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Acidic and neutral polar NSO compounds in Smackover oils of different thermal maturity revealed by electrospray high field Fourier transform ion cyclotron resonance mass spectrometry

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Abstract

Negative ion electrospray ionization (ESI) coupled with high field Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) allows for the direct detection of acidic NSO compounds in petroleum. The technique requires no chromatographic separation, is able to distinguish 18 different compound classes (e.g., neutral nitrogen, carboxylic acids and oxygenates), and can identify ~14,000 distinct masses by ultra-high mass resolution and mass accuracy. We previously studied three crude oils from different geological origins [Organic Geochemistry 33 (2002b) 743–759]. Here, we expand our research by comparing two source-equivalent Smackover oils of different levels of thermal maturity. We observe clear differences in the distribution of NSO compound classes, types (number of rings plus double bonds within a class), and number of alkyl carbons. With increasing thermal stress, the relative amount of sulfur and oxygen containing compounds decreases, condensation and aromatization of the polar cores increase, and the number of alkyl carbons decreases, reflecting the distribution of saturated hydrocarbons.
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1. Introduction

Typical crude oils are composed mostly of saturated and aromatic hydrocarbons with minor amounts of thiophenoaromatics, sulfides, neutral nitrogen, and polar compounds (Table 1). The polar compounds each contain one or more heteroatoms (NSO), may be complexed with inorganic ions and metals, and can be separated into sub-fractions (e.g., asphaltenes and resins) based on their relative solubility in light alkanes. These compounds may constitute the majority of the components in non-expelled bitumens, and in very immature and biodegraded oils.

Although polar compounds are generally minor (<10 wt%) constituents of petroleum, they have significant influence on field development, producibility, and refining

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Table 1
Average petroleum compositions by chemical group-type

	%Sat.	%Aro.	%Thio.	%Sulf.	%Pyrroles	%Pyridines	%Acids	%Res.
Average	59.18	18.93	4.57	2.17	1.14	0.57	0.17	13.13
Standard deviation	11.68	5.76	5.63	2.81	1.34	0.64	0.31	10.49
Minimum	27.19	7.73	0.04	0.01	<0.01	<0.01	<0.01	<0.01
Maximum	91.83	40.99	26.90	13.39	9.45	4.79	1.79	46.7

%Sat., % saturated hydrocarbons; %aro., % aromatic hydrocarbons; %thio., % sulfur-aromatics; %sulf., % sulfides (reactive sulfur); %res., % residuum (>570 °C b.p.).

Based on complete characterization by chemical separation and field ionization mass spectrometry of 152 oils from around the world, representative of regions with current major production. Heavily biodegraded oil and bitumens may have appreciably higher content of NSO compounds than the maximum values indicated.

costs. For example, asphaltenes may precipitate in the reservoir, forming non-producible tar mats (Wilhelms and Larter, 1995); oil viscosity is greatly influenced by the proportion of polar compounds (Werner et al., 1996); and asphaltenes may form emulsions and scales resulting in field equipment failure and pipeline plugging (Becker, 1997; Joshi et al., 2001). Asphaltenes may precipitate during transportation and within the refinery when incompatible oils are mixed (Wiehe and Kennedy, 2000). NSO compounds are particularly problematic to the refining process. Sulfur compounds must be removed to meet EPA standards. That removal is often by a hydrotreatment process in which the catalysts may become inhibited by the presence of basic nitrogen compounds (La Vopa and Satterfield, 1988). Nitrogen compounds also contribute to fuel instability during storage (Chmielowiec et al., 1987; Worstell et al., 1981). Petroleum acids present another potential problem by causing liquid-phase corrosion at elevated temperatures (Jayaraman and Saxena, 1995). High TAN (total acid number) petroleums are increasingly exploited, and savings of several dollars per barrel could be made if the corrosivity of naphthenic acids could be properly measured and controlled (Turnbull et al., 1998).

Although considerable advances have been made in determining the molecular composition of the hydrocarbon fraction, the bulk of the polar material in petroleum remains largely uncharacterized. Previous studies have focused mainly on low molecular weight (<500 Da) NSO compounds that are readily amenable to gas- or liquid- chromatographic analysis. Compound classes such as phenols (Taylor et al., 1997, 2001; Bennett and Larter, 1997; Galimberti et al., 2000), naphthenic acids and their derivatized methyl esters (Green et al., 1985; Jaffé et al., 1988a,b; Jaffé and Gallardo, 1993; Nascimento et al., 1999; Barakat et al., 2000; Meredith et al., 2000; Rodrigues et al., 2000), and carbazoles (Bakel and Philp, 1990; Larter et al., 1996; Li et al., 1995, 1997, 1999; Clegg et al., 1997, 1998; Galimberti et al., 2000) have been shown

to be useful indicators of source facies, thermal maturity, migration, and reservoir alteration processes. Specific NSO-containing biomarkers such as steroid and hopanoid carboxylic acids (e.g., Jaffé and Gallardo, 1993; Rodrigues et al., 2000; Seifert et al., 1979), sulfurized terpanoids and isoprenoids (e.g., Kohnen et al., 1991; Sinninghe Damsté et al., 1993), and porphyrins (e.g., Ocampo et al., 1993; Sundararaman and Raedeke, 1993), have also received attention. These chemical groups, however, represent only a small fraction of the polar compounds present in crude oils. The majority of the heteroatoms are found in polar cores that link to form larger asphaltenes.

Characterization of the non-volatile polar compounds in petroleum is typically based on chromatographically enriched fractions of basic nitrogen (pyridines), "strong" acids (including the naphthenic acids), and "weak" acids, that may be further fractionated to neutral nitrogen (pyrroles) and phenolic compounds. Non-polar sulfur-aromatic (thiophenes) and sulfides usually elute with the hydrocarbon fractions. The isolated fractions are then further characterized by gas chromatography/mass spectrometry (GC/MS) (with and without derivatization) or liquid chromatography/mass spectrometry (LC/MS). Although such methods are suitable for many biochemical and recent sediment studies, petroleum fractions are very complex mixtures and typically yield few resolved peaks (e.g., Behar and Albrecht, 1984; Meredith et al., 2000). Even when resolved, peak identification is difficult because authentic reference compounds may not be available (Galimberti et al., 2000), fragmentation patterns are not unique, and mass resolution is insufficient to yield unambiguous molecular formula. Even conventional double-focusing sector mass spectrometers lack the resolving power and mass accuracy necessary to distinguish very narrow mass doublets common in petroleum samples (e.g., the C_3/SH_4 doublet, with a mass difference of 3.4 mDa) across a broad mass range (e.g., 200–1200 Da).

In addition, analysis of polar compounds, in general, suffers from their thermal instability, low volatility, and inefficient ionization by traditional mass spectrometric ionization sources.

Electrospray ionization (ESI) coupled to high-field (9.4 T) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) offers a very promising and powerful tool for detailed characterization of heteroatomic species in crude oils and crude oil distillates (Zhan and Fenn, 2000) and complex environmental mixtures (Kujawinski, 2002; Stenson et al., 2002). Positive- (or negative-) ion electrospray selectively ionizes strongly basic (or acidic) polar heteroatomic compounds within the predominately hydrocarbon matrix of petroleum samples, thereby eliminating the need for pre-chromatographic isolation. FT-ICR-MS (Marshall et al., 1998) routinely affords ultrahigh mass resolving power ($m/\Delta m_{50\%} > 350,000$, in which $\Delta m_{50\%}$ denotes mass spectral peak full width at half-maximum height) and mass accuracy <1 ppm, allowing for molecular formula assignment of singly charged heteroatomic ions between 250 and 1000 Da (see below). By resolving mass differences down to ~ 1 mDa, FT-ICR MS provides for unambiguous determination of molecular formulas for more than 20 polar compounds having the same nominal (i.e., rounded off to the nearest integer number of Dalton) mass.

Although ESI FT-ICR MS offers geochemists a new and powerful tool in the identification of polar compounds, we must mention that our current instrumental set-up does not allow for the identification of stereoisomers or low molecular weight compounds (<250 Da). Since stereoisomers have the same exact mass, they must be chromatographically separated prior to their identification by mass spectrometry. We have yet to implement chromatography in our petrochemical and geochemical analyses. We have, however, interfaced liquid chromatography (LC) with ESI FT-ICR MS for biological analyses (Blakney et al., 2003). Second, current ion optics limit the mass range to ~ 250–1000 Da. Low molecular weight ions, which often provide useful geochemical information, do not reach the ICR cell for excitation/detection. Current efforts are underway to extend the lower mass range. To compensate, GC/MS was used to collect low molecular weight data (which itself is limited to a mass range <500 Da). Despite these current limitations, ESI FT-ICR MS shows great promise in the analysis of polar petroleum compounds.

We previously demonstrated that petroliferous basic nitrogen compounds can be selectively analyzed by positive-ion electrospray (i.e., protonation) (Hughey et al., 2001a; Qian et al., 2001b), and that petroleum acids (Hughey et al., 2001b; Hughey et al., 2002b; Qian et al., 2001a), and weakly acidic neutral nitrogen (Hughey et al., 2002b) compounds can be selectively analyzed by negative-ion electrospray (i.e., deprotonation). (Neutral compounds, like sulfides, are not ionized by ESI.) ESI FT-ICR MS has proved extremely effective in resolving more than $\sim 14,000$ singly charged masses of which $\sim 75\%$ can be assigned a unique elemental composition ($C_cH_hO_oN_nS_s$). Some of the unassigned masses likely correspond to the same molecules but with one ^{13}C or [34]S instead of ^{12}C and [32]S, but at signal-to-noise ratio too low for definitive assignment (Hughey et al., 2002a). In prior work (Hughey et al., 2002b), we compared the negative ion ESI FT-ICR MS spectra of three oils from different source facies: lacustrine (China), carbonate-evaporite (Middle East), and marine shale (Northern Alaska). Of the ~ 4000–8000 masses present in each oil spectrum, $>85\%$ could be assigned with high confidence to molecular formulas that fall into 18 heteroatomic classes, each consisting of a different combination of N, S, and O. In this paper, we compare the mass spectra of two oils derived from the lower Smackover formation carbonate that differ in thermal maturity. Our goal is to demonstrate the potential of ESI FT-ICR MS for geochemical applications and to familiarize geochemists with the ultrahigh mass resolution and ultrahigh mass accuracy of FT-ICR MS for analysis of crude oils.

2. Experimental methods

2.1. Oil samples

Oils from the Toxey, Turkey Creek, and Chunchula fields, located onshore Alabama, were selected to examine the effect of thermal maturity on the distribution of polar compounds. The Upper Jurassic petroleum of the Mississippi Interior Salt Basin is particularly suitable to study petroleum maturation because variations imparted by other influences are minimized. The Oxfordian lower Smackover carbonate source facies is fairly homogeneous, having been deposited under continuous hypersaline, marine conditions. Migrational effects are also minimized because the reservoir rocks are upper Smackover carbonates, which are sealed by the Buckner anhydrite (Claypool and Mancini, 1989; Mancini, 2000; Mancini et al., 1993; Oehler, 1984; Sassen and Moore, 1988). Light hydrocarbon, biomarker, and $\delta^{13}C$ isotopic analyses of bulk fractions and individual hydrocarbons prove that these oils are genetically related and their compositions have not been altered by secondary reservoir processes, such as biodegradation or thermochemical sulfate reduction (Claypool and Mancini, 1989; Rooney, 1995; Sofer, 1988; Sofer, 1990). Several investigations have exploited the constraints in the geochemical and geologic variability within the Smackover petroleum system to study the changes in molecular and isotopic compositions imparted by source maturation and reservoir cracking (Dahl et al., 1997; Kuo and Michael, 1994; Wingert, 1992).

Table 2
Crude oil geographic, physical, and chemical data

Field[a]	Toxey	Turkey Creek	Chunchula
County, Alabama, USA	Choctaw	Choctaw	Mobile
Reservoir Fm.	Smackover	Smackover	Smackover
Reservoir depth, m	3200	3770	5628
Reservoir temp, °C[b]	87	93	160
GOR[b]	1.8	1.6	48.0
%Ro equivalent[c]	0.70	0.85	1.63
API Gravity	17.1	40.9	56.0
% Sulfur	5.2	0.8	0.1
% Nitrogen	0.34	0.02	0.001
C_{15+} chemical fractions			
% Saturates	23.6	58.7	84.9
% Aromatics	43.7	35.4	12.1
% Polars	8.1	3.9	2.0
% Asphaltenes[d]	24.8	2.1	1.0
$\delta^{13}C$ whole oil, ‰	−24.1	−23.9	−23.7
$\delta^{13}C$ C_{15+} fractions			
Saturates, ‰	−24.4	−24.4	−24.2
Aromatics, ‰	−23.6	−23.4	−22.4
Polars, ‰	−24.3	−24.3	n.d.
Asphaltenes, ‰	−24.4	n.d.	n.d.
$\delta^{34}S$ whole oil[b], ‰	5.5	−0.9	2.4
Pristane/(pristane + phytane)	0.36	0.45	0.56
Pristane/(pristane + n-C_{17})	0.22	0.22	0.18
Phytane/(phytane + n-C_{18})	0.35	0.26	0.17
CPI-1[e]	0.75	0.88	0.95
n-C_{27}/(n-C_{27} + n-C_{17})	0.20	0.22	0.13

[a] Toxey, Jimmerson 4-6; Turkey Creek, Pruet 28-5#1 and Alco 28-7#1; Chunchula, A. M. Hill 8-10#1 well.
[b] Data from Claypool and Mancini, 1989. GOR, gas oil ratio, in standard cubic feet of gas per stock tank barrel of oil or condensate at standard conditions (60 °F and 14.65 psia).
[c] Based on the regional vitrinite reflectance vs. depth trend defined as %Ro = 0.23 exp(depth ft./9440 ft). (Claypool and Mancini, 1989).
[d] Hexane precipitation.
[e] As defined by (Marzi et al., 1993).

Oil from the Toxey Field is a low gravity, high-sulfur crude, representing petroleum expelled from Smackover source rocks under relatively low maturity conditions (Tables 2 and 3). Turkey Creek Field oil has appreciably higher gravity and lower sulfur, representing oil expelled from the Smackover source rocks under conditions associated with main-stage generation. Condensate from the Chunchula Field represents a post-mature fluid that has undergone hydrocarbon cracking while in the reservoir.

2.2. Conventional geochemical analyses

The Smackover petroleums were analyzed for their molecular and isotopic compositions by use of a variety of conventional methods. Chemical group-type separations and chromatographic (GC and GC/MS) analyses

of oils and saturated and aromatic fractions were performed by methods described in Isaksen (1996). Light hydrocarbons were analyzed for composition by a multidimensional GC method (Walters and Hellyer, 1998). Stable carbon isotopic analysis of individual components was based on methods described in Rooney et al. (1998). Geographical, physical and basic geochemical data on these samples are given in Table 2.

Whole-oil (Fig. 1) and light hydrocarbon (Fig. 2) gas chromatograms for oils are shown for the Toxey and Turkey Creek oils. The m/z 191 and 217 selected-ion gas chromatograms of the saturated hydrocarbon fractions show the distribution of steranes, tricyclic terpanes, and hopanes (Fig. 3). Molecular indicators of thermal stress are listed in Table 3. As discussed below, the condensate from the Chunchula Field produced an ESI FT-ICR MS signal too weak to provide reliable measurement of its

Table 3
Indicators of thermal maturation

	Toxey	Turkey Creek
Light hydrocarbon parameters		
Heptane ratio[a] $100(n\text{-}C_7)/(\Sigma\ C_7$ hydrocarbons + cyclohexane)	29.6	22.3
Isoheptane ratio[a] (2-methyl + 3-methyl-hexanes/Σ DMCP)	3.30	2.85
(2,2-DMP + 3,3-DMP)/Σ (DMP)[b]	0.05	0.18
1,1-DMCP/Σ DMCP[b]	0.04	0.15
$^\circ C_{temp} = 140 + 15 \times \ln(2,4\text{-DMP}/2,3\text{-DMP})$[c]	117	127
Steranes		
C_{29} $\alpha\alpha\alpha$ (20S)/(20S + 20R)	0.45	0.49
C_{29} $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$	0.49	0.60
C_{27}–C_{29} diasteranes/(diasteranes + steranes)	0.18	0.34
Hopanes		
C_{27} T_s/T_m	0.19	0.77
C_{29} T_s/T_m	0.07	0.33
C_{32} 22S/(22S + 22R)	0.58	0.59
Naphthalenes, phenanthrenes, dibenzothiophenes		
DMN = (2,6- + 2,7-DMN)/1,5-DMN[d]	1.51	3.43
TMN 1 = 2,3,6-TMN/(1,3,5- + 1,4,6-TMN)[d]	0.39	0.52
TMN 2 = (1,3,7- + 2,3,6-TMN)/(1,3,5- + 1,4,6- + 1,3,6-TMN)[d]	0.93	0.97
MPI 1 = 1.5(3-MP + 2-MP)/(P + 9-MP + 1-MP)[e]	0.59	0.78
MPI 2 = 3(2-MP)/(P + 9-MP + 1-MP)[e]	0.68	0.88
MPI 3 = (3-MP + 2-MP)/(9-MP + 1-MP)[e]	0.59	0.76
MDBT = 4-MDBT/1-MDBT[e]	1.09	3.18
Aromatized steroids		
$C_{20}/(C_{20} + C_{27}$ (20S))	0.20	0.66
TAS C_{27}(20S)/(TAS C_{27}(20S) + MAS 5βC_{28}(20S))	0.65	0.78
TAS C_{28}(20R)/(TAS C_{28}(20R) + MAS 5αC_{29}(20S + 20R))	0.72	0.85

DMP, dimethylpentanes; DMCP, dimethylcyclopentane; DMN, dimethylnaphthalenes; TMN, trimethylnaphthalenes; P, phenanthrene; MP, methylphenanthrene; MDBT, methyldibenzothiophenes; TAS, triaromatic steroids; MAS, monoaromatic steroids

[a] Thompson (1983).
[b] Based on Chung et al. (1998) from Hunt et al. (1980).
[c] Bement et al. (1995) and Mango (1997).
[d] Alexander et al. (1985).
[e] Radke and Welte (1983) and Radke et al. (1986).

polar NSO components, so there is no further discussion of the geochemistry of that sample.

2.3. Sample preparation for negative ion ESI FT-ICR MS analysis

Solutions of the oil samples were prepared according to the procedures described in Hughey et al. (2002b). For the Toxey Field sample, 20 mg of crude was first dissolved in 3 mL of toluene, then diluted with 17 mL of methanol to give a final volume of 20 mL. The samples with low sulfur content (Turkey Creek at 0.8%, and Chunchula 0.1%) were prepared at a higher concentration (30 and 40 mg/20 mL solvent, respectively) in order to give an adequate ESI response. The final solutions were spiked with 30% NH_4OH to give a final base

concentration of 0.05% to facilitate deprotonation of the acids and neutral nitrogen compounds found in the crude.

2.4. FT-ICR MS mass analysis

Mass analyses were carried out with a homebuilt FT-ICR mass spectrometer (Senko et al., 1996b) equipped with a 9.4 T magnet (Oxford Instruments America Inc., Concord MA). Data were collected and processed by a modular ICR data acquisition system (MIDAS) (Senko et al., 1996a; Blakney et al., 2001). Negative ions were generated, accumulated, excited and detected under the same conditions as described in Hughey et al. (2002b). One hundred to 200 co-added time domain data sets were Hanning apodized, followed by a single zero-fill

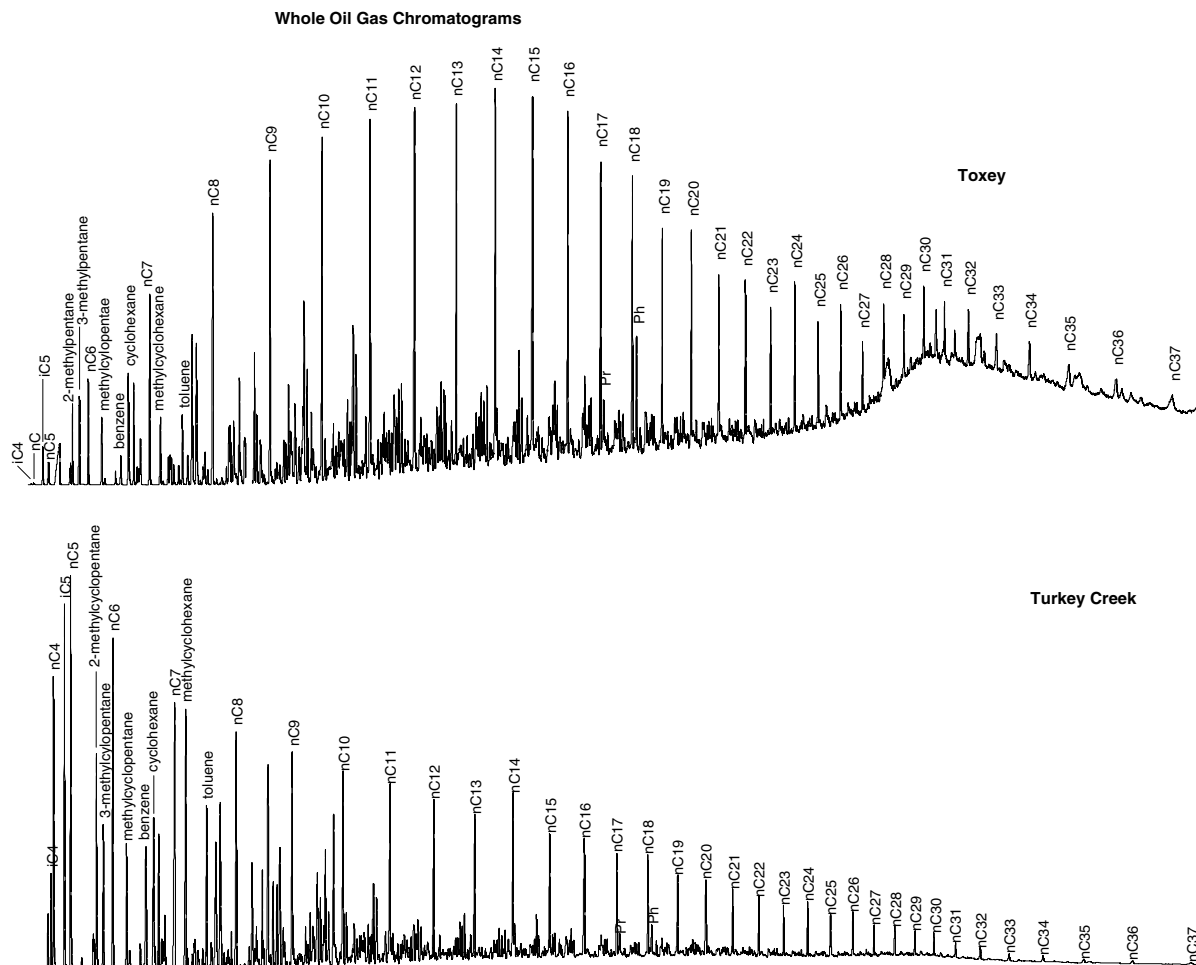**Whole Oil Gas Chromatograms**

Fig. 1. Whole oil gas chromatograms of Toxey and Turkey Creek oil field samples. Normal alkanes are labeled by carbon number. Pr, pristane; Ph, phytane.

before fast Fourier transformation and magnitude calculation. Frequency was converted to mass-to-charge ratio by quadrupolar electric trapping potential approximation (Ledford Jr. et al., 1984; Shi et al., 2000) to generate the spectra shown in Fig. 4. The Chunchula contains <2 wt% polar compounds and asphaltenes, an order of magnitude less than in whole oils previously analyzed by ESI FT-ICR MS. Although a mass spectrum was obtained, the data quality was too poor for reliable extraction of compound chemical formulae and distributions.

2.5. Mass calibration and high mass accuracy

Mass spectra were initially frequency-to-m/z calibrated externally with respect to a #G2421A Electrospray "tuning mix" from Agilent (extending down to 734 Da). The mass spectra were then recalibrated with respect to a homologous series within each crude

oil, spanning a $250 < m/z < 1000$ mass range. For example, the homologous series, $C_nH_{2n}SO_4$, was used for internal calibration of the Toxey crude; and $C_nH_{2n-21}N$ to calibrate Turkey Creek oil. Each recalibration yielded an rms error of <0.5 ppm. All species in the present mass spectra are singly charged, evidenced by the ∼1 Da spacing between each monoisotopic species and its corresponding nuclide containing one ^{13}C atom. Thus, from here on, we shall denote peaks by their mass in Da rather than as mass-to-charge ratio, m/z.

2.6. Data analysis: sorting, assignment of elemental compositions and Z-series (ring plus double bond) distributions

The mass values for (singly-charged) ions of 225–1000 Da and peak height greater than 3 standard deviations of baseline noise were imported into an
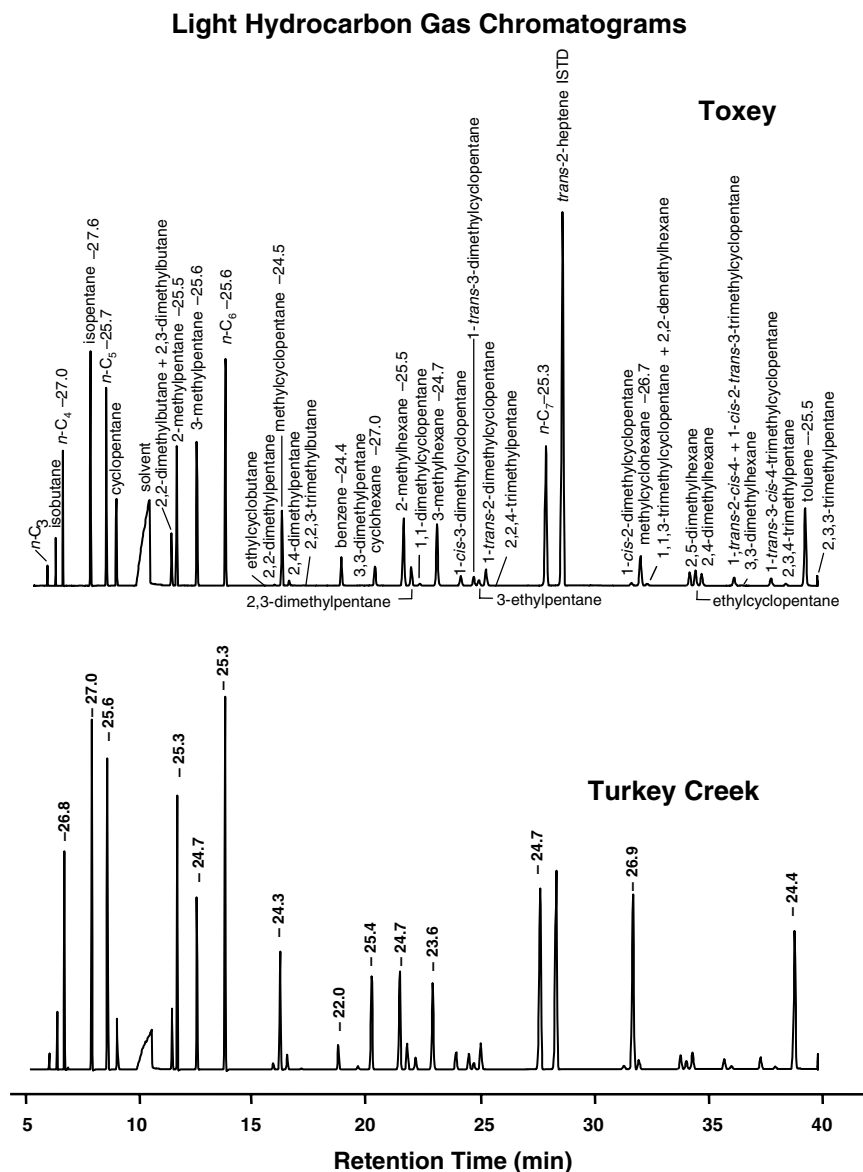
Light Hydrocarbon Gas Chromatograms

Fig. 2. Light hydrocarbon (C4–C7) gas chromatograms of Toxey and Turkey Creek field samples. δ^{13}C values were measured for the major components.

Excel spreadsheet. Measured masses were converted from the IUPAC mass scale ($CH_2 = 14.01565$ Da) to the Kendrick mass scale ($CH_2 = 14.00000$ Kendrick mass units) as previously described (Kendrick, 1963; Hsu et al., 1992; Hughey et al., 2001b). Even and odd nominal Kendrick masses were then sorted by an Excel macro, and the Kendrick mass defect (i.e., difference between exact and nominal (nearest-integer) Kendrick mass) calculated. Even and odd nominal Kendrick masses were then sorted (Hsu et al., 1992)

into homologous series, based on their identical Kendrick mass defects. Molecular formulas of species less than ~400 Da in mass could be assigned uniquely based solely on mass measurement to ±1 ppm. Elemental compositions were assigned by use of a mass calculator program limited to molecular formulas consisting of up to 100 ^{12}C atoms, 2 ^{13}C, 200 ^{1}H, 5 ^{14}N, 5 ^{16}O, 5 ^{32}S, and 1 ^{34}S. If two (or more) elemental compositions were found within the mass tolerance of ±1 ppm, one formula could usually be

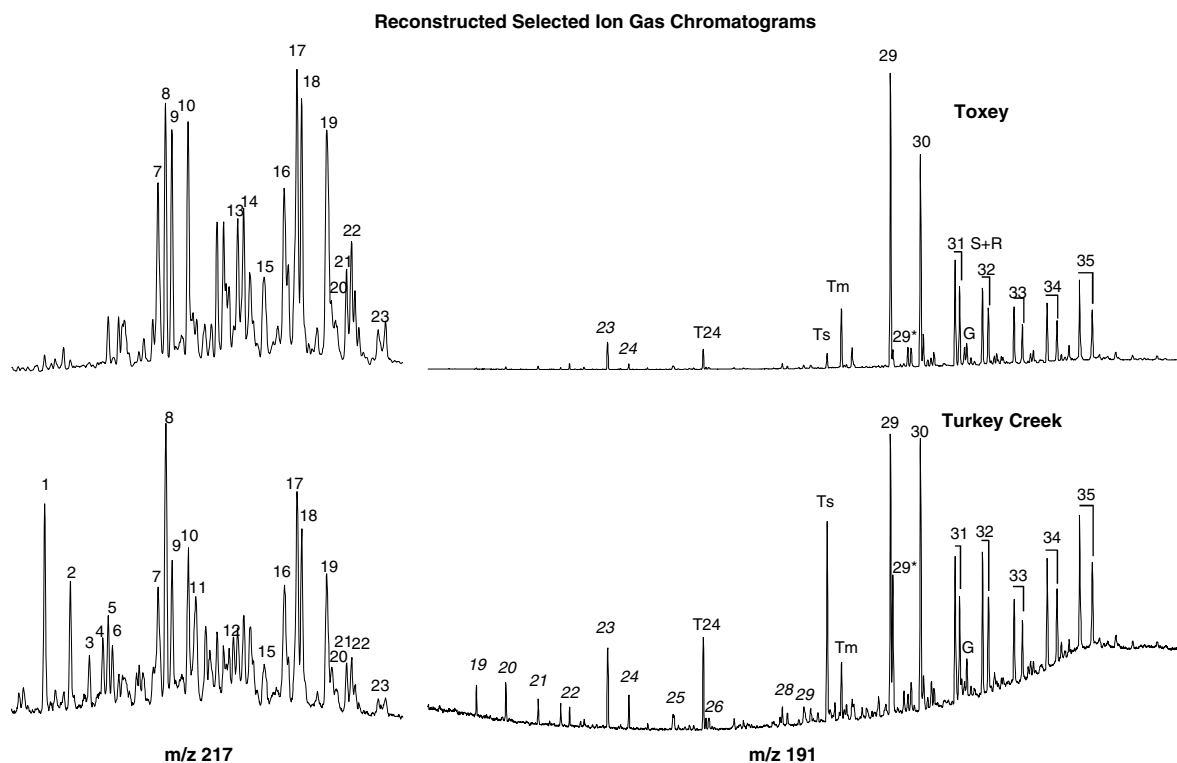**Reconstructed Selected Ion Gas Chromatograms**

Fig. 3. Reconstructed ion (m/z 191 and 217) selected ion gas chromatograms of saturated hydrocarbon fractions from Toxey and Turkey Creek field samples, showing the distribution of saturated biomarkers. Diasteranes, steranes, and hopanes are identified according to the Appendix key. Tricyclic terpanes are identified by carbon number. $T_{24} = C_{24}$ tetracyclic terpane.
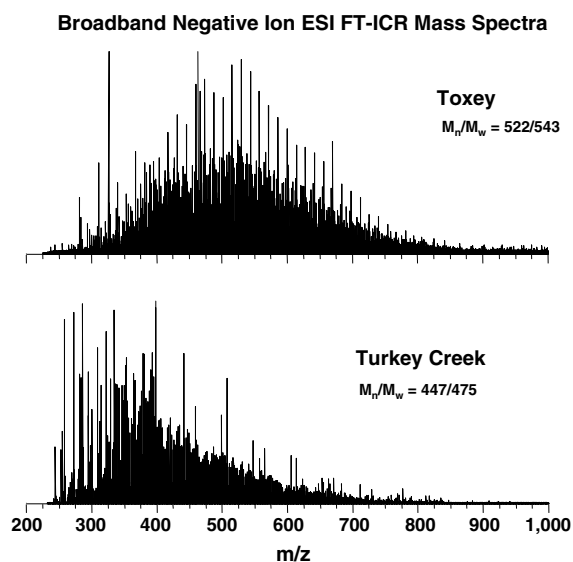

Fig. 4. Broadband negative-ion ESI FT-ICR mass spectra of Toxey and Turkey Creek oils.

confirmed/eliminated unequivocally by the presence/absence of the corresponding nuclide containing one [13]C. Because members of a homologous series differ only by integer multiples of CH_2, assignment of a single member of such a series usually sufficed to identify all higher-mass members. Thus, by recognizing homologous series, one can assign unique elemental compositions for species up to ~1000 Da, even though mass accuracy alone would not suffice.

Once identified, a homologous series within each formula class is described by its Z-value or hydrogen deficiency index. The Z-value is determined by the number of rings and double bonds in a molecule. Every two unit decrease in Z represents one degree of unsaturation (i.e., one additional double bond) or one additional ring. For example, the homologous series $C_nH_{2n-15}N$ found in the Toxey oil is abbreviated as $-15N$. For this series, carbazole is the core molecule, which collectively includes carbazole and all of its alkylated forms. For convenience, we have also designated molecules by the number of rings plus double bonds or double bond equivalents (DBE) present. Carbazole ($-15N$) has nine rings plus double bonds.

3. Results and discussion

3.1. Thermal maturity of Smackover oils

The Smackover oils yield mostly consistent molecular and isotopic indicators of maturity (Tables 2 and 3). The Toxey oil is revealed to be marginally mature with respect to oil generation and Turkey Creek oil is characterized as fully mature, main-stage oil generation. The $\delta^{13}C$ values for individual light hydrocarbons in the Toxey and Turkey Creek oils follow a consistent trend as expected for oils from the same source facies. The Turkey Creek oil exhibits heavier $\delta^{13}C$ values, consistent with a higher level of thermal stress (Rooney, 1995). However, a few anomalies are observed. Although maturity indicators based on the isomeric distribution within the C_7 hydrocarbon class indicate that the Toxey oil is less mature than Turkey Creek oil, C_7 light hydrocarbon ratios based on compound class distribution (e.g., the heptane and isoheptane ratios) are inverted from expected trends. The cause for the relatively high proportion of *n*-heptane and isoheptane relative to the C_7 cycloalkanes in the Toxey sample may be related to the preferential early release of these compounds as sulfur-bound moieties, an effect that would later be masked as the source rock matures.

3.2. Molecular weight distributions of polar compounds

The broadband ESI FT-ICR mass spectra clearly show that the molecular weight distribution of polar compounds is greatly influenced by thermal maturation (Fig. 4). The observed compound mass range (~250–1000 Da) is similar to those previously reported by high-resolution mass spectrometry (Hughey et al., 2002b; Tomczyk et al., 2001) and by fluorescence depolarization techniques (Groenzin and Mullins, 1999; Groenzin and Mullins, 2000). However, the weight-average molecular weight for the Toxey and Turkey Creek oils is 543 and 475, respectively. In this regard, the Turkey Creek sample resembles other oil samples expelled during peak generation (Hughey et al., 2002b), whereas the Toxey sample resembles that reported for a San Joaquin Valley sample that is a low-maturity, biodegraded oil derived from siliceous Monterey formation source rocks (Tomczyk et al., 2001).

The shift in the overall molecular weight distribution may be attributed to two thermal effects. Sulfur-rich kerogens generate petroleum enriched in polar NSO compounds under conditions of low thermal stress. These compounds contain many weak C–S and C–O bonds that may crack at reservoir temperatures, liberating defunctionalized hydrocarbons and smaller polar core molecules. Further maturation of the source rock results in similar cracking of retained fluids and of the cracking of stronger C–C bonds within the kerogen,

resulting in an expelled petroleum that is enriched in hydrocarbons and smaller polar compounds. The net effect of thermal maturity is reservoir cracking of large polar compounds and a dilution of early expelled high molecular weight polar compounds with later expelled smaller polar compounds.

3.3. Compound class distributions

High field FT-ICR mass spectrometry provides unambiguous identification of the deprotonated molecular negative ion species generated by ESI. Fig. 5 displays a highly expanded mass segment for the two oils. Between 486.1 and 486.5 Da, at least 10 chemically different species are resolved and identified in Toxey crude. The identifications may be abbreviated according to the values of Z and X values as in the general formula of $C_nH_{2n+Z}X$. Turkey Creek spectrum is considerably simpler and contains species with fewer S and O atoms.

The relative concentrations of polar compounds by formula class can be approximated by dividing the sum of all abundances for that class by the total abundance of all species. This approach does not account for inherent differences in ionization efficiency between different formula classes or mass-dependent ionization efficiency differences within a formula class. For example, carboxylic acids are known to ionize much more readily than neutral nitrogen species, producing a disproportionately larger signal. Nevertheless, such
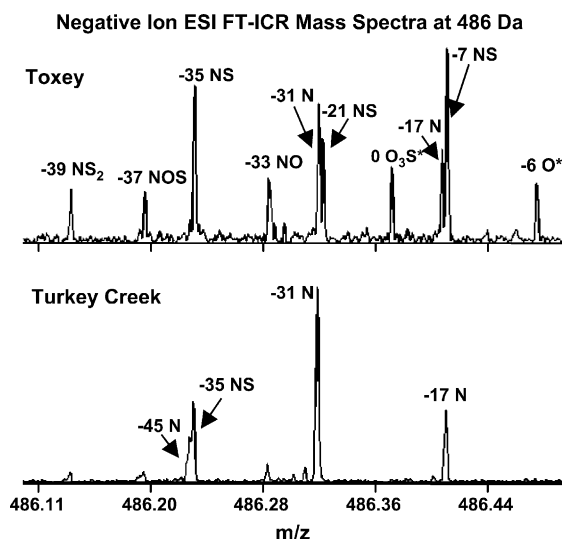

Fig. 5. IUPAC mass scale-expanded segment of the spectrum of Fig. 4, for ions of nominal mass, 486 Da. Molecular formulas are abbreviated with their class and type (Z series that define the number of rings plus double bonds) designation. For example, –39 NS$_2$ represents the homologous series $C_nH_{2n-39}NS_2$. This molecule would contain 21 rings plus double bonds. Asterisks denote nuclides containing one (*) ^{13}C atom.

comparisons do provide insight into the relative composition of the polar molecules. These comparisons do generally reflect elemental composition data (Hughey et al., 2002b). The large differences observed between the Toxey and Turkey Creek oils indicate that thermal maturation is a major influence on that distribution (Fig. 6). The most obvious difference is the higher proportion of sulfur and oxygen-containing species in the Toxey oil, including the NS, NS_2, NSO, O, SO, SO_3 and SO_4 classes. In contrast, the Turkey Creek sample is dominated by nitrogen-containing species, suggesting that during the course of thermal maturation (again, either due to cracking of kerogen and retained polars within the source or expelled oil within the reservoir),

sulfur compounds are preferentially destroyed and/or neutral nitrogen compounds are preferentially produced. O_2 compounds are low in both oils, supporting the concept that high concentrations of carboxylic acids in oils result from biodegradation (Meredith et al., 2000).

3.4. Z-series distributions within formula classes

An obvious pattern seen in all formula series is an increase in relative abundance at six Z-unit intervals, corresponding to the addition of one more aromatic ring fused to an already aromatic core (Fig. 7). Examples of likely core molecules for the formula series are shown in
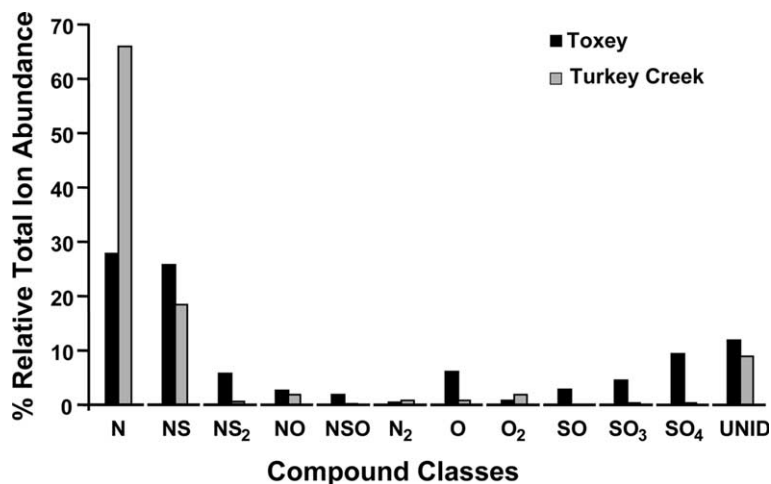

Fig. 6. Compound class distributions found in Toxey and Turkey Creek oils, normalized to 100%.
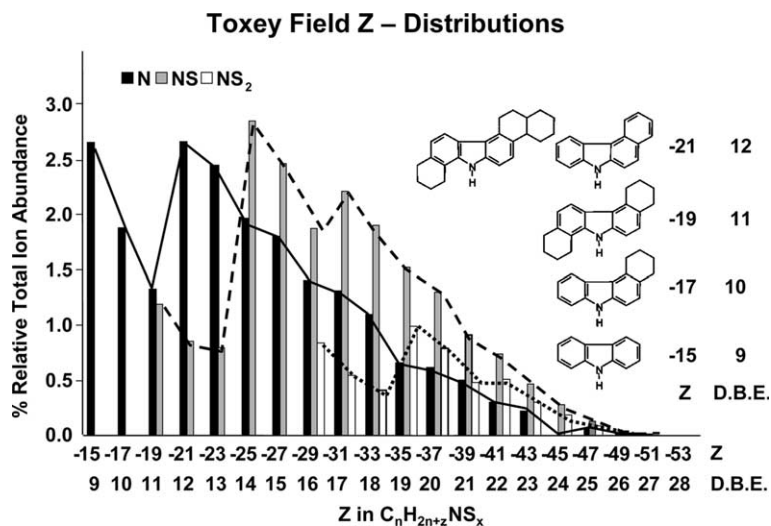

Fig. 7. Normalized Z-series distribution for $C_nH_{2n+z}N$, $C_nH_{2n+z}NS$, and $C_nH_{2n+z}NS_2$ compounds in Toxey Field oil. Double bond equivalent (DBE) designations are also given. Structures are representative.
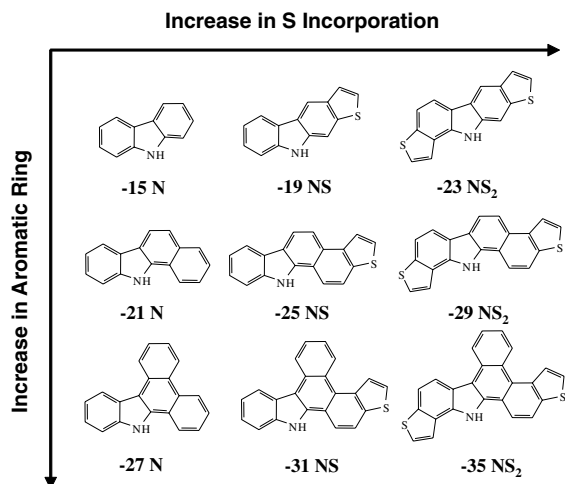
Fig. 8. Evolution of potential N-core structures as a function of Z number and sulfur.

Fig. 8. Note that each structure represents only one of many possible isomers.

A comparison of the Z-series distribution for pyrrolic compounds ($C_nH_{2n+Z}N$) observed in the Toxey and Turkey Creek oils shows clear differences attributable to thermal maturation (Fig. 9). The low maturity Toxey sample contains a far greater proportion of smaller core molecules (carbazoles and naphtheno-carbazoles) than the more mature oil from Turkey Creek. The proportion of potentially fully aromatized species ($Z = -15 - 6_n$ or DBE $= 9 + 3_n$) to those with napthenic rings is approxi-

mately equal in the two oils if one considers the full range ($Z = -15$ to -53 or DBE $= 9-28$). However, the pyrrolic compounds in the Turkey Creek are measurably more prone to be fully aromatic than the Toxey compounds beginning with benzocarbazoles ($Z = -21$ or DBE $= 12$) and continuing to the end of the series.

The pattern is repeated in other formula classes. For example, Toxey oil exhibits a greater relative abundance of low molecular weight cores and cores with a greater number of naphthenic rings than the Turkey Creek oil in both $C_nH_{2n+Z}NS$ and $C_nH_{2n+Z}NO$ classes (Fig. 10).

The SO, SO_3 and SO_4 formula classes are particularly interesting. These compounds are only present in significant relative abundance in the Toxey oil, suggesting that they are highly sensitive indicators of early oil expulsion and/or to thermal stress. Needless to say, the presence of such oxidized species resulting from kerogen deposited under strongly anoxic conditions is problematic. SO compounds may include species such as dibenzothiophenes with a hydroxyl group or possibly sulfoxides, which are formed readily via the photooxidation of sulfides but are not likely to be ionized in negative ion ESI. The SO_3 and SO_4 compounds are dominated by naphthenic and monoaromatic species and are most likely sulfonic acids (Fig. 11). Sulfonic acids are not detected much above background in the Turkey Creek sample, indicating that these compounds are readily degraded at advanced levels of thermal stress.

Sulfonic acids have only recently been reported to occur in natural crude oils. Tomczyk et al. (2001) reported SO_3 compounds in San Joaquin Valley oil by high-resolution magnetic sector mass spectrometry.
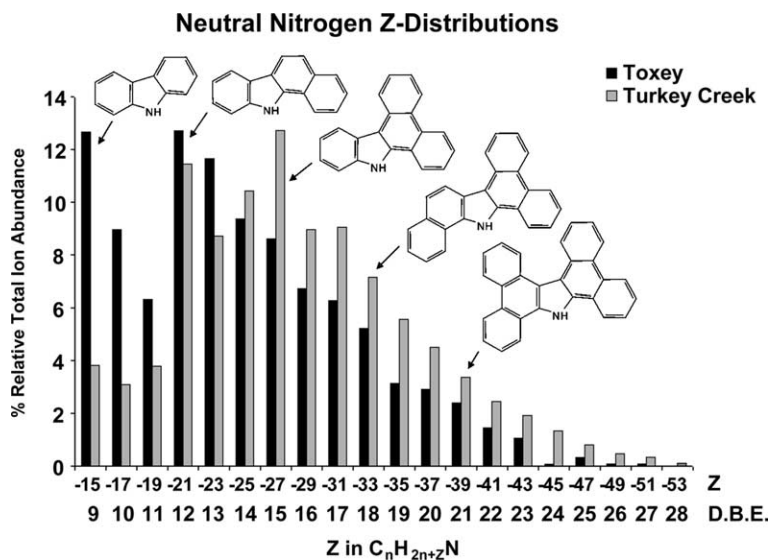

Fig. 9. Normalized Z-series distribution for $C_nH_{2n+z}N$ compounds for Toxey and Turkey Creek oils. Double bond equivalent (DBE) designations are also given. Structures are representative.
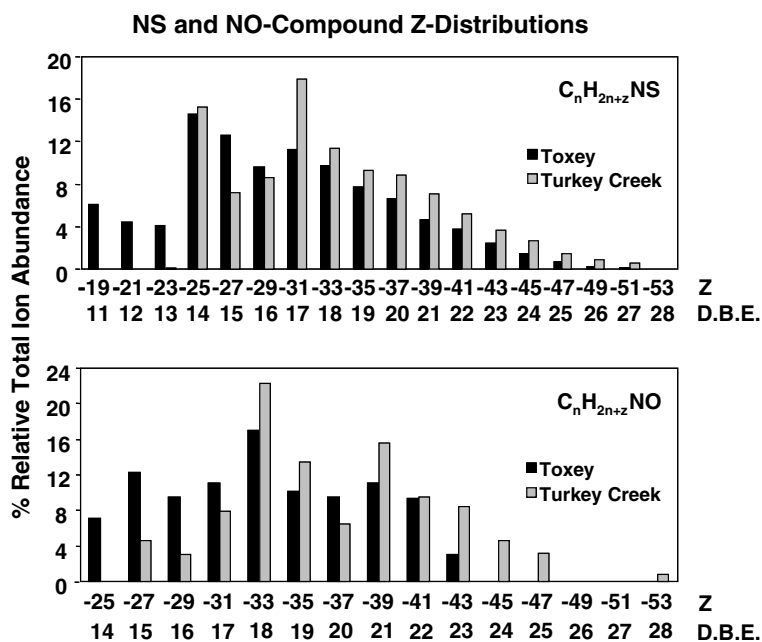
NS and NO-Compound Z-Distributions

Fig. 10. Normalized Z-series distribution for $C_nH_{2n+z}NS$ and $C_nH_{2n+z}NO$ compounds for Toxey and Turkey Creek oils. Double bond equivalents (DBE) designations are also given.
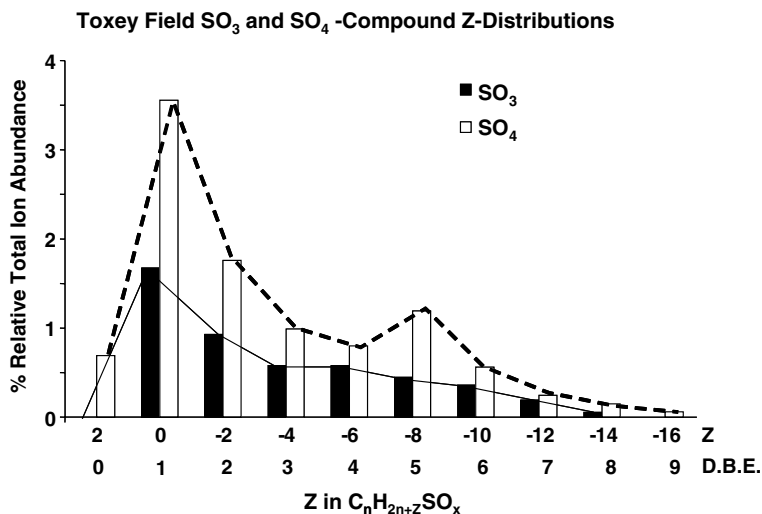
Toxey Field SO$_3$ and SO$_4$-Compound Z-Distributions

Fig. 11. Normalized Z-series distribution for $C_nH_{2n+z}SO_3$ and $C_nH_{2n+z}SO_4$ compounds found in Toxey Field oil. Double bond equivalent (DBE) designations are also given.

That oil is relatively immature and heavily biodegraded. Rudzinski et al. (2002) reported compounds with SO_3 moieties in a Maya crude by use of ESI-MS/MS. The occurrence of sulfonic acids in the Maya crude is particularly relevant because that sample is a blend of Bay of Campeche oils derived from a source that is equivalent to the Smackover Formation (Guzmán-Vega and Mello, 1999). However, both the San Joaquin Valley and Maya crudes were fractionated prior to analysis by methods that could promote oxidation. For example, isolated aliphatic sulphides are readily oxidized to sulphoxides and sulphones (Gorbaty et al., 1992). In the ESI FT-ICR MS analysis of whole crude oils, Qian et al. (2001a) and Hughey et al. (2002b) reported minor amounts of SO_2, SO_3, and SO_4 compounds. In ESI FT-ICR MS, oxidation of analyte species is less likely.

3.5. Alkylation distributions within homologous series

Thermal maturation has a significant influence on the carbon number distributions in a homologous series (i.e., formula-specific Z-series). For example, the relative abundances for N-compounds with Z numbers of −15 or DBE of 9 (carbazoles), −21 or 12 (benzocarbazoles), and −27 or 15 (dibenzocarbazoles) differ significantly between the two Smackover oils (Fig. 12). These distributions approximate that seen for the *n*-alkanes (Fig. 1), extending from 0 to ∼40 carbons. The number of alkyl carbons in the Toxey oil maximizes around 15–24, whereas the Turkey Creek sample shifts to lower molecular weight species. Similarity between the alkyl distributions within the neutral nitrogen and saturated hydrocarbons is observed in other oils (Hughey et al., 2002b). Note that the distribution for the −15N carbazoles is incomplete because the C_0 to ∼C_6 species are not observed due to limited detection efficiency for species less than ∼250 Da.

It is reasonable to assume that alkyl groups cleave from these nitrogen compounds as the kerogen, retained bitumen, and expelled oil is subjected to increasing

thermal stress. Furthermore, as for the *n*-alkanes, any carbon number preference within alkyl groups attached to polar cores will diminish as maturation proceeds. Indeed, there is appreciably more irregularity in carbon number distribution in the Toxey oil which resembles, but does not exactly mirror, the even-carbon number preference of its *n*-alkanes. We can expect such divergences because the carbon numbers reflect the sum of all alkyl groups, which are not necessarily expressed as a single alkyl chain. Nevertheless, there is a suggestion that the even-carbon number preference of the *n*-alkanes is apparent in the polar compounds of the Toxey oil.

4. Conclusions

ESI FT-ICR MS analysis of the polar compounds in two Smackover-derived oils reveals appreciable differences. These oils were selected to minimize variations that could be attributed to source facies, expulsion, migration, and post-reservoir alteration processes, such as phase separation and biodegradation. Thermal maturation is the major factor influencing the differences in composition. The Toxey oil was generated and expelled at relatively low thermal stress (early oil window), whereas the Turkey Creek oil was generated and expelled under thermal conditions associated with main-stage oil generation. Because the reservoir rocks are only slightly cooler than the source, oil composition may reflect cumulative thermal reactions that occur within the kerogen and unexpelled bitumen within the source carbonates, and in expelled oil in the reservoir rocks.

The present results clearly demonstrate the efficacy of analyzing weakly acidic compounds by coupling electrospray ionization to Fourier transform-ion cyclotron resonance mass spectrometry. The selective deprotonation induced by negative-ion ESI minimizes the need for fractionation, and the ultrahigh mass resolution allows for the identification of unique elemental formulations and assignment of masses to distinct classes (NSO composition), type (Z series that define the number of rings plus double bonds), and carbon number distributions.

We can offer the following conclusions concerning the effects of thermal maturation on acidic polar compounds:

1. The low maturity oil contains a high proportion of sulfur and oxygen compound classes with more than one NSO heteroatom (NS, NS_2, NSO, SO, SO_3 and SO_4 groups). In contrast, the high maturity oil is dominated by compound classes containing nitrogen (mostly N and NS). Thus, the sulfur and oxygen compounds are preferentially destroyed and/or neutral nitrogen compounds are preferentially produced during catagenesis.

2. Thermal maturation promotes aromatization and condensation of acidic polar compounds. Within a
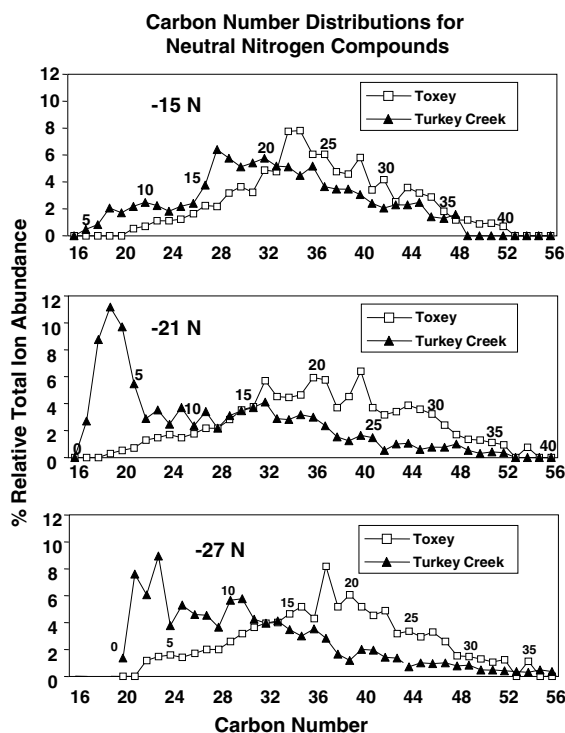

Fig. 12. Normalized carbon number distributions for individual compounds in three pyrrolic $C_nH_{2n+z}N$ Z-series ($Z = -15$, −21, and −27) Note that instrument limitations prevent the measurement of species below a mass of ∼250 Da. Consequently, the low molecular weight carbazoles, ∼C_0 to ∼C_5, are not observable.

given formula class, the relative distribution shifts toward compounds with a higher degree of un-saturation and favors fully aromatized species relative to those with partially unsaturated naphthenic rings.

3. For a given molecular class (numbers of N, S, and O atoms) and type (*Z*-number, or number of rings plus double bonds), the degree of alkylation decreases with increasing maturation. The carbon number distribution for the alkyl groups on aromatic rings resembles that for the *n*-alkanes. Carbon number preferences are present in the low maturity oil but diminish with increasing thermal stress.

The above conclusions are based only on the limited present data set and must be verified by analysis of additional samples, both from within the Smackover trend and from other well-constrained petroleum systems. Meanwhile, it is encouraging that the present conclusions are consistent with results previously published for three different oils (Hughey et al., 2002b), even though a direct comparison is not possible because of the interfering effects of source variations and biodegradation.

Associate Editor – **Simon George**

Appendix A. Key to Fig. 3

Peak number	Name	Carbon number
m/z 217: steranes and diasteranes		
1	13β,17α-diacholestane 20*S*	27
2	13β,17α-diacholestane 20*R*	27
3	13α,17β-diacholestane 20*S*	27
4	13α,17β-diacholestane 20*R*	27
5	13β,17α-24-methyldiacholestane 20*S*	28
6	13β,17α-24-methyldiacholestane 20*R*	28
7	5α,14α,17α-cholestane 20*S*	27
8	5α,14β,17β-cholestane 20*R* + 13β,17α-ethyldiacholestane 20*S*	27 + 29
9	5α,14β,17β-cholestane 20*S*	27
10	5α,14α,17α-cholestane 20*R*	27
11	13β,17α-24-ethyldiacholestane 20*R*	29
12	5α,14α,17α-24-methylcholestane 20*S*	28
13	5α,14β,17β-24-methylcholestane 20*R*	28
14	5α,14β,17β-24-methylcholestane 20*S*	28
15	5α,14α,17α-24-methylcholestane 20*R*	28
16	5α,14α,17α-24-ethylcholestane 20*S*	29
17	5α,14β,17β-24-ethylcholestane 20*R*	29
18	5α,14β,17β-24-ethylcholestane 20*S*	29
19	5α,14α,17α-24-ethylcholestane 20*R*	29
20	5α,14α,17α-24-*n*-propylcholestane 20*S*	30
21	5α,14β,17β-24-*n*-propylcholestane 20*R*	30
22	5α,14β,17β-24-*n*-propylcholestane 20*S*	30
23	5α,14α,17α-24-*n*-propylcholestane 20*R*	30

Appendix A (*continued*)

Peak number	Name	Carbon number
m/z 191: triterpanes		
Ts	18α-22,29,30-Trisnorneohopane	27
Tm	17α-22,29,30-Trisnorhopane	27
28	(17α + 18α)-28,30-Bisnorhopane	28
29	17α,21β-Norhopane	29
29*	18α-30-Norneohopane	29
30	17α,21β-Hopane	30
30M	17β,21α-Hopane	30
31S	17α,21β-Homohopane (22*S*)	31
31R	17α,21β-Homohopane (22*R*)	31
G	Gammacerane	30
32S	17α,21β-Bishomohopane (22*S*)	32
32R	17α,21β-Bishomohopane (22*R*)	32
33S	17α,21β-Trishomohopane (22*S*)	33
33R	17α,21β-Trishomohopane (22*R*)	33
34S	17α,21β-Tetrakishomohopane (22*S*)	34
34R	17α,21β-Tetrakishomohopane (22*R*)	34
35S	17α,21β-Pentakishomohopane (22*S*)	35
35R	17α,21β-Pentakishomohopane (22*R*)	35

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