes can survive, even when the host geomacromolecules undergo serious biodegradation alteration.^{19,26,30,31} This can be attributed to the preservation of the geomacromolecular structures, which alleviate the transformative effects of later geochemical processes and preserve the primary organic geochemical information.^{20–22}

Some unusual compounds have been detected in the occluded fractions of solid bitumen and asphaltenes, such as bicyclic terpenoid sulfides,²⁶ tricyclic terpenes (C_{23} tricyclic terp-12(13)-ene), and hopenes (22,29,30-trisnorhop-17(21)-ene, C_{29} 18 α -30-norneohop-13(18)-ene, and 17 α -hop-20(21)-ene) (Figure 4).⁶⁶ Some tricyclic terpenes and hopenes have also been detected in the pyrolysis products of kerogen^{67,68} and asphaltenes,⁶⁹ and the researchers suggested that these compounds were the original constituents covalently bonded to kerogen structures, but neglected that they maybe belong to the components trapped inside the macromolecules as free molecules which would be released by hydropyrolysis. Bicyclic terpenoid sulfide was presumably derived from a thermal maturation reaction of a carotenoid precursor under anaerobic conditions.⁷⁰ Terpenes are usually considered as precursors of the corresponding terpanes or secondary products from reactions of terpanes generation in the early stage of diagenesis.^{67,71} Therefore, formation of these components will be earlier than their host geomacromolecules (asphaltene or solid bitumen). Yang et al.⁶⁶ suggested that terpene found in the occluded fractions of the asphaltenes were the thermal pyrolysis products of kerogens at an early stage of hydrocarbon generation. Those studies indicate that the occluded hydrocarbons from later forming geomacromolecules have a close correlation with their earlier ones.

A series of even-carbon-numbered n -alk-1-enes, are often detected in the trapped fractions of geomacromolecules (kerogen, asphaltene, and solid bitumen), but not in the free or adsorbed fractions.^{17–19,26–29,34,66} Alkenes are believed to be generated from the corresponding esters at an early stage of deposition through concerted reactions at a quite low

maturation stage, which can be illustrated with the chemical scheme as follows:^{72,73}



The even-carbon-numbered *n*-alk-1-enes are assumed to be degradation products of esters with even-carbon-numbered linear alkyl chains that are commonly present in organisms,¹⁸ but are thermally unstable.^{35,74,75} Actually, *n*-alk-1-enes are frequently found in modern sediments,⁷⁶ but reports of the presence of such compounds in crude oil have hitherto been scarce. Therefore, the *n*-alk-1-enes released from asphaltene and solid bitumen are not from the thermal cracking of geomacromolecule, but from the occluded fraction of kerogen. The preserving effect of the geomacromolecule skeleton is helpful for *n*-alk-1-enes surviving in the geological environment. The suggestion of the *n*-alk-1-ene origin is consistent with the discoveries that esters and even-carbon-numbered *n*-alkenes are present in trapped fractions from humic matter,^{77–79} which can be considered as a precursor of kerogen.

Therefore, it seems that the occluded components inside the geomacromolecular structure can be persistently retained through the evolution process of kerogen → asphaltene → solid bitumen, which is illustrated in Figure 5. The two-dimensional (2D) structure of a Type I kerogen from Green River shale (Figure 3) is selected as a model to construct the 3D skeleton using the software Materials Studio 7.0 in Amorphous Cell (kerogen density set at 0.95 g/cm³ for convenience). The different spheres (C-gray, H-white, O-red, N-blue, and S-yellow) are interconnected in the 3D space and represent the kerogen skeleton, while the individual yellow sticks represent the occluded molecules. A lot of occluded molecules are seen occupying the microporous structural units of the raw kerogen. When the kerogen skeleton is cracked to generate a soluble fragment (e.g., cracking along the blue

dotted line in Figure 5a, the soluble fragment or the precursor of asphaltene derived from kerogen will contain some occluded molecules. As the primary or early components, this portion of occluded molecules will be preserved inside the asphaltene or solid bitumen with the evolution of fragment → asphaltene → solid bitumen.

3.1.3. Occluded Compounds of Asphaltene from Kerogen—Insight from Stable Carbon Isotope Characteristics. In previous studies, it has been found that the stable carbon isotopes of the organic fractions and individual hydrocarbons occluded inside the asphaltene structure are generally heavier than those of the adsorbed or free fraction. For instance, the occluded fractions of asphaltene from the central Tarim Basin, NW China, were found to have a heavier stable carbon isotope composition than the free and adsorbed fractions.⁸¹ From the occluded fraction of ZG31 asphaltene, the even-carbon-numbered *n*-alk-1-enes proved to be enriched in ¹³C by up to 3–8‰ compared to the doublet alkanes,²⁷ while the occluded *n*-alkanes of asphaltenes were enriched in ¹³C by more than 2‰, more than the corresponding *n*-alkanes from oils.²⁸ Maybe the heavier occluded alkenes are mainly derived from the first oil charge and the adsorbed alkanes are from a later charge,²⁷ or the occluded components originated from different source rocks.²⁸

As a ¹²C–¹²C bond will be broken more readily than a ¹²C–¹³C bond during kerogen cracking, the oil and gas products will be enriched in ¹²C while the residual kerogen enriched in ¹³C. Early studies showed that the oil can be depleted in ¹³C by up to 1–2‰ compared with the corresponding source kerogen,⁸² and thermal maturation can further fractionate the oils by up to 2–3‰.⁸³ The occluded compounds of kerogen represent its primary components, and hence their stable carbon isotope composition might be close to that of the raw kerogen. Thus, the liquid hydrocarbons (adsorbed hydrocarbons) derived from the cracking of kerogen will have a lighter stable carbon isotope distribution than the occluded hydrocarbons (Figure 6). Of course, the occluded fraction inside the macromolecular (kerogen and its broken fragment) may also be thermally cracked. However, the residual

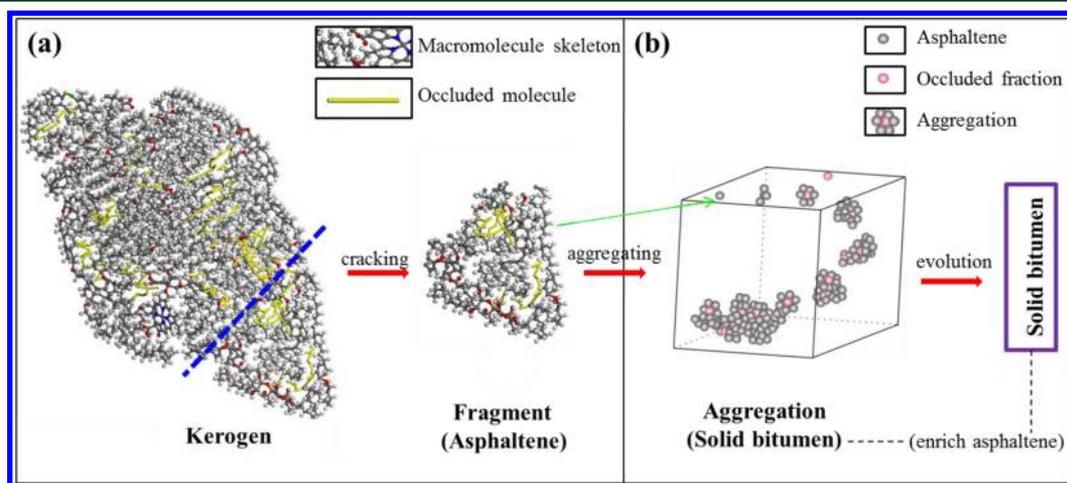


Figure 5. Schematic model showing the primary occluded components being transferred and new components being trapped inside geomacromolecules during the evolution of kerogen → asphaltene → solid bitumen. (a) Type I-a kerogen from Green River shale (Figure 3) was selected to model the 3D skeleton using the software Materials Studio 7.0 in Amorphous Cell (kerogen density set at 0.95 g/cm³ for convenience). The different spheres (C-gray, H-white, O-red, N-blue, and S-yellow) interconnect in the 3D space and represent the skeleton of the macromolecule, while the individual yellow sticks represent the occluded molecules. (b) Asphaltene aggregation adapted from ref 80. Copyright 2006 American Chemical Society.

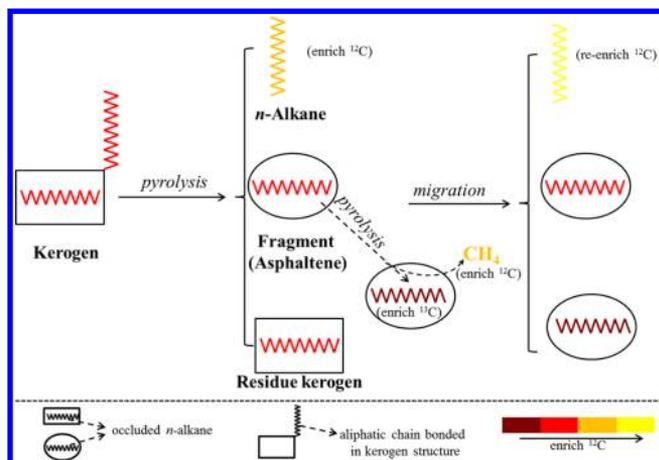


Figure 6. Schematic diagram showing the stable carbon isotope fractionation of the occluded vs bonded hydrocarbons from kerogens.

hydrocarbons from the occluded fraction would also be enriched in ^{13}C , because the lighter or gaseous hydrocarbons derived from the raw occluded fraction, such as CH_4 and C_2H_6 , will take away more ^{12}C via C–C bond cleavage. Therefore, the occluded components will start with a heavier stable carbon isotope distribution than the liquid oils during kerogen cracking. Second, the liquid hydrocarbons or oil will be further fractionated and enriched with ^{12}C during migration from source rock to reservoir, while the occluded compounds will not be influenced because they remain trapped inside the kerogen fragment or asphaltene (Figure 6). Oil migration could cause fractionation of the stable carbon isotopes of the individual hydrocarbons, and the fractionation level will be related to the migrated distance.⁸⁴ One study reported that migration could cause the biomarkers of oil samples to fractionate by more than 1‰.⁸⁵

Through the aforementioned kerogen thermal degradation and oil migration processes, it is possible to generate huge fractionation of the stable carbon isotopes between the occluded fractions and the free or adsorbed ones. Therefore, the fact that the occluded fractions contain many earlier compounds from kerogen and undergo a relatively independent

evolution may be one of the major reasons why the stable carbon isotopes of occluded compounds from asphaltene are heavier than those of the free and adsorbed fractions.

3.1.4. Occluded Compounds in Solid Bitumen from Asphaltene—Insight from an Asphaltene Thermal Simulation Experiment. To test and verify the adsorption–occlusion within the asphaltene structure, Zhao et al.³⁴ carried out a simulated experiment using a low-matured asphaltene ($R_o < 0.5\%$) and deuterated paraffin $n\text{-C}_{20}\text{D}_{42}$ as a target compound under a high pressure of 20 MPa and varying temperatures of 240 °C (held for 72 h), 270 °C (held for 48 h), and 290 °C (held for 24 h). The occluded components were released by mild oxidative degradation with $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$. In this way, they detected a series of alkanes in the occluded fraction of the raw asphaltene and its residues from different simulated experiments.³⁴ The organic residue from the thermal degradation of asphaltene could be regarded as solid bitumen, and the results indicated that occlusion can be found in the solid bitumen. Thus, the detected n -alkanes trapped inside the residue after thermal degradation must have been derived from the occluded fractions of the raw asphaltene. Traditional biomarkers, such as terpanes and steranes, were also detected in the occluded fractions of the residues from the thermal degradation of asphaltene (Figure 7; raw asphaltene and its 240 and 290 °C residues as examples). These biomarkers occluded inside the residues showed similar distributions to those inside the raw asphaltene.

3.2. Later-Forming Geomacromolecules Subsequently Occluding Other Molecules. According to the above discussion, later-forming geomacromolecules inherit the occluded components of the earlier ones, but they may also occlude new small molecules during their formation and evolution processes.

First, the asphaltene structure may develop new spaces or cracks to accommodate new small molecules when it is developed from kerogen cracking. Second, asphaltene are liable to flocculate in oils to form stable aggregates,^{63,86–90} which have similar 3D spatial structures as kerogen. This kind of aggregates can also adsorb and even occlude other small molecules (Figure 5b),^{34,91} which causes the occluded

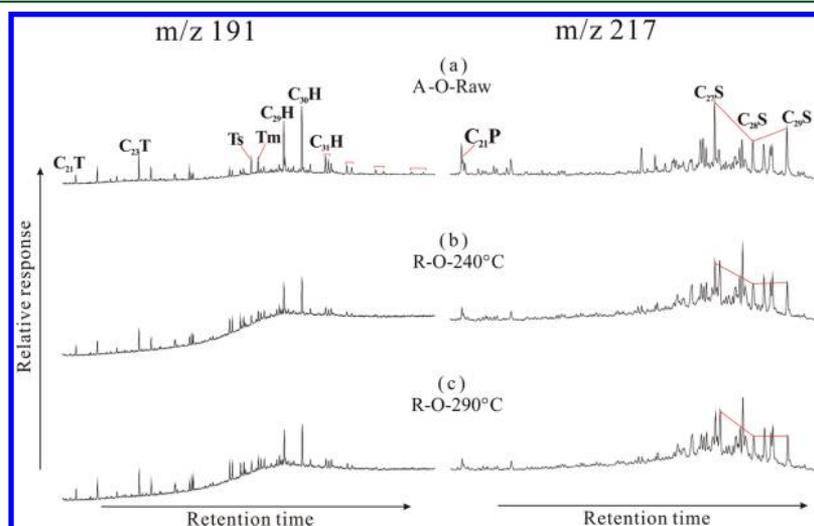


Figure 7. Chromatograms of terpanes and steranes in the occluded fractions of the raw asphaltene and its pyrolysis residues: (a) the raw asphaltene; (b, c) the residues from 240 and 290 °C asphaltene pyrolyses. The biomarker assignments are listed in Table 1.

components therein to differ significantly from those from the early asphaltene.⁶⁴

Similarly, solid bitumen not only inherits the occluded components of the parent asphaltene, but may also trap new components during the process of its evolution from asphaltene, which has been observed in the simulated experiment on adsorption/occlusion phenomena inside the asphaltene structure.³⁴

3.3. Influencing Factors on the Occluded Components in Geomacromolecules. During the processes of kerogen cracking to oils (including asphaltene), and oil (asphaltene) evolving to solid bitumen, thermodynamic activity is the main driving force. Both adsorbed and occluded components within the geomacromolecular structure will be influenced by thermal stress as verified by a thermal simulation experiment performed on a low-matured source rock.³⁵

Previous studies have shown that, based on biomarker indices, the maturity of the occluded fractions does not match that of the adsorbed fractions. Guo et al.^{30,31} found that the ratios of C_{31} hopanes $22S/(22S+22R)$ and C_{29} steranes $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$ from CS_2/NMP extracts of MaoMing oil shale kerogen were higher than those from chloroform extracts. Zhao et al.²⁷ observed a similar phenomenon that the ratios of $Ts/(Ts+Tm)$ (for explanations of these abbreviations, see Table 2) and C_{29} steranes $20S/(20S+20R)$ in the occluded fraction of ZG31 asphaltene from the Tarim Basin were higher than those from its adsorbed fraction. However, Yang⁸¹ found the ratios of C_{29} steranes $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$ in the occluded fractions lower than those in the adsorbed fractions for 14 asphaltene from the Tarim Basin. Thermal simulation of a low-matured source rock showed that the adsorbed and occluded hydrocarbons had similarities in terms of biomarker features in the early stage of kerogen thermal evolution, but different with increasing thermal levels.³⁵

Thermal evolutions of the two kinds of fractions of geomacromolecules are not always the same. This may be because the adsorbed components are influenced by other factors, such as mineral catalysis, thermochemical sulfate reduction, or biodegradation, while the occluded components are controlled mainly by thermal stress because they are present in a relatively closed environment and avoid contact with outside matters.

4. GEOCHEMICAL SIGNIFICANCE OF THE EVOLUTION CHARACTERISTICS OF OCCLUDED COMPONENTS IN GEOMACROMOLECULES

Geochemical studies on adsorption–occlusion phenomenon within geomacromolecule structures have progressed, but previous studies focused on isolating one from the others and ignored the association between different geomacromolecules. The occluded components inside geomacromolecular structures are persistently retained through the evolution process of kerogen \rightarrow asphaltene \rightarrow solid bitumen.

Later-forming geomacromolecules inherit the occluded components of the earlier ones and retain these components within their microporous structural units. Compared with the adsorbed components, which will be influenced by many other factors besides thermodynamic activity, the occluded components undergo a relatively simple thermal evolution, and so they may be more useful for oil (bitumen)–source correlation and the identification of mixed-source reservoirs. For different geomacromolecules originated from the same parent biomass,

studies on the characteristics of their adsorbed and occluded hydrocarbons will be helpful for understanding the geochemical evolution of oil and gas other than thermal stress.

Furthermore, due to the fact that later-forming geomacromolecules may occlude new free molecules during their formation processes, developing a means to identify these inheritances and new components inside the later geomacromolecules is a challenging task worth more efforts.

5. SUMMARY

As the evolution products of sedimentary organic matter at different stages, kerogen, asphaltene, and solid bitumen have a close correlation in terms of origin. During the evolution process of kerogen \rightarrow asphaltene \rightarrow solid bitumen, the occluded components inside geomacromolecule structures are persistently retained through the carrier action of a macromolecule fragment. Later-forming geomacromolecules inherit the occluded components of the earlier ones, but may also occlude new small molecules. The occluded components have a relatively independent thermal evolution, whereas the adsorbed components will be influenced by many other factors besides thermal stress.

Studying the evolution characteristics of occluded hydrocarbons within the changing structures of geomacromolecules is important for the geochemical information encoded with them, which can be used in the field such as oil (bitumen)–source correlation, identification of mixed-source reservoirs, and characterization of hydrocarbon accumulation and evolution.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*; Springer–Verlag, New York, 1984.
- (2) Curiale, J. A. Origin of solid bitumens, with emphasis on biological marker results. *Org. Geochem.* **1986**, *10* (1–3), 559–580.
- (3) Hwang, R. J.; Teerman, S. C.; Carlson, R. M. Geochemical comparison of reservoir solid bitumens with diverse origins. *Org. Geochem.* **1998**, *29* (1–3), 505–517.
- (4) Schulten, H. R.; Schnitzer, M. Three-dimensional models for humic acids and soil organic matter. *Naturwissenschaften* **1995**, *82*, 487–498.
- (5) Schulten, H. R. Three-dimensional molecular structures of humic acids and their interactions with water and dissolved contaminants. *Int. J. Environ. Anal. Chem.* **1996**, *64*, 147–162.
- (6) Schulten, H. R.; Schnitzer, M. Chemical model structures for soil organic matter and soils. *Soil Sci.* **1997**, *162*, 115–130.
- (7) Vandenbroucke, M. Kerogen, from types to models of chemical structure. *Oil Gas Sci. Technol.* **2003**, *58*, 243–269.
- (8) Vandenbroucke, M.; Largeau, C. Kerogen origin, evolution and structure. *Org. Geochem.* **2007**, *38*, 719–833.

- (9) Speight, J. G. Developments in Petroleum Science. In *Asphaltenes and Asphalts*. I; Yen, T. F., Chilingarian, G. V., Eds.; Elsevier: Amsterdam, 1994.
- (10) Rogel, E.; Carboognani, L. Density estimation of asphaltenes using molecular dynamics simulations. *Energy Fuels* **2003**, *17*, 378–386.
- (11) Acevedo, S.; Castro, A.; Negrin, J. G.; Fernández, A.; Escobar, G.; Piscitelli, V.; Delolme, F.; Dessalces, G. Relations between asphaltene structures and their physical and chemical properties, the rosary-type structure. *Energy Fuels* **2007**, *21*, 2165–2175.
- (12) Tan, K. H. *Humic Matter in Soil and the Environment*; CRC Press: FL, 2003.
- (13) Surhorne, L. M.; Tennoe, M. T.; Henssonow, S. F. *Asphaltene*; Betascript Publishing, 2010.
- (14) Hill, R. J.; Tang, Y. C.; Kaplan, I. R.; Jenden, P. D. The influence of pressure on the thermal cracking of oil. *Energy Fuels* **1996**, *10*, 873–882.
- (15) Kelemen, S. R.; Walters, C. C.; Kwiatek, P. J.; Freund, H.; Afeworki, M.; Sansone, M.; Lamberti, W. A.; Pottorf, R. J.; Machel, H. G.; Peters, K. E.; Bolin, T. Characterization of solid bitumens originating from thermal chemical alteration and thermochemical sulfate reduction. *Geochim. Cosmochim. Acta* **2010**, *74*, 5305–5332.
- (16) Liao, Z.; Geng, A. Characterization of nC_7 -soluble fractions of the products from mild oxidation of asphaltenes. *Org. Geochem.* **2002**, *33* (12), 1477–1486.
- (17) Cheng, B.; Liao, Z.; Tian, Y.; Zhao, J. Release of the hydrocarbons occluded inside solid bitumen in Jurassic Shaximiao formation of Northwestern Sichuan Basin and its geochemical significance. *Geochimica* **2012**, *41* (5), 425–432.
- (18) Cheng, B.; Yang, C.; Du, J.; Zhao, J.; Liao, Z. Determination of the series of even carbon numbered n -alk-(1)-enes trapped inside geomacromolecules. *Mar. Pet. Geol.* **2014**, *51*, 49–51.
- (19) Cheng, B.; Liao, Z.; Wang, T.; Liu, H.; Tian, Y.; Yang, S. Multiple charges to Sinian reservoirs in the middle Sichuan basin, SW China, Insight from the adsorbed/occluded hydrocarbons in solid bitumens. *J. Pet. Sci. Eng.* **2015**, *127*, 359–366.
- (20) Behar, F.; Pelet, R.; Roucache, J. Geochemistry of asphaltenes. *Org. Geochem.* **1984**, *16*, 587–595.
- (21) Ekweozor, C. M. Tricyclic terpenoid derivatives from chemical degradation reactions of asphaltenes. *Org. Geochem.* **1984**, *6*, 51–61.
- (22) Ekweozor, C. M. Characterization of the non-asphaltene products of mild chemical degradation of asphaltenes. *Org. Geochem.* **1986**, *10*, 1053–1058.
- (23) Russell, C. A.; Snape, C. E.; Meredith, W.; Love, G. D.; Clarke, E.; Moffatt, B. The potential of bound biomarker profiles released via catalytic hydroxyprolysis to reconstruct basin charging history for oils. *Org. Geochem.* **2004**, *35* (11–12), 1441–1459.
- (24) Lockhart, R. S.; Meredith, W.; Love, G. D.; Snape, C. E. Release of bound aliphatic biomarkers via hydroxyprolysis from type II kerogen at high maturities. *Org. Geochem.* **2008**, *39* (8), 1119–1124.
- (25) Liao, Y.; Fang, Y.; Wu, L.; Geng, A.; Hsu, C. The characteristics of the biomarkers and $\delta^{13}C$ of n -alkanes released from thermally altered solid bitumens at various maturities by catalytic hydroxyprolysis. *Org. Geochem.* **2012**, *46*, 56–65.
- (26) Cheng, B.; Hu, S.; Shen, C.; Liao, Z.; Liu, H.; Du, J.; Tian, Y. The geochemical characterization of adsorbed/occluded hydrocarbons inside solid bitumen in the Kuangshanliang area of northwestern Sichuan Basin and its significance. *Pet. Sci. Technol.* **2014**, *32* (18), 2203–2211.
- (27) Zhao, J.; Liao, Z.; Zhang, L.; Creux, P.; Yang, C.; Chrostowska, A.; Zhang, H.; Graciaa, A. Comparative studies on compounds occluded inside asphaltenes hierarchically released by increasing amounts of H_2O_2/CH_3COOH . *Appl. Geochem.* **2010**, *25*, 1330–1338.
- (28) Tian, Y.; Zhao, J.; Yang, C.; Liao, Z.; Zhang, L.; Zhang, H. Multiple-sourced features of marine oils in the Tarim Basin, NW China—Geochemical evidence from occluded hydrocarbons inside asphaltenes. *J. Asian Earth Sci.* **2012**, *54–55*, 174–181.
- (29) Tian, Y.; Yang, C.; Liao, Z.; Zhang, H. Geochemical quantification of mixed marine oils from Tazhong area of Tarim Basin, NW China. *J. Pet. Sci. Eng.* **2012**, *90–91*, 96–106.
- (30) Shaohui, G.; Shuyuan, L.; Kuangzong, Q. CS_2 /NMP extraction of immature source rock concentrates. *Org. Geochem.* **2000**, *31*, 1783–1795.
- (31) Guo, S. Solubility of MaoMing oil shale kerogen. *Oil Shale* **2000**, *17* (1), 11–16.
- (32) Zhu, J.; Guo, S.; Xu, G.; Wang, P. Hydrocarbons entrapped in the petroleum asphaltene. *Petrol. Explor. Develop.* **2002**, *29* (2), 61–63.
- (33) Zhu, J.; Li, S.; Guo, S. New methods for the study of biodegraded crude oil. *J. Fuel Ch. Technol.* **2003**, *31* (1), 1–5.
- (34) Zhao, J.; Liao, Z.; Chrostowska, A.; Liu, Q.; Zhang, L.; Graciaa, A.; Creux, P. Experimental studies on the adsorption/occlusion phenomena inside the macromolecular structures of asphaltenes. *Energy Fuels* **2012**, *26* (3), 1746–1755.
- (35) Cheng, B.; Du, J.; Tian, Y.; Liu, H.; Liao, Z. Thermal evolution of adsorbed/occluded hydrocarbons inside kerogens and its significance as exemplified by one low-matured kerogen from Santanghu Basin, Northwest China. *Energy Fuels* **2016**, *30*, 4529–4536.
- (36) Rubinstein, I.; Strausz, O. P. Thermal treatment of the Athabasca oil sand bitumen and its component parts. *Geochim. Cosmochim. Acta* **1979**, *43*, 1887–1893.
- (37) Rubinstein, I.; Spyckerelle, C.; Strausz, O. P. Pyrolysis of asphaltenes, a source of geochemical information. *Geochim. Cosmochim. Acta* **1979**, *43*, 1–6.
- (38) Jones, D. M.; Douglas, A. G.; Connan, J. Hydrous pyrolysis of asphaltenes and polar fractions of biodegraded oils. *Org. Geochem.* **1988**, *13*, 981–993.
- (39) Wilhelms, A.; Larter, S. R. Characterization of asphaltenes by pyrolysis-field ionization mass spectrometry—some observations. *Org. Geochem.* **1993**, *20* (7), 1049–1062.
- (40) Magnier, C.; Huc, A. Y. Pyrolysis of asphaltenes as a tool for reservoir geochemistry. *Org. Geochem.* **1995**, *23*, 963–967.
- (41) Bowden, S. A.; Farrimond, P.; Snape, C. E.; Love, G. D. Compositional differences in biomarker constituents of the hydrocarbon, resin, asphaltene and kerogen fractions: An example from the Jet Rock (Yorkshire, UK). *Org. Geochem.* **2006**, *37* (3), 369–383.
- (42) Wu, L.; Liao, Y.; Fang, Y.; Geng, A. The comparison of biomarkers released by hydroxyprolysis and Soxhlet extraction from source rocks of different maturities. *Chin. Sci. Bull.* **2013**, *58*, 373–383.
- (43) Wu, L.; Geng, A. Differences in the thermal evolution of hopanes and steranes in free and bound fractions. *Org. Geochem.* **2016**, *101*, 38–48.
- (44) Khaddor, M.; Ziyad, M.; Amblès, A. Structural characterization of the kerogen from Youssoufia phosphate formation using mild potassium permanganate oxidation. *Org. Geochem.* **2008**, *39*, 730–740.
- (45) Liao, Z.; Zhou, H.; Graciaa, A.; Chrostowska, A.; Creux, P.; Geng, A. Adsorption/occlusion characteristics of asphaltenes, some implications for asphaltene structural features. *Energy Fuels* **2005**, *19* (1), 180–186.
- (46) Liao, Z.; Geng, A.; Graciaa, A.; Creux, P.; Chrostowska, A.; Zhang, Y. Different adsorption-occlusion properties of asphaltenes associated with their secondary evolution processes in oil reservoirs. *Energy Fuels* **2006**, *20* (3), 1131–1136.
- (47) Liao, Z.; Graciaa, A.; Geng, A.; Chrostowska, A.; Creux, P. A new low-interference characterization method for hydrocarbons occluded inside asphaltene structures. *Appl. Geochem.* **2006**, *21* (5), 833–838.
- (48) Liao, Z.; Geng, A.; Graciaa, A.; Creux, P.; Chrostowska, A.; Zhang, Y. Saturated hydrocarbons occluded inside asphaltene structures and their geochemical significance, as exemplified by two Venezuelan oils. *Org. Geochem.* **2006**, *37* (3), 291–303.
- (49) Valkova, D.; Grasset, L.; Ambles, A. Molecular compounds generated by ruthenium tetroxide oxidation and preparative off-line thermochemolysis of lignite humic acids from South Moravia, Implication for molecular structure. *Fuel* **2009**, *88*, 2113–2121.

- (50) Hayashi, J.; Chiba, T. Quantitative description of oxidative degradation of brown coal in aqueous phase on the basis of Bethe Lattice statistics. *Energy Fuels* **1999**, *13*, 1230–1238.
- (51) Calemma, V.; Rausa, R.; D'Anton, P.; Montanari, L. Characterization of asphaltene molecular structure. *Energy Fuels* **1998**, *12*, 422–428.
- (52) Strausz, O. P.; Mojelsky, T. W.; Faraji, F.; Lown, E. M.; Peng, P. Additional structural details on Athabasca asphaltene and their ramifications. *Energy Fuels* **1999**, *13*, 207–227.
- (53) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M.; Kowalewski, I.; Behar, F. Structural features of Boscan and Duri asphaltene. *Energy Fuels* **1999**, *13*, 228–247.
- (54) Sheremata, J.; Gray, M.; Dettman, H.; McCaffrey, W. Quantitative molecular representation and sequential optimization of Athabasca asphaltenes. *Energy Fuels* **2004**, *18*, 1377–1384.
- (55) Marshall, C. P.; Love, G. D.; Snape, C. E.; Hill, A. C.; Allwood, A. C.; Walter, M. R.; Van Kranendonk, M. J.; Bowden, S. A.; Sylva, S. P.; Summons, R. E. Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia. *Precambrian Res.* **2007**, *155* (1–2), 1–23.
- (56) Budinova, T.; Razvigorova, M.; Tsytsarski, B.; Petrova, B.; Ekinci, E.; Yardim, M. F. Characterization of Bulgarian oil shale kerogen revealed by oxidative degradation. *Chem. Erde* **2009**, *69* (3), 235–245.
- (57) Vandenbroucke, M.; Largeau, C. Kerogen origin, evolution and structure. *Org. Geochem.* **2007**, *38* (5), 719–833.
- (58) Schabron, J. F.; Speight, J. G. The solubility and three-dimensional structure of asphaltenes. *Pet. Sci. Technol.* **1998**, *16*, 361–375.
- (59) Murgich, J.; Abanero, J. A.; Strausz, O. P. Molecular recognition in aggregates formed by asphaltene and resin molecules from the Athabasca oil sand. *Energy Fuels* **1999**, *13*, 278–286.
- (60) Lynch, L. J.; Webster, D. S. Proton NMR-thermal scanning methods for the study of oil shale pyrolysis. In *Geochemistry and Chemistry of Oil Shale*; Miknis, F. P., McKay, J. F., Eds.; ACS Symposium Series, Vol. 230; American Chemical Society: Washington DC, 1983.
- (61) Fu, J.; Qin, K. *Kerogen Geochemistry*; Guangdong Scientific Publication Press: Guangzhou, 1995.
- (62) Leon, O.; Contreras, E.; Rogel, E.; Dambakli, s.; Acevedo, S.; Carbognani, L.; Espidel, J. Adsorption of native resins on asphaltene particles: A correlation between adsorption and activity. *Langmuir* **2002**, *18*, 5106–5112.
- (63) Acevedo, S.; Escobar, G.; Ranaudo, M. A.; Piñate, J.; Amorín, A.; Diaz, M.; Silva, P. Observations about the structure and dispersion of petroleum asphaltene aggregates obtained from dialysis fractionation and characterization. *Energy Fuels* **1997**, *11*, 774–778.
- (64) Snowdon, L. R.; Volkman, J. K.; Zhang, Z.; Tao, G.; Liu, P. The organic geochemistry of asphaltenes and occluded biomarkers. *Org. Geochem.* **2016**, *91*, 3–15.
- (65) Behar, F.; Vandenbroucke, M. Chemical modelling of kerogen. *Org. Geochem.* **1987**, *11* (1), 15–24.
- (66) Yang, C.; Liao, Z.; Zhang, L.; Creux, P. Some biogenic-related compounds occluded inside asphaltene aggregates. *Energy Fuels* **2009**, *23* (2), 820–827.
- (67) Qu, D.; Shi, J.; Xiang, M. Novel extended side-chain-unsaturated hopenes released from the kerogen macromolecules under artificial conditions. *Org. Geochem.* **1996**, *24* (8–9), 815–823.
- (68) Greenwood, P. F.; Arouri, K. R.; George, S. C. Tricyclic terpenoid composition of *Tasmanites* kerogen as determined by pyrolysis GC-MS. *Geochim. Cosmochim. Acta* **2000**, *64* (7), 1249–1263.
- (69) Meredith, W.; Snape, C. E.; Carr, A. D.; Nytoft, H. P.; Love, G. D. The occurrence of unusual hopenes in hydrolyrolysates generated from severely biodegraded oil seep asphaltenes. *Org. Geochem.* **2008**, *39*, 1243–1248.
- (70) Mathis, P.; Sehenck, C. C. The functions of carotenoids in photosynthesis. In *Carotenoid Chemistry and Biochemistry*; Britton, G., Goodwin, T. W., Eds.; Pergamon Press, 1982.
- (71) McCaffrey, M. A.; Simoneit, B. R. T.; Aquino Neto, F. R.; Moldowan, J. M. Functionalized biological precursors of tricyclic terpanes: Information from sulfur-bound biomarkers in a Permian tasmanite. *Org. Geochem.* **1994**, *21* (5), 481–487.
- (72) Alexander, R.; Kralert, P. G.; Kagi, R. I. Kinetics and mechanism of the thermal decomposition of esters in sediments. *Org. Geochem.* **1992**, *19*, 133–140.
- (73) Alexander, R.; Kralert, P. G.; Sosrowidjojo, I. B.; Kagi, R. I. Kinetics and mechanism of the thermal elimination of alkanes from secondary Stanyl and triterpenyl esters: implications for sedimentary processes. *Org. Geochem.* **1997**, *26*, 391–398.
- (74) Tsonopoulos, C.; Ambrose, D. Vapor-liquid critical properties of elements and compounds. 6. Unsaturated aliphatic hydrocarbons. *J. Chem. Eng. Data* **1996**, *41* (4), 645–656.
- (75) Nikitin, E. D.; Popov, A. P. Critical temperatures and pressures of linear alk-1-enes with 13 to 20 carbon atoms using the pulse-heating technique. *Fluid Phase Equilib.* **1999**, *166* (2), 237–243.
- (76) Van Bree, L. G. J.; Rijpstra, W. I. C.; Cocquyt, C.; Al-Dhabi, N. A.; Verschuren, D.; Sinninghe Damste, J. S.; De Leeuw, J. W. Origin and palaeoenvironmental significance of C25 and C27 *n*-alk-1-enes in a 25,000-year lake-sedimentary record from equatorial East Africa. *Geochim. Cosmochim. Acta* **2014**, *145*, 89–102.
- (77) Grasset, L.; Ambles, A. Aliphatic lipids released from a soil humin after enzymatic degradation of cellulose. *Org. Geochem.* **1998**, *29* (4), 893–897.
- (78) Grasset, L.; Guignard, C.; Ambles, A. Free and esterified aliphatic carboxylic acids in humin and humic acids from a peat sample as revealed by pyrolysis with tetramethylammonium hydroxide or tetraethylammonium acetate. *Org. Geochem.* **2002**, *33*, 181–188.
- (79) Deport, C.; Lemee, L.; Ambles, A. Comparison between humic substances from soil and peats using TMAH and TEAAc thermochemolysis. *Org. Geochem.* **2006**, *37*, 649–664.
- (80) Aguilera-Mercado, B. A.; Herdes, C.; Murgich, J.; Muller, E. A. Mesoscopic simulation of aggregation of asphaltene and resin molecules in crude oils. *Energy Fuels* **2006**, *20*, 327–338.
- (81) Yang, C. Geochemical Study about the Origin and Mechanism of the Diversity of Marine Crude Oils from the Tazhong Area, Tarim Basin, NW China. Ph.D. Thesis, Guangzhou Institute of Geochemistry, CAS, Guangzhou, China, 2008.
- (82) Machel, H. G.; Krouse, H. R.; Sassen, R. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Appl. Geochem.* **1995**, *10* (4), 373–389.
- (83) Peters, K. E.; Walters, C. C.; Moldowan, J. M. *Biomarker and Isotopes in Petroleum Exploration and Earth History*; The Biomarker Guide, Vol. 2; Cambridge University Press: Cambridge, 2005.
- (84) Dzou, L. I. P.; Hughes, W. B. Geochemistry of oils and condensates, K Field, offshore Taiwan: a case study in migration fractionation. *Org. Geochem.* **1993**, *20* (4), 437–462.
- (85) Curiale, J. A.; Bromley, B. W. Migration induced compositional changes in oils and condensates of a single field. *Org. Geochem.* **1996**, *24* (12), 1097–1113.
- (86) Buenrostro-Gonzalez, E.; Groenzin, H.; Lira-Galeana, C.; Mullins, O. C. The overriding chemical principles that define asphaltenes. *Energy Fuels* **2001**, *15*, 972–978.
- (87) Roux, J.; Broseta, D.; Deme, B. SANS study of asphaltene aggregation, concentration and solvent quality effects. *Langmuir* **2001**, *17*, 5085–5092.
- (88) Strausz, O. P.; Peng, P.; Murgich, J. About the colloidal nature of asphaltenes and the MW of covalent monomeric units. *Energy Fuels* **2002**, *16*, 809–822.
- (89) Porte, G.; Zhou, H.; Lazzeri, V. Reversible description of asphaltene colloidal association and precipitation. *Langmuir* **2003**, *19*, 40–47.
- (90) Mujica, V.; Nieto, P.; Puerta, L.; Acevedo, S. Caging of molecules by asphaltenes: A model for free radical preservation in crude oils. *Energy Fuels* **2000**, *14*, 632–639.
- (91) Acevedo, S.; Cordero, T. J. M.; Carrier, H.; Bouysiere, B.; Lobinski, R. Trapping of paraffin and other compounds by asphaltenes detected by laser desorption ionization–time of flight mass

spectrometry (LDI-TOF MS), Role of A1 and A2 asphaltene fractions in this trapping. *Energy Fuels* **2009**, *23*, 842-848.