Organic Geochemistry 51 (2012) 13–16

Contents lists available at SciVerse ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Note

$^2H/^1H$ ratio of hopanes, tricyclic and tetracyclic terpanes in oils and source rocks from the Potiguar Basin, Brazil

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ARTICLE INFO

Article history:
Received 16 February 2012
Received in revised form 21 July 2012
Accepted 22 July 2012
Available online 1 August 2012

ABSTRACT

We report the hydrogen isotope ratio $^2H/^1H$ (expressed as δ^2H values) of 8 selected hopanes, tricyclic and tetracyclic terpanes from oils and source rocks in the Potiguar Basin, and of associated formation water. Hopanes ranged in δ^2H value from −79‰ to −142‰, whereas tri- and tetracyclic terpanes (TTTs) ranged from −137‰ to −225‰. Formation water δ^2H values ranged from −23‰ to −32‰. The most significant pattern in the data is the systematic ^2H enrichment of hopanes relative to TTTs, by an average of 45‰ in oils and 78‰ in source rock extracts. The hopanes appear close to hydrogen isotopic equilibrium with coeval formation water, whereas TTTs are significantly more ^2H depleted. Given the similarities in structure between the two compound classes, it is unlikely that hopanes would be exchanged completely while the others would not. More likely, both classes have undergone a limited extent of exchange, but with the hopanes being biosynthesized with δ^2H values closer to equilibrium. Our data suggest that at least some primary environmental and/or biotic information can be retained in the δ^2H values of biomarkers in oils and extracts, and is not completely obscured by hydrogen exchange.

1. Introduction

The hydrogen isotopic composition (δ^2H) of lipids and saturated hydrocarbons in sediments has been used as a proxy for paleoclimatic and paleoenvironmental research, based on the premise that the source of hydrogen for such compounds is ocean and/or meteoric water (Santos Neto et al., 1998; Sauer et al., 2001; Schimmelmann et al., 2004; Tuo et al., 2006; Nabbefeld et al., 2010; Sachs and Schwab, 2011). In addition, several studies have observed a correlation between the sedimentary record of saturated hydrocarbon δ^2H values and the maturity of sedimentary organic matter. The observations provide consistent evidence for gradual ^2H enrichment of organic matter with increasing maturity (Dawson et al., 2005, 2007; Schimmelmann et al., 2006; Pedentchouk et al., 2006; Kikushi et al., 2010).

Most of the studies were based on compound-specific ^2H analysis of *n*-alkanes and fatty acids and more rarely of isoprenoid lipids such as sterols and hopanols, and even some aromatic compounds. However, there are virtually no data for three of the most commonly used classes of biomarkers in petroleum: hopanes, and tricyclic terpanes and tetracyclic terpanes (TTTs). Like the acyclic isoprenoids, these compounds contain multiple tertiary carbons that could stabilize tertiary carbocations and so facilitate extensive H exchange at adjacent positions (Alexander et al., 1984). Thus hopanes and TTTs should also be quite susceptible to hydrogen exchange and might serve as an early indicator of isotopic exchange in oil and bitumen.

Here we present a first report of δ^2H measurements for selected hopanes and TTTs isolated from source rocks and crude oils, together with associated formation water, in order to examine the hydrogen isotopic characteristics of these important biomarkers. Samples were from the Potiguar Basin of Brazil, a Cretaceous basin deposited during the rifting of Gondwana (Santos Neto and Hayes, 1999). Such information should improve the use of the $^2H/^1H$ ratio (expressed as δ^2H values) for assessment of the depositional conditions of source rocks and strengthen oil–oil and oil–source correlations.

2. Material and methods

A total of 7 source rock samples, 12 lacustrine oils and 11 formation water samples were collected from wells, cores and one sample of cuttings was from the Potiguar Basin (Supplementary

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0146-6380/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.orggeochem.2012.07.007

material), with age corresponding to the Early Cretaceous (Santos Neto and Hayes, 1999 and references therein). Source rock samples from the Pendência Formation were chosen on the basis of their respective Rock–Eval parameters, total organic carbon (TOC) content and biomarker ratios (Supplementary material). Related oils from the Pendência, Alagamar and Açu formations were selected on the basis of geochemical characteristics and had no evidence of biodegradation or other secondary alteration such as water washing or evaporative fractionation. Samples PO1, PO4 and PO6 were the exception, with evidence for slight biodegradation. The oils and water were sampled from production wells not subject to water injection or any other enhanced oil recovery (EOR) method, so the original isotopic signatures of the formation waters should be preserved.

Biomarkers from powdered source rocks were extracted in a microwave-accelerated reaction system (MARS Xpress, CEM Corp.) using 20 ml dichloromethane (DCM)/MeOH (20 ml, 9:1 v/v at 100 °C for 15 min with continuous stirring. The extracts were filtered and the solvent removed under N_2. Both oils and rock extracts were separated on a silica gel column into sub-fractions using hexane and DCM. After solvent evaporation, the saturate fractions were eluted through silicalite to remove *n*-alkanes. Hopanes and TTTs were then further isolated at the Moldowan Laboratory at Stanford University using a proprietary series of zeolite molecular sieves. Since some zeolites are known to catalyze hydrogen exchange activity, we tested the procedure by processing standards containing pristane, squalane, cholestane, stigmastane and moretanes. The overall mean difference between compounds before and after the zeolite procedure was +0.5‰.

The δ^2H values of hopanes and TTTs were measured at Caltech using a Thermo-Finnigan Trace GC^{ULTRA} equipped with a DB-1 column (30 m × 0.25 mm, 1 μm film thickness) and a PTV injector operated in splitless mode, coupled to a Delta^{Plus}XP isotope ratio mass spectrometer via a pyrolysis interface (Thermo GC/TC) operated at 1430 °C. Data were calibrated by comparison with CH_4 reference gas peaks as described by Wang and Sessions (2008) and are reported in the conventional δ^2H notation (Coplen, 2011) relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. Accuracy was checked with a standard mixture of 8 fatty acid methyl esters (FAMEs) of known ^{2}H/^{1}H values after every 4–5 analyses. The standards had been calibrated to the Vienna standard mean ocean water (VSMOW) and standard light Antarctic precipitation (SLAP) scale, but no further attempt at normalization was made. The root-mean-squared (RMS) error for δ^2H values of the FAME standard was 5.4‰ (n = 57) during the period the samples were analyzed. The H_3^+ factor was measured daily and was typically <6.5 ppm/mV during the analyses. Samples were analyzed in duplicate or triplicate and the mean values are reported.

The δ^2H values of formation waters samples were measured at Indiana University via conversion to H_2 gas at 500 °C in contact with Indiana Zinc (Schimmelmann and DeNiro, 1993), followed by dual inlet analysis using a Thermo-Finnigan Delta^{Plus}XP isotope ratio mass spectrometer. Samples were analyzed in duplicate or triplicate and results were normalized to the VSMOW and SLAP standards.

3. Results and discussion

The δ^2H values of hopanes ranged from −79‰ to −142‰, whereas those of the TTTs ranged from −137‰ to −225‰ (Table 1). Water δ^2H values ranged from −23‰ to −32‰, with little variation between samples. Although the δ^2H values of biomarkers appear to co vary somewhat with those of formation water (Fig. 1), especially for sample P07 relative to the others, the small variation between samples results in a low correlation coefficient (R^2 0.42). It is thus impossible to assess on the basis of correlation alone whether significant exchange between water and organic biomarkers has occurred. The clearest trend in the data is that the hopanes were ^{2}H-enriched relative to TTTs in all samples by 40–90‰. The enrichment averaged 78‰ for the extracts and 45‰ for the oils.

To test whether these offsets might reflect differences in equilibrium isotopic fractionation (ε_{eq}), presumably due to hydrogen exchange phenomena, we estimated ε_{eq} values for the relevant molecular structures using the approach of Wang et al. (2009) and Wang et al. (submitted for publication). Details of the calculations are in the Supplementary material. The results indicate that δ^2H values for hopanes and TTTs in hydrogen isotopic equilibrium should be essentially identical and fall in the range −95‰ to

Table 1
δ^2H values (‰, VSMOW)[a] of selected biomarkers and formation waters.

Sample[b]	H29[c]	H30[c]	H31R[c]	H31S[c]	T19[d]	T20[d]	T21[d]	Tet23[d]	Water
FC1	−142 (0)	−123 (3)	−95 (3)	−110 (5)	−202 (4)	−210 (0)	−225 (2)	−198 (1)	–
FC2	−133 (3)	−123 (0)	−115	−109	−199 (1)	−203 (2)	−214 (3)	−188 (6)	–
UC2	−105 (0)	−87 (3)	−89 (4)	−110 (1)	–	−159 (4)	−171 (0)	−157 (3)	–
PC1	**−129** (4)	**−116** (5)	**−119** (3)	**−127** (4)	–	−174	**−188** (10)	**−178** (5)	–
PC2	**−92** (6)	**−82** (5)	−79 (0)	−94 (0)	**−166** (10)	**−167** (4)	**−176** (5)	**−168** (2)	–
PC3	−105 (2)	−90 (1)	−79 (3)	−79 (0)	−178 (3)	−182 (2)	−196 (1)	−177 (1)	–
PC4	−115 (7)	−100 (3)	−104 (7)	−116 (4)	−180	−180 (1)	−195 (1)	−178 (2)	–
FO2	**−137** (3)	**−135** (3)	−106 (5)	−126 (5)	–	−165 (5)	**−178** (3)	−156 (2)	–
PO6	−112 (0)	−106 (3)	−97 (0)	−115 (1)	−141 (3)	−159 (0)	−168 (1)	−145 (2)	−24 (0)
PO4	−115 (7)	−109 (2)	−103 (2)	−118	−145 (4)	−158 (3)	−171 (2)	−150 (1)	−23 (1)
PO1	−114 (2)	−108 (1)	−94 (5)	–	−147 (0)	−159 (1)	−167 (1)	−150 (2)	**−24** (2)
PO7	−139 (3)	−126 (2)	−104 (4)	−115 (4)	–	−177 (1)	−195 (1)	−174 (2)	**−32** (2)
PO5	−123 (2)	−109 (0)	−100 (0)	−120 (0)	–	−155 (6)	−171 (1)	−152 (0)	−25 (2)
PO2	−121	−108	−105	−122	–	−169	−166	−145.2	**−25** (2)
PO3	**−133** (2)	−121 (1)	−111 (4)	−106 (7)	−155 (1)	−167 (4)	−183 (2)	−163 (4)	**−25** (2)
MO1	−117 (3)	−113 (1)	−100 (2)	−119	−155 (3)	−165 (1)	−172 (1)	−156 (2)	−31 (0)
FO1	−128 (6)	−118 (2)	−116 (15)	−106 (6)	−137 (11)	−168 (4)	−178 (4)	−153 (9)	**−30** (1)
RO1	−129 (5)	−129 (3)	−116 (12)	−141	–	–	−157	–	–
RO2	−130 (4)	−127 (5)	−122 (2)	−141 (3)	–	–	−164 (13)	–	–

[a] Mean δ^2H (1σ) from replicate injections; values in bold indicate average of triplicates, all others corresponding to single measurements or duplicates (standard deviation in parentheses).
[b] Italicized names are rock extracts (UC2 is cuttings), all others are oils and co-produced water.
[c] See Supplementary material for structures; H29, H30 and H31 are the regular hopanes with 29, 30 and 31 carbons (H29 includes the coeluting C_{29}Ts. H31R and H31S are the C-22 stereoisomers).
[d] See Supplementary material for structures; TTTs: T19, T20 and T21 are the tricyclic terpanes with 19, 20 and 21 carbons; Tet23 is the tetracyclic terpane with 23 carbons.

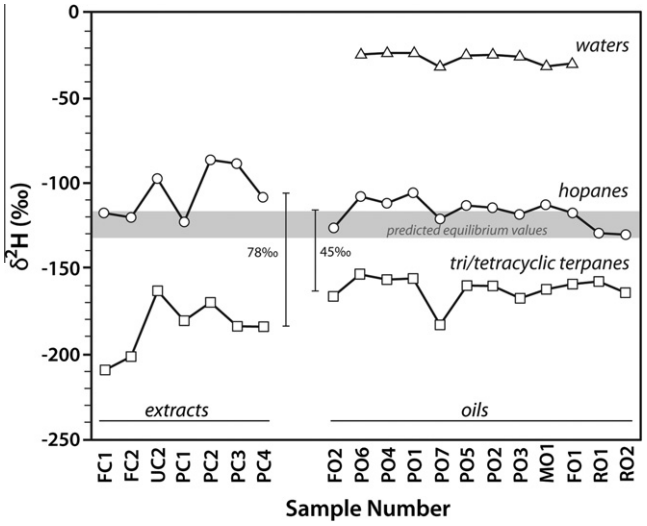

Fig. 1. Average δ^2H values (‰, VSMOW) of hopanes (circles), tri- and tetracyclic terpanes (TTTs; squares) and formation water (triangles). Each point represents the mean of all related compounds in that sample. Gray box represents range of predicted equilibrium fractionation for all biomarkers relative to measured formation water. The offsets between the average δ^2H values of hopanes and TTTs in extracts and oils are indicated (78‰ and 45‰, respectively).

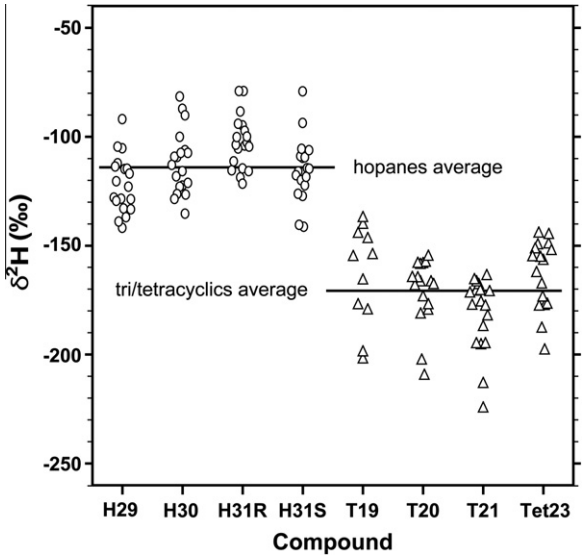

Fig. 2. Values of δ^2H (‰, VSMOW) for biomarkers grouped by compound. Averages were calculated as the unweighted mean of the average values for each compound.

−100‰ depletion relative to water (Fig. 1). Thus the hopanes appear to be very close to isotopic equilibrium with coeval formation water, whereas the TTTs remain significantly depleted relative to equilibrium values. The latter result clearly precludes complete hydrogen isotopic exchange of TTTs with formation water. However, the similarity of hopanes/water fractionation to that predicted at equilibrium does not require complete isotopic exchange. Alternatively, the precursor hopanoids could have been biosynthesized with δ^2H values that appear close to isotopic equilibrium but without significant participation of exchange processes. Regarding TTTs, average δ^2H values for T21 and Tet23 do exhibit a robust covariance ($y = 0.89x + 0.09$, R^2 0.91), but this seems to reflect mostly change in organic facies (Santos Neto et al., 1998) rather than exchange with formation water. Still, significant correlation exists between other pairs of biomarkers, like T20 and Tet23 ($y = 0.93x - 3.48$, R^2 0.81).

When all hopanes from all samples are compared, H29 appears slightly ^{2}H depleted whereas H31R is slightly ^{2}H enriched (Fig. 2). Similarly, T21 is slightly depleted relative to all TTTs, while T19 and Tet23 are slightly enriched. The causes of these systematic variations, which we tentatively attribute to their biotic origins, are not understood. The fact that closely related compounds have slightly different δ^2H values does suggest that neither class of biomarker has completely achieved hydrogen isotopic equilibrium.

4. Conclusions

The use of advanced, zeolite-based separation techniques to isolate hydrocarbon biomarkers allowed us to measure for the first time the hydrogen isotopic composition of individual hopanes, tri- and tetracyclic terpanes (TTTs) in oils and source rock extracts from the Potiguar Basin. The results show two unexpected effects. First, there was a systematic ^{2}H enrichment of hopanes vs. TTTs, by an average of 45‰ for oils and 78‰ for extracts. Second, the hopanes appeared very nearly at hydrogen isotopic equilibrium with coeval formation water, whereas TTTs were substantially depleted relative to predicted equilibrium values.

Given the similarities in structure between the two compound classes, it is unlikely that hopanes had exchanged completely while TTTs had not. More likely, the hopanes were biosynthesized with a more ^{2}H enriched composition, close to that expected at equilibrium, perhaps by heterotrophic bacteria (Zhang et al., 2009), and both groups of compounds then underwent partial isotopic exchange with formation water. If correct, the greater fractionation between hopanes and TTTs in extracts relative to oils could be indicative of greater hydrogen exchange in the oils. Regardless, our data indicate that the primary (biotic) ^{2}H/^{1}H ratio values of these biomarkers are not completely reset by way of hydrogen exchange during oil generation and may retain some useful information about the environment and/or organisms from which they originated.

Acknowledgements

We thank L. Zhang for assistance with compound-specific ^{2}H measurements, P. Velloso and R. Marins for generation and improvements of the images, and PETROBRAS for permission to publish the results of this investigation. The manuscript greatly benefited from constructive reviews by C. Eiserbeck and D. Dawson. A.L.S. was supported by NSF Grant EAR-0645502 and A.S. was funded by U.S. Department of Energy, Basic Energy Research Grant DEFG02-00ER15032.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orggeochem.2012.07.007.

Associate Editor—**K. Grice**

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