PSFrom Here to Maturity: Estimating Thermal Maturity of Crude Oils*

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Abstract

Combining gas chromatography with tandem mass spectrometry to assess unresolved structural and stereoisomeric mixtures of steranes in crude oils began 35 years ago. C27-C29 20S/20R and diasterane/regular sterane ratios were often used to determine oil and source rock maturity and GC- MSMS techniques allowed for more precise measurements of these thermally sensitive biomarker ratios. Today, GC combined with triple quadrupole mass spectrometers not only allows for the better resolution of steranes and other biomarkers (e.g., carotenoids) found in oils, source rock bitumen and kerogen but also measures a wide variety of other, more volatile thermally dependent compounds such as alkyl naphthalenes/phenanthrenes and diamondoids. Simple 'Dilute & Shoot' injections of whole crude oils preclude evaporative loss, while the specificity of the tandem spectrometers allows for the discrimination of saturate and aromatic hydrocarbons, eliminating the need for liquid chromatographic separations. A combination of these thermally sensitive biomarker ratios can be subjected to principal component analysis, and the resulting first or primary factor often carries over 75% of the total variation in the dataset. The principal component calculated for each oil in each family can be converted to a 'vitrinite reflectance equivalent' (VRE) value in order to place each oil within the confines of the oil generation window (~0.6-1.2% Ro) and likely records the maturity of the corresponding source rock at the time the oil was expelled (primary migration). It is important to evaluate maturity in oils that are from the same source facies since some of these maturity ratios may also have a significant genetic or source component. At advanced oil maturity levels that yield volatile oils or condensates (~1.0-1.3% Ro), terpane and sterane biomarkers are thermally degraded and are often insufficient in abundance to be useful in predicting maturity levels. Also, these biomarker-derived maturity estimations reflect the maturity of the heavier-ends (C20+) of the oil; lighter components of the same oil may have been derived from more mature, biomarker-deficient fluids expelled from the same source rock at a later time, due to increasing geothermal heating during subsidence. Since many of the fluids produced from unconventional lateral completions are light oils or condensates with minimal biomarker concentrations, or may have high maturity lighter-end components in addition to typical biomarker distributions, we have developed an oil maturity calculation based on known differences in the thermal stability of alkyl-substituted benzenes, naphthalenes, and phenanthrenes. To derive VREQ values (vitrinite reflectance equivalent based on the triple quadrupole), a series of thirteen alkyl- substituted naphthalene and phenanthrene ratios are constructed such that they increase with increasing maturity, with the more thermally stable isomer in the numerator. The percentages of all thirteen are simply added together with the higher total values corresponding to higher maturity levels. To calibrate the scale, the upper end of fluid maturity is

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fixed at 1.35% Ro and given to a number of clear condensates analyzed with the highest alkyl aromatic summations measured. Lower values are equated to oil standards of known or suspected maturities, as well as source rock extracts. Source rocks, with measured Ro values and Tmax determinations from pyrolysis, are crushed but not powdered, and the DCM extract (never taken to dryness to minimize evaporation) is injected on the GC-triple quadrupole after deuterated internal standards are added. Crude oils often have multiple maturity signals with the VRE from the heavier biomarkers recording the early, less mature products and the VREQ values the later, lighter, and more mature signal. This presentation will illustrate the 35+ year evolution of both Instrumental and Interpretive approaches to determine the thermal maturity of generated hydrocarbon fluids and their relationships to parent organic matter.

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From Here to Maturity: Estimating Thermal Maturity of Crude Oils

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This poster illustrates the evolution of both instrumental and interpretive approaches to determine the thermal maturity of generated hydrocarbon fluids and their relationship to parent organic matter. Combining gas chromatography with tandem mass spectrometry to assess unresolved structural and stereoisomeric mixtures of steranes in crude oils began 35 years ago (Warburton and Zumberge, 1983). C27-C29 20S/20R and diasterane/regular sterane ratios were often used to determine oil and source rock maturity (e.g., Mackenzie et al., 1980; Zumberge 1987), and GC-MSMS techniques allowed for more precise measurements of these thermally-sensitive

Today, GC combined with triple quadrupole mass spectrometers not only allows for the better resolution of steranes and other biomarkers (e.g., carotenoids; French et al., 2015) found in oils, source rock bitumen and kerogen (e.g., Zumberge et al., 2018), but also measures a wide variety of other, more volatile thermally-dependent compounds such as alkyl naphthalenes/phenanthrenes and diamondoids (e.g. Zumberge et al., 2016a; Zumberge et al., 2017a; Zumberge et al., 2017b). Simple 'Dilute & Shoot' injections of whole crude oils precludes evaporative loss, while the specificity of the tandem spectrometers allows for the discrimination of saturate and

A combination of these thermally-sensitive biomarker ratios can be subjected to principal component analysis, and the resulting first or primary factor often carries over 75% of the total variation in the dataset. The principal component calculated for each oil in each family can be converted to a 'vitrinite reflectance equivalent' (VRE) value in order to place each oil within the confines of the oil generation window (~0.6-1.2% Ro) and likely records the maturity of the corresponding source rock at the time the oil was expelled (primary migration). It is important to evaluate maturity in oils that are from the same source facies since some of these maturity ratios may also have a significant genetic or source component (Zumberge et al., 2016b)

At advanced oil maturity levels that yield volatile oils or condensates (~1.0-1.3% Ro), terpane and sterane biomarkers are thermally degraded and are often insufficient in abundance to be useful in predicting maturity levels. Also, these biomarker-derived maturity estimations reflect the maturity of the heavier-ends (C20+) of the oil; lighter components of the same oil may have been derived from more mature, biomarker-deficient fluids expelled from the same source rock. Since many of the fluids produced from unconventional lateral completions are light oils or condensates with minimal biomarker concentrations, or may have high maturity lighter-end components in addition to typical biomarker distributions, we have developed an oil maturity calculation based on known differences in the thermal stability of alkylsubstituted benzenes, naphthalenes, and phenanthrenes (e.g., van Aarssen et al., 1999).

In order to derive VREQ values (vitrinite reflectance equivalent based on the triple quadrupole), a series of thirteen alkyl-substituted naphthalene and phenanthrene ratios are constructed such that they increase with increasing maturity, with the more thermally stable isomer in the numerator. The percentages of all thirteen are simply added together with the higher total values corresponding to higher maturity levels. To calibrate the scale, the upper end of fluid maturity is fixed at 1.35% Ro and given to a number of clear condensates analyzed with the highest alkyl aromatic summations measured. Lower values are equated to oil standards of known or suspected maturities, as well as source rock extracts. Source rocks, with measured Ro values as well as Tmax determinations from pyrolysis, are crushed but not powdered, and the DCM extract (never taken to dryness to minimize evaporation) is injected on the GC-triple guadrupole after deuterated internal standards are added.

Crude oils often have multiple maturity signals with the VRE from the heavier biomarkers recording the early, less mature products and the VREQ values the later, lighter, and more mature signal. This can also be seen in an oil maturity series from Eagle Ford laterals using compound specific isotope ratios (Barrie et al, 2016)

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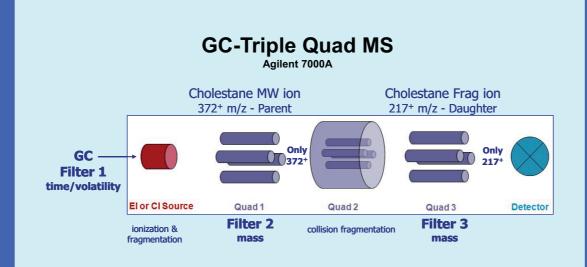
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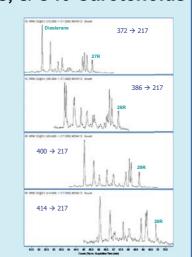
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The NEW--QQQ



'Usual' Biomarker Suspects, Diamondoids, & C40 Carotenoids

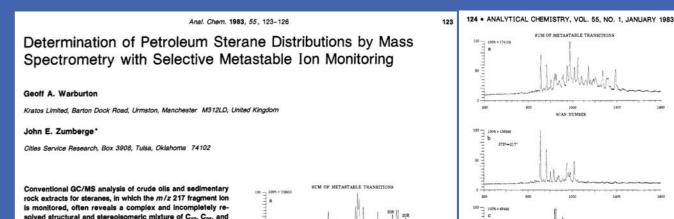
% VREQ	0.92	1.10	1.22
ppm Diamondoids	51	68	382
ppm Naphthalenes	146	90	61
ppm Phenanthrenes	37	21	7
ppm Dibenzothiophenes	30	12	1
ppm Methylchrysenes	4	4	1
ppm Steranes	31	9	0
ppm Tricyclic Terpanes	19	6	2
ppm Pentacyclic Terpanes	14	1	0
ppm Carotenoids	3	1	0
ppm Triaromatic Steroids	4	1	0
ppm Monoaromatic Steroids	5	1	0



C27-C30 Steranes

'Dilute & Shoot'

The OLD--SMIM



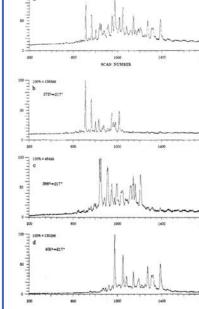
Steroidal hydrocarbons are common constituents of crude oils and ancient sedimentary rocks. Sterane distributions can be used as indicators of petroleum source rock depositional ments because the carbon atom skeleton of sterane s a remnant of the biochemical precursor steroidal structure (1). For example, a relatively greater abundance of C₂₉ steranes (e.g., stereoisomers of 24-ethylcholestane) over C steranes could suggest that the precursor organic matter contained more land-derived biochemical compounds rather than those derived from marine organisms since sterol disributions dominated by C29 components are characteristic of vascular land plants (1). Steranes are also useful parameter to vascular lain plants (f). Steames are also useful parameters in pertoleum exploration as correlation and thermal maturity indicators (2-4). With increasing temperature, the biologically derived 20R isomer of $5\alpha(H),14\alpha(H),17\alpha(H)$ -steranes is isomerized to the 20S configuration, which is not found in biological systems (3-5). Oils and sedimentary rocks which have exsystems (3-5). Oils and sedimentary rocks which have ex-perienced different degrees of thermal maturation can, herefore, have correspondingly different 20S/20R sterane ratios. In oil-oil and oil-source rock correlation studies

C20 steranes. Increased specificity can be achieved by

terane parent lons occurring in the first field-free region a double focusing mass spectrometer. The sterane meta-stable parent ion transitions, corresponding to 372⁺ → 217⁺,

served during a single GC/MS run by using a program

terane distributions are used to identify oils which share a sommon source and thermal history (4). Routine capillary gas chromatographic/mass spectrometric (GC/MS) analysis of aliphatic hydrocarbon fractions of crude In order to increase the specificity of petroleum sterandeterminations, we used selective metastable ion monitoring (SMIM) in the GC/MS analyses of a number of crude of ntary rock extracts allows the monitoring of th electron impact (EI) m/z 217 fragment ion which is the base peak in $14\alpha(H)$ -sterane EI mass spectra (6). The resulting aliphatic hydrocarbon fractions. Monitoring the spontaneou nass fragmentograms frequently reveal complex and incor ecular) fragmentation of sterane parent ions occurring pletely resolved structural and stereoisomeric mixtures of Co in the first field-free region of a double focusing mass spec C_{29} , and C_{29} steranes. Most problematic is the coelution of rearranged C_{29} steranes (also known as diasteranes) with C_{28} and C_{27} normal steranes (3, 4). Thus, chromatographic coelutions molecular weights. The most common steranes (both regular lution of sterane homologues places constraints on the accurate amu (C27H48), 386 amu (C28H50), and 400 amu (C29H52). The

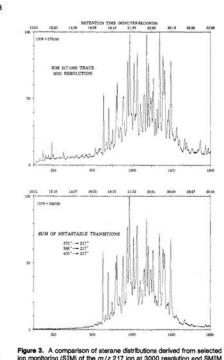




sterane metastatore parent for transitions (of $2-\epsilon_L$), one -217^4 , and $400^4 \rightarrow 217^4$) are known to occur readily in the first field-free region (7). Gallegos (7) used metastable ion methods to measure the abundances of C_{27} , C_{28} , and C_{29} steranes in a Green River shale extract, although only direct insertion mass spectrometry (not GC/MS) was used. Separation of isomers was therefore not achieved. More recently Gaskell and Millington (8) and Finlay and Gaskell (9) use selected metastable peak monitoring in quantitative GC/MS to detect and measure dihydrotestosterone and testosterone in human blood plasma. In the present study, we have combined the features of an abundant metastable sterane fra omed the reatures of an abundant metastable sterane fragment ion with high-resolution capillary gas chromatography to greatly increase the specificity of petroleum sterane deter-minations. In addition, the three different sterane parent ion metastable transitions were monitored in a single GC/MS run by using a programmable power supply to vary the acceler-ating voltage, all under data system control.

EXPERIMENTAL SECTION

Aliphatic hydrocarbon fractions were obtained from pen-tane-deasphalted crude oil samples (subsequent to light end evaporation) which were subjected to combined alumina/silica column liquid chromatography. Also, a cyclic/branched aliphatic hydrocarbon fraction from a sediment extract of a sample Coupyray) from the Paris Basin (3) was examined. The aliphati hydrocarbon fractions were then analyzed with a Kratos MS25/DS55 GC/MS system equipped with metastable ion monitoring facilities. The GC was a Carlo Erba 4160 fitted with

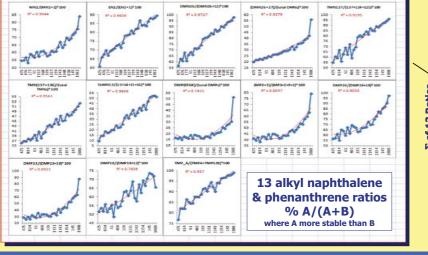


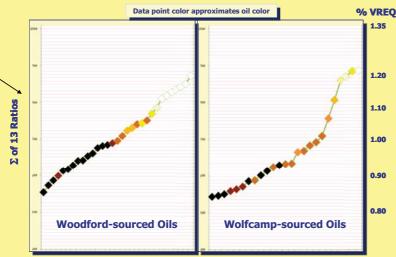
a Grob type split/splitless injector (at 270 °C) and a 20-m fused silica capillary column coated with OV-1 (methylsilicone). Analyses were performed in the split mode (25:1). The GC column oven temperature program was the following: 60 °C to 100 °C at 35 °C/min and then to 230 °C at 10 °C/min, subsequently ramping to 280 °C at 2 °C/min. The He flow rate through the GC column was about 1 mL/min made up to 30 mL/min prior to entering the GC/MS interface which consisted of a jet separator held at 250 °C. Mass spectrometer parameters used were the following: source temperature = 220 °C; electron beam current = 100 μ A; and electron voltage = 60 eV. The three metastable parent ion transitions monitored were

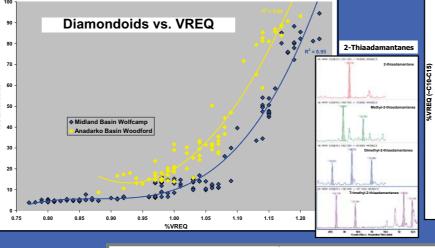
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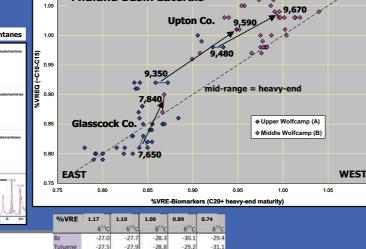
The three metastable parent ion transitions monitored were 372.3756* → 217.1956*, 386.3913* → 217.1956*, and 400.4069* → 217.1956* which correspond to C₂₇H₄₈, C₂₈H₅₀, and C₂₉H₅₂ sterane isomers, respectively. By use of an authentic cholestane standard in the direct insertion probe, the m/z 217 ion was located by adjusting the magnet setting. The electrostatic voltage (E) and acceleration voltage (V) supplies were unlinked, and the E reference voltage was supplied by the internal reference of the mass spectrometer. The V reference was supplied by a binary programmable power supply driven by DS55 software. Increasing the accelerating voltage from 2 kV to 3.429 kV allowed the transition 372* → 217* occurring in the first field-free region to be located at the collector (10). Similarly, increasing V to 3.558 kV and 3.887 kV allowed the transitions 386* → 217* and 400* → 217* to be located, respectively. The data system, DS55, was programmed to switch to each of these voltages repetitively during the GC/MS run and record the signal obtained. The dwell time on each transition was 150 ms; a sweep of ±50 ppm was applied on each transition was 150 ms; a sweep of ±50 ppm was applie to the V reference supply to ensure collection of peak top data. Data from the MS25 were acquired through a 200-kHz preprocessor interface operating at a sampling rate of 100 μ s. The MS25

Thermal Maturity of Light Oils & Condensates - 'VREQ'









%VRE

--- 1.10 → 1.00 **→** 0.89

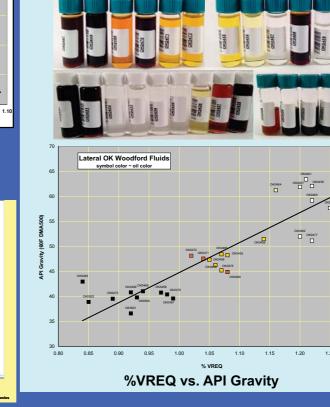
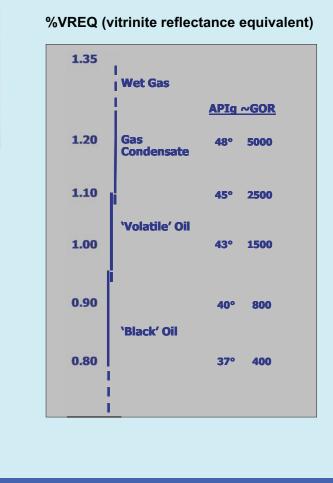
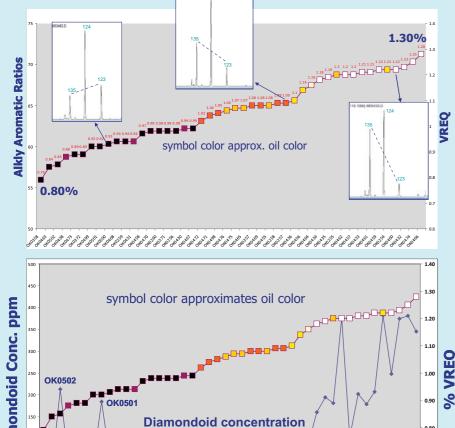


Figure 1. (a) Sterane distributions in a crude oil from the Willisto



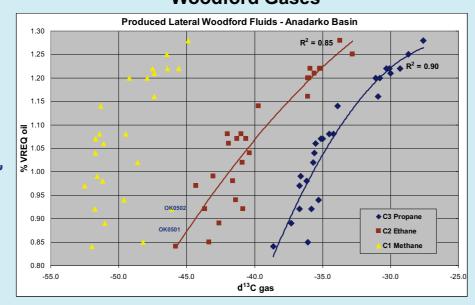
Oils from Stack Woodford Laterals



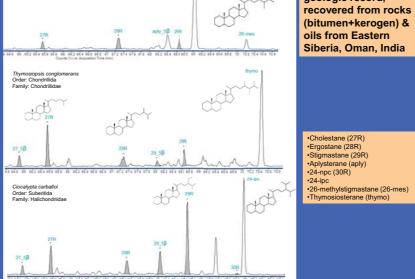
Woodford Source Rocks

		%VRE	Measured		
UD Woodford Fm.		Tmax*	%Ro**	%VREQ5	
Kingfisher Co. OK Core 1	Ave	0.98	0.97	1.02	
9,393-9,432 ft	Std Dev	0.02	0.06	0.01	n=6
Canadian Co. OK Core 2	Ave	1.07	1.05	1.09	
10,326-10,426 ft	Std Dev	0.03	0.07	0.02	n=7
		*After Extraction			
		** C. La	ndis		

Woodford Gases



QQ of 3 Demosponge HyPy Pyrolysates Verified the oldest animals in the geologic record, recovered from rocks (bitumen+kerogen) 8 oils from Eastern Siberia, Oman, India



Carotenoids: water depth-light penetration



