Oil and gas geochemistry and petroleum systems of the Fort Worth Basin

Ronald J. Hill, Daniel M. Jarvie, John Zumberge, Mitchell Henry, and Richard M. Pollastro

ABSTRACT

Detailed biomarker and light hydrocarbon geochemistry confirm that the marine Mississippian Barnett Shale is the primary source rock for petroleum in the Fort Worth Basin, north-central Texas, although contributions from other sources are possible. Biomarker data indicate that the main oil-generating Barnett Shale facies is marine and was deposited under dysoxic, strong upwelling, normal salinity conditions. The analysis of two outcrop samples and cuttings from seven wells indicates variability in the Barnett Shale organic facies and a possibility of other oil subfamilies being present. Light hydrocarbon analyses reveal significant terrigenous-sourced condensate input to some reservoirs, resulting in terrigenous and mixed marine-terrigenous light hydrocarbon signatures for many oils. The light hydrocarbon data suggest a secondary, condensate-generating source facies containing terrigenous or mixed terrigenous-marine organic matter. This indication of a secondary source rock that is not revealed by biomarker analysis emphasizes the importance of integrating biomarker and light hydrocarbon data to define petroleum source rocks. Gases in the Fort Worth Basin are thermogenic in origin and appear to be cogenerated with oil from the Barnett Shale, although some gas may also originate by oil cracking. Isotope data indicate minor contribution of biogenic gas. Except for reservoirs in the Pennsylvanian Bend Group, which contain gases spanning the complete range of observed maturities, the gases appear to be stratigraphically segregated, younger reservoirs contain less mature gas, and older reservoirs contain more mature gas. We cannot rule out the possibility that other source units within the Fort Worth Basin, such as the Smithwick Shale, are locally important petroleum sources.

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INTRODUCTION

The Fort Worth Basin in north-central Texas has produced approximately 2 billion bbl of oil and 7 tcf of gas since production began in the early 1900s (Ball and Perry, 1996; Pollastro, 2003). Reservoirs range in age from Ordovician to Permian, with most being in middle and upper Pennsylvanian rocks. Lower Permian reservoirs are important in the western area of the basin. The primary source rock for Fort Worth Basin oils and gases is the Mississippian Barnett Shale (Figure 1) (Jarvie et al., 2001), which averages 4 wt.% total organic carbon (TOC) with values reaching 14% in outcrop samples along the Llano uplift and the south flank of the Fort Worth Basin (Henk et al., 2000; Jarvie et al., 2001). The highest average TOC approximately coincides with the formation's depocenter that follows the paleoaxis of the Fort Worth Basin. The organic-rich strata are thermally mature throughout most of the basin (Pollastro et al., 2003), and fractured shale units themselves are gas exploration targets. Jarvie et al. (2001) interpreted the Barnett Shale to be a source rock based primarily on light hydrocarbon analysis integrated with vitrinite reflectance and geologic data. The purpose of this article is to further investigate the origin of petroleum in the Fort Worth Basin through bulk geochemical and detailed molecular analyses of its oils and gases.

Geologic Summary

The Fort Worth Basin is an asymmetric, wedge-shaped basin containing as much as 12,000 ft (3657 m) of sedimentary rocks along the west side of the Muenster arch (Pollastro et al., 2007). This foreland basin formed in front of the advancing Ouachita structural belt as it was thrusted onto the margin of the North America craton during a late Mississippian–early Pennsylvanian episode of plate convergence (Flippin, 1982; Walper, 1982; Grayson et al., 1990). The Bend arch is a broad, north-plunging, subsurface anticline that extends northward from the Llano uplift (Pollastro et al., 2007). The arch forms the westernmost limit of a migrating hinge zone, where Pennsylvanian and younger sediments were deposited on the Eastern shelf of the Permian Basin.

The Fort Worth Basin is bounded by the Ouachita structural front to the east and southeast, the Llano uplift to the south, and the Muenster and Red River arches to the north and northeast, and the Bend arch to the west (Figure 1). For the purpose of resource appraisal, the U.S. Geological Survey defined the Fort Worth Basin to include areas where Fort Worth Basin–derived petroleum may have migrated (Figure 1). A generalized stratigraphic section of the Bend arch–Fort Worth Basin is shown in Figure 2. From the Cambrian to the Ordovician, the area that is now the Fort Worth Basin was part of a stable cratonic shelf with deposition dominated by carbonates. The Barnett Shale was deposited over the Ellenburger unconformity during a period of foreland basin formation in the late Mississippian. The formation is present throughout most of the Fort Worth Basin–Bend

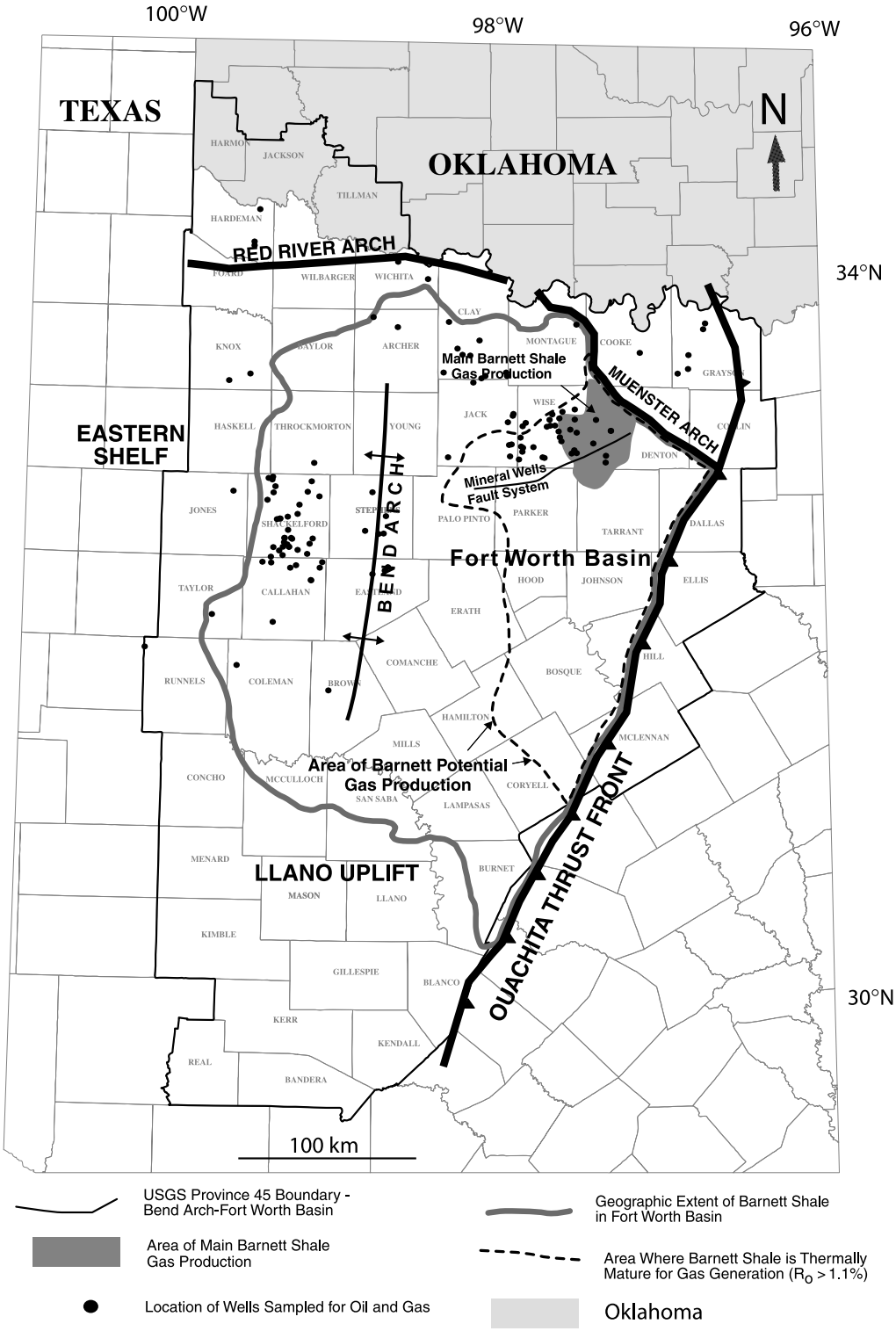
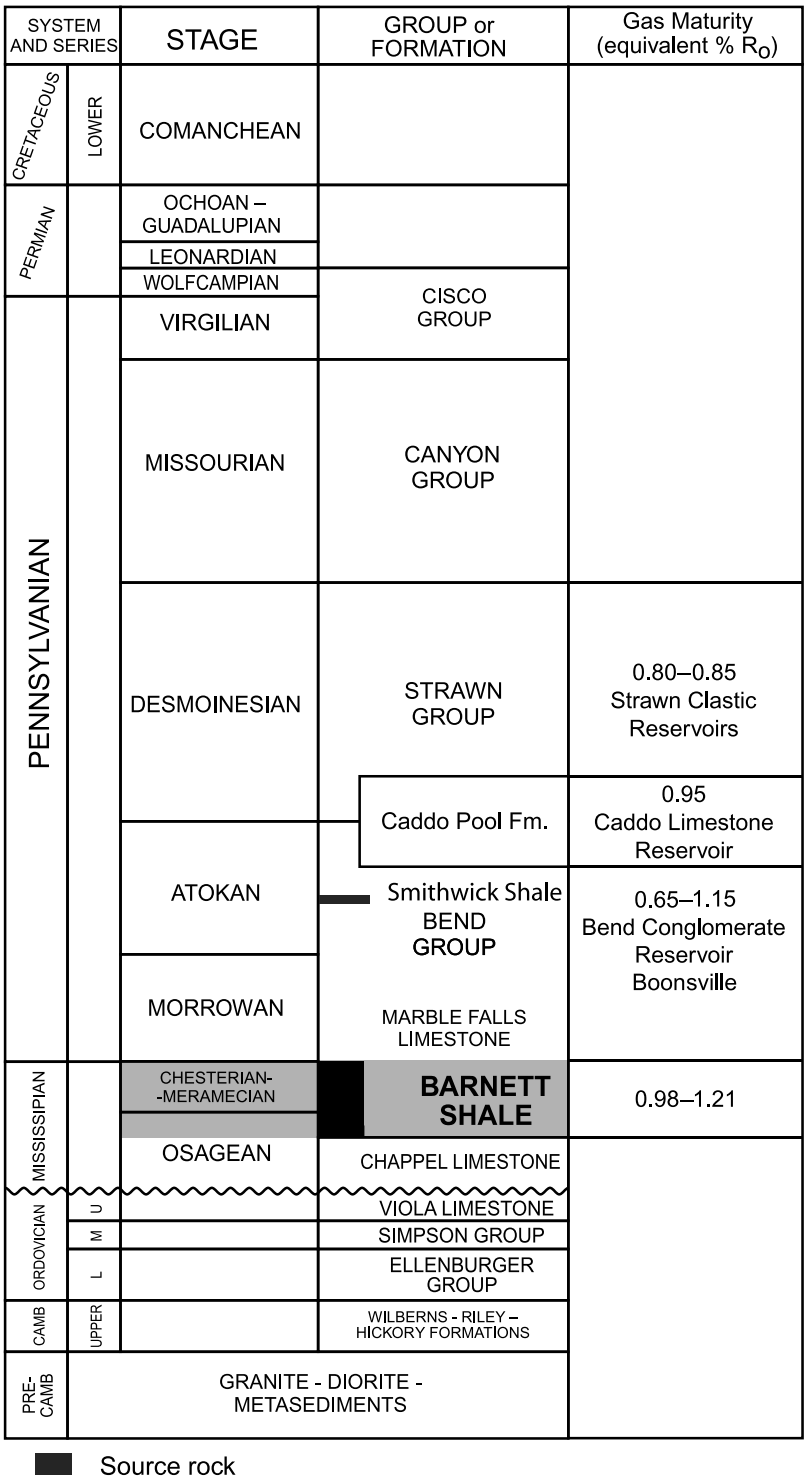


Figure 1. Map of Fort Worth Basin showing boundaries of major geologic structures and location of oil and gas wells sampled. The main producing area of the Newark East field is shown in the darker shaded area.

arch area and ranges in thickness from a few tens of feet along its western limit to more than 1000 ft (304 m) adjacent to the Muenster arch (Pollastro, 2003). Although burial depth is a major factor in Barnett Shale thermal maturity, gas generation and consequent gas production are largely controlled by high heat flow related to Ouachita thrusting and fault systems within the Fort Worth Basin (Bowker, 2003; Pollastro et al., 2003). The formation is presently in the oil-generation window in the northern and western parts of the basin.

Figure 2. Generalized Fort Worth Basin stratigraphy with gas-maturity values indicated. The name Boonsville conglomerate is of local usage in the Boonsville field, north-central Texas.



METHODS

Sampling

Oil (34) and gas (34) samples were collected from the Newark East area in Wise County, Texas, and surrounding counties (Figure 1), with permission from Republic Energy. Oil samples were collected in brown glass bottles at the well head or from the holding tank associated with each well. Gas samples were collected at the well head in brown glass bottles, by displacement of water containing zephrin chloride (an antibacterial agent) from the bottles. The bottles were sealed with snap caps and transported with the seals facing downward.

Forty oil samples and seven cuttings samples from the western Fort Worth Basin and two outcrop samples from the Llano uplift were obtained by Humble Geochemical Services, Houston, Texas. The data for the 74 oils and 9 rock samples are included in Table 1. An additional 63 oils were analyzed as part of this study available through GeoMark Research. GeoMark data are included in the figures, but are not present in Table 1.

Gas Analysis

Hydrocarbon and nonhydrocarbon gases were analyzed using a two-channel Hewlett Packard (HP) 6890 series gas chromatograph (GC) custom configured by Wasson ECE Instrumentation, with two capillary and seven packed columns in conjunction with a flame ionization detector (FID), two thermal conductivity detectors (TCD), and a Wasson AS200 autosampler. Each sample was introduced into the GC using three 5-mL sample loops through a series of precolumns and backflushes, thus allowing three analytical separation and detection schemes. The C_1–C_5 hydrocarbons were analyzed on channel A using helium as a carrier gas, two Wasson KC5 capillary columns for gas separation, and the HP-FID A for component detection. The CO_2, H_2S, O_2/Ar, N_2, and CO gases were separated on Wasson K1 and K2S packed columns using helium as the carrier gas and detected on the HP single-filament TCD B. The H_2 and He gases were separated on Wasson K1 and K2 packed columns using nitrogen as the carrier gas and analyzed on a standard Gow-Mac TCD C. Detectors B and C are tied by a summing board to provide a single analog signal. The detectors were calibrated using Scott Specialty Gases standards with a precision of ±1 mol% for each compound. The GC temperature was programmed from 85°C (3 min isothermal) to 180°C (5 min) at a rate of 15°C/min. Each three-part analysis was completed in 10 min.

Stable carbon analyses ($\delta^{13}C$) of C_1–C_3 and CO_2 gas components were performed on a Micromass Optima mass spectrometer interfaced with a HP 6890 GC. The GC was equipped with a J&W Scientific GS-Q 30-m (98-ft) × 0.32-mm (0.01-in.) column and the column flow rate was 2.5 mL/min. The GC oven was programmed to hold at 30°C for 4 min, then increased to 240°C at 15°C/min, and held at 240°C for 5 min. The separated gas components enter the combustion furnace (1000°C) for conversion to CO_2 prior to analysis. The interface between the GC and the mass spectrometer was maintained at 350°C.

API Gravity, Weight Percent Sulfur, and Hydrocarbon $\delta^{13}C$

Oil and condensate API gravities were determined using an Anton Parr DMA 4500 density meter. Weight percent sulfur was determined using a Carlo Erba Model 1100 elemental analyzer equipped with a combustion tube containing copper metal and tungsten trioxide for conversion of S to SO_2 and a Poropak PQS column 0.5 m (1.6 ft) × 0.25 in. (0.635 cm) for separation of combustion products. Magnesium perchlorate is also present in the combustion tube for water removal. Approximately 1–3 mg of oil or condensate sample was loaded in tin capsules and combusted at 1000°C. The SO_2 is detected on a Gow-Mac TCD.

Oil Liquid Chromatography

The oil's saturated and aromatic hydrocarbon fractions were obtained by column chromatography. Columns were prepared in disposable 5.0-mL serological pipettes by filling with alumina and silica-type 923 and silica-type 62 gel slurries. The column preparation procedure and oil column chromatography methods are summarized at the U.S. Geological Survey Web site (2004).

The rock samples were extracted with dichloromethane by soaking the powdered rock sample in solvent overnight and repeating until the solvent extract is clear. Asphaltenes were precipitated using pentane overnight at room temperature. Columns were prepared in disposable 5.0-mL serological pipettes by filling with silica gel. Saturated hydrocarbons were eluted using 15 mL of pentane; aromatic hydrocarbons were eluted using 40 mL of 90:10 pentane/dichloromethane mixture, and the polars eluted using 87:13 chloroform/methanol mixture.

Saturated hydrocarbon and aromatic hydrocarbon fraction $\delta^{13}C$ values were determined using a Micromass Optima mass spectrometer interfaced to a Carlo Erba Model 1100 elemental analyzer. Approximately 0.1 mg of saturated and aromatic hydrocarbons were loaded into tin capsules and combusted in the elemental analyzer at 1000°C to generate the CO_2 for analysis in the mass spectrometer. All carbon isotope ratios are relative to the Peedee belemnite standard.

Gas Chromatography

Whole-oil gas chromatography was performed on a Hewlett Packard 6890 GC using temperature and flow programming. In this procedure, (1) a 50 m (164 ft) × 0.20 mm

Table 1. Fort Worth Basin Outcrop and Oil Biomarker and Light Hydrocarbon Data

Name	Pristane/ Phytane	API Gravity (°)	Weight% S*	Saturate $\delta^{13}C$ (‰)	Aromatic $\delta^{13}C$ (‰)	C_{19}/C_{23}**	C_{22}/C_{21}**	$C_{24}Tet/C_{23}$†
Barnett outcrop (TOC¶¶ = 11.6%)	1.45	–	–	–		0.02	0.24	0.09
Barnett outcrop (TOC¶¶ = 13.1%)	1.26	–	–	–		0.02	0.24	0.08
Truitt 1 6870–6880-ft (2093–2097-m) cuttings	1.42	–	–	–		0.15	0.41	0.10
Truitt 1 6945-ft (2116-m) cuttings	1.39	–	–	–		0.09	0.39	0.10
Truitt 1 7040–7050-ft (2145–2148-m) cuttings	1.29	–	–	–		0.08	0.39	0.07
Gaskins 1 5120–5140-ft (1560–1566-m) cuttings	2.06	–	–	–		0.50	0.36	0.38
Gaskins 1 6970–6980-ft (2124–2127-m) cuttings	1.35	–	–	–		0.19	0.57	0.20
Gaskins 1 7060–7070-ft (2151–2154-m) cuttings	1.30	–	–	–		0.05	0.57	0.10
Gaskins 1 7190–7200-ft (2191–2194-m) cuttings	1.40	–	–	–		0.06	0.44	0.07
A. D. Huff 1	1.41	35.64	0.01	−31.23	−30.06	0.04	0.26	0.08
Aaron Hall 3	1.56	42.11	0.09	−30.98	−29.29	0.03	0.26	0.08
Arizona	1.56	–	–	−30.2	−29.32	–	–	–
Beaman 2	1.49	40.27	0.11	−30.74	−28.89	0.06	0.25	0.09
Beaman 3	1.50	48.43	0.00	−30.45	−28.85	0.08	0.29	0.11
Benda 71 no. 1	1.36	35.95	0.13	−31.57	−29.79	0.04	0.22	0.08
Blanton 49 no. 1	1.60	35.8	0.04	−30.77	−30.35	0.10	0.20	0.07
Bogy A 2	1.47	41.17	0.06	−30.98	−29.83	0.05	0.26	0.08
Booth 2	1.43	42.83	0.13	−31.09	−29.7	0.05	0.20	0.07
Brown "1602" 1	1.56	39.07	0.20	−31.26	−30.24	0.05	0.23	0.08
Burleson 34 no. 2	1.65	41.82	0.13	−31.19	−30.39	0.07	0.22	0.05
Casey 1	1.49	46.71	0.00	−30.20	−28.97	0.03	0.27	0.09
Caswell 1	1.58	52.37	0.00	−29.89	–	–	–	–
Collins 3	1.51	49.26	0.06	−30.66	−28.43	0.07	0.28	0.10
Cosey "A" 1	1.51	36.33	0.23	−31.42	−30.29	0.03	0.23	0.10
Craft TWB 2	1.44	43.23	0.11	−30.77	−29.29	0.03	0.21	0.06
Crawford 2	1.40	39.11	0.07	−31.09	−29.91	0.03	0.28	0.08
D. O. Lawson 3	–	56.28	0.00	–	–	0.04	0.26	0.09
Dawson-Conway B	1.28	35.62	0.40	−31.62	−30.95	0.03	0.24	0.07
Dell Newell 1	1.36	34.79	0.35	−31.75	−31.16	0.02	0.23	0.08
Della Christian WB 3	1.38	40.13	0.28	−31.29	−30.21	0.04	0.27	0.08
Dyer 2051 no. 1	1.44	40.58	0.13	−30.96	−29.69	0.06	0.22	0.07
Dyer 2988 no. 3	1.50	51.52	0.11	−31.16	−30.43	0.07	0.19	0.08
Elliot 45 no. 1	1.48	38.32	0.06	−31.19	−31.26	0.05	0.24	0.08
F. B. Ledbetter 1	1.48	39.98	0.16	−31.13	−30.82	0.07	0.22	0.10
Glenn George 2	1.44	49.81	0.00	−30.41	−28.07	0.09	0.30	0.08
Glenn George no. 3	–	57.18	0.00	–	–	–	–	–

Gammacerane/ hopane	Norhopane/ hopane	C_{35}/C_{34}[††]	C_{33}/C_{32}[††]	% C_{27} Sterane	% C_{28} Sterane	% C_{29} Sterane	C_{27} Diasterane/ C_{27} Sterane	C_{29} S/R[‡]	C_{29} αββ/ (ααα + αββ)[‡‡]	TAS[¶]	Terpane/ Sterane
0.08	0.79	0.74	0.95	0.41	0.11	0.47	0.70	0.28	0.36	0.09	0.74
0.07	0.80	0.76	0.86	0.42	0.11	0.47	0.65	0.28	0.35	0.08	0.74
0.09	0.33	0.62	0.80	0.44	0.13	0.44	2.70	0.45	0.63	0.61	0.54
0.07	0.35	0.48	0.75	0.40	0.17	0.43	2.45	0.46	0.64	0.60	0.56
0.07	0.37	0.46	0.76	0.38	0.17	0.45	2.12	0.47	0.63	0.60	0.59
0.02	0.60	0.47	0.50	0.41	0.14	0.45	1.54	0.40	0.39	0.19	0.21
0.09	0.29	0.49	0.71	0.41	0.16	0.43	3.35	0.47	0.62	0.59	0.40
0.06	0.34	0.49	0.76	0.38	0.16	0.46	2.33	0.45	0.64	0.58	0.41
0.06	0.38	0.47	0.73	0.37	0.15	0.48	1.50	0.43	0.64	0.55	0.53
0.07	0.40	0.92	0.89	0.50	0.15	0.35	1.41	0.42	0.64	0.36	1.08
0.07	0.42	1.11	0.94	0.51	0.15	0.35	1.50	0.41	0.64	0.41	1.17
	–	–	–	–	–	–	–	–	–	–	
0.08	0.40	1.04	0.94	0.51	0.15	0.34	1.79	0.42	0.64	0.48	1.00
0.09	0.47	1.17	0.95	0.52	0.15	0.33	1.49	0.43	0.64	0.44	1.04
0.10	0.55	1.06	1.11	0.46	0.14	0.40	1.27	0.41	0.64	0.56	0.92
0.72	0.70	–	1.11	0.51	0.18	0.31	1.60	0.45	0.60	0.59	1.94
0.07	0.40	1.04	0.90	0.48	0.16	0.36	1.59	0.43	0.64	0.42	1.13
0.13	0.56	1.32	0.90	0.48	0.11	0.41	1.43	0.42	0.63	0.53	1.44
0.09	0.48	0.94	1.00	0.49	0.14	0.37	1.10	0.42	0.63	0.48	0.92
0.24	0.48	2.43	0.98	0.51	0.19	0.30	1.53	0.43	0.63	0.79	1.63
0.08	0.44	1.34	0.84	0.52	0.16	0.33	1.58	0.43	0.64	0.45	1.04
	–	–	–	–	–	–	–	–	–	0.67	
0.09	0.35	1.45	0.93	0.51	0.14	0.34	1.73	0.40	0.62	0.51	1.17
0.12	0.51	1.01	0.87	0.37	0.19	0.44	1.88	0.42	0.63	0.47	1.13
0.11	0.48	1.57	0.92	0.50	0.15	0.35	1.71	0.42	0.63	0.59	1.38
0.07	0.37	1.01	0.92	0.49	0.15	0.35	1.46	0.43	0.64	0.43	1.08
0.07	0.40	1.08	0.86	0.50	0.14	0.36	1.47	0.40	0.63	0.42	0.96
0.08	0.55	0.92	0.98	0.44	0.15	0.41	0.81	0.42	0.58	0.16	0.82
0.08	0.52	0.92	0.93	0.45	0.15	0.40	0.86	0.42	0.58	0.19	0.79
0.07	0.38	1.01	0.90	0.49	0.15	0.35	1.43	0.43	0.64	0.42	1.04
0.15	0.58	1.35	0.84	0.50	0.14	0.35	1.22	0.44	0.63	0.59	1.38
0.23	0.43	1.46	0.99	0.53	0.17	0.30	1.47	0.45	0.63	0.80	2.33
0.09	0.53	1.06	0.91	0.39	0.18	0.43	0.71	0.42	0.59	0.16	0.96
0.17	0.37	0.90	0.83	0.51	0.17	0.33	1.30	0.43	0.64	0.53	1.38
0.19	0.47	3.09	0.83	0.56	0.17	0.26	1.98	0.44	0.61	0.75	1.44
	–	–	–	–	–	–	–	–	–	–	

Table 1. Continued

Name	Pristane/ Phytane	API Gravity (°)	Weight% S*	Saturate $\delta^{13}C$ (‰)	Aromatic $\delta^{13}C$ (‰)	C_{19}/C_{23}**	C_{22}/C_{21}**	$C_{24}Tet/C_{23}$†
Grimes 75 no. 1	1.69	39.2	0.05	−30.92	−30.37	0.08	0.24	0.07
Hatchel no. 2	–	61.42	0.00	−28.62	–	–	–	–
Herr King 7-18	1.67	41.72	0.11	−31.25	−30.22	0.08	0.24	0.13
J. H. Nail "A" 29	1.34	34.98	0.40	−31.7	−30.05	0.03	0.22	0.08
J. H. Nail "A" 5	1.35	36.85	0.41	−31.85	−31.21	0.04	0.22	0.07
Jerry North no. 1	2.01	59.30	0.00	−28.35	–	–	–	–
McComas 1	1.38	38.57	0.17	−31.28	−29.73	0.05	0.23	0.09
McConnell 2A	1.44	37.95	0.00	−30.85	−29.36	0.04	0.24	0.08
McConnell 6	1.45	39.60	0.06	−30.86	−29.41	0.03	0.25	0.07
Mildred A. Durham 14	1.41	41.80	0.07	−30.56	−29.53	0.03	0.27	0.09
Mitcham 3	1.63	37.57	0.18	−31.09	−30.32	0.05	0.20	0.09
Montgomery "20" 1	1.52	39.38	0.09	−31.12	−29.96	0.05	0.23	0.10
Nail 124A 1	1.40	37.09	0.35	−32.1	−30.08	0.03	0.23	0.07
Nail 135 no. 5	1.38	36.51	0.27	−31.88	−31.04	0.03	0.24	0.09
Nail M 35	1.44	36.63	0.32	−31.74	−30.87	0.04	0.23	0.08
Newell 10 no. 3	1.62	41.24	0.13	−31.45	−30.48	0.07	0.19	0.09
Newell 11 no. 1	1.38	35.73	0.38	−31.79	−31.17	0.03	0.23	0.07
Newell 12 no. 1	1.61	43.33	0.12	−31.45	−30.08	0.06	0.19	0.06
North no. 2	–	61.91	0.00	–	–	–	–	–
Odom 165 no. 1	1.59	39.37	0.08	−30.42	−29.8	0.07	0.27	0.20
Parr no. 2	1.48	45.14	0.17	−31.05	−29.39	–	–	–
Perkins no. 1	–	54.54	0.00	−30.28	–	–	–	–
Pitzer 372 no. 2	1.55	40.62	0.21	−31.6	−31.12	0.05	0.19	0.08
Raney no. 6	–	56.59	0.00	–	–	–	–	–
S. Green 46 no. 2	1.50	37.98	0.15	−30	−29.22	0.05	0.23	0.10
S. Green 54 no. 1	1.67	38.92	0.00	−31.12	−30.48	0.06	0.16	0.10
S. Green 58 no. 1	1.40	–	0.20	−31.75	−30.00	0.04	0.23	0.08
S. Green 58 no. 15	1.37	38.06	0.10	−31.37	−30.03	0.04	0.23	0.07
S. Green 60 no. 1	1.55	41.58	0.07	−31.07	−30.49	0.08	0.19	0.05
S. Green 68C 1	1.48	36.21	0.11	−31	−29.05	0.05	0.23	0.07
S. Green 72 no. 2	1.39	40.27	0.14	−31.65	−30.31	0.02	0.24	0.08
Scott 1	1.46	39.44	0.10	−30.90	−28.92	0.03	0.26	0.10
Seagraves 3	1.46	41.09	0.05	−30.89	−29.13	0.04	0.25	0.10
Seagraves 4	1.46	43.50	0.09	−30.50	−29.04	0.06	0.26	0.10
Snyder 32C 1	1.54	39.67	0.08	−31	−30.26	0.16	0.24	0.10
T. G. Rogers 2	1.43	41.93	0.16	−30.75	−28.92	0.07	0.27	0.09
Tarrant County Waterboard unit 1 no. 3	1.50	56.56	0.00	−30.73	–	0.07	0.27	0.08
Tarrant County Waterboard unit 6 no. 4	1.42	42.40	0.00	−31.22	−29.72	0.03	0.26	0.05
W. B. 522-523 no. 1	1.43	36.88	0.17	−30.69	−29.66	0.03	0.25	0.11
W. H. Green "A" 1	1.63	37.42	0.00	−30.82	−30.22	0.08	0.22	0.08
W. H. Green Key 2	1.45	38.94	0.17	−31.41	−30.12	0.04	0.23	0.08
W. W. A. Murphy no. 4	1.42	53.29	0.00	−29.25	–	–	–	–
William 2976 no. 7	1.48	39.19	0.10	−31.35	−29.54	0.04	0.22	0.08

Gammacerane/ hopane	Norhopane/ hopane	C_{35}/C_{34} ††	C_{33}/C_{32} ††	% C_{27} Sterane	% C_{28} Sterane	% C_{29} Sterane	C_{27} Diasterane/ C_{27} Sterane	C_{29} S/R ‡	C_{29} αββ/ (ααα + αββ) ‡‡	TAS ¶	Terpane/ Sterane
0.37	1.12	2.28	1.11	0.54	0.12	0.33	1.44	0.38	0.56	0.63	1.50
	–	–	–	–	–	–	–	–	–	–	
0.13	0.37	1.16	0.76	0.60	0.13	0.27	1.42	0.45	0.68	0.50	1.38
0.08	0.54	0.85	0.97	0.44	0.15	0.41	0.81	0.43	0.59	0.18	0.79
0.08	0.55	0.84	0.95	0.44	0.14	0.42	0.80	0.41	0.58	0.18	0.82
	–	–	–	–	–	–	–	–	–	–	
0.10	0.57	1.21	0.90	0.47	0.14	0.39	1.00	0.41	0.61	0.49	1.17
0.08	0.45	1.11	0.98	0.48	0.17	0.35	1.39	0.42	0.64	0.50	1.04
0.12	0.41	1.47	1.06	0.53	0.15	0.32	1.80	0.41	0.64	0.54	1.13
0.08	0.43	1.09	0.98	0.49	0.15	0.36	1.58	0.41	0.64	0.47	1.00
0.10	0.45	0.95	0.85	0.50	0.15	0.35	1.14	0.43	0.64	0.32	1.08
0.14	0.47	1.27	0.77	0.48	0.15	0.37	1.44	0.43	0.61	0.47	1.44
0.08	0.51	0.91	1.02	0.44	0.15	0.40	0.89	0.42	0.58	0.16	0.79
0.08	0.50	0.89	0.92	0.46	0.15	0.40	0.90	0.41	0.58	0.16	0.82
0.08	0.51	0.84	0.95	0.45	0.14	0.41	0.91	0.41	0.58	0.18	0.89
0.23	0.50	1.39	0.66	0.54	0.16	0.31	1.49	0.45	0.65	0.83	1.78
0.08	0.53	0.91	0.96	0.44	0.14	0.41	0.83	0.41	0.57	0.17	0.79
0.16	0.47	1.43	0.86	0.54	0.14	0.32	1.41	0.42	0.65	0.84	1.27
	–	–	–	–	–	–	–	–	–	–	
0.22	0.49	1.98	1.11	0.49	0.21	0.30	1.32	0.46	0.61	0.45	2.23
	–	–	–	–	–	–	–	–	–	–	
	–	–	–	–	–	–	–	–	–	–	
0.13	0.41	0.95	0.83	0.44	0.16	0.40	1.50	0.42	0.63	0.44	1.13
	–	–	–	–	–	–	–	–	–	–	
0.12	0.45	1.07	0.80	0.55	0.15	0.30	1.25	0.44	0.62	0.27	1.27
0.35	0.57	2.45	0.94	0.48	0.20	0.32	1.34	0.44	0.61	0.84	2.57
0.08	0.54	1.06	1.08	0.44	0.15	0.41	1.04	0.42	0.63	0.51	0.92
0.08	0.54	1.05	1.00	0.46	0.14	0.39	1.01	0.42	0.63	0.51	1.04
0.27	0.53	2.56	1.09	0.55	0.14	0.31	1.46	0.39	0.61	0.81	2.13
0.16	0.56	2.03	0.96	0.48	0.18	0.34	1.27	0.44	0.63	0.55	1.70
0.08	0.56	1.01	0.99	0.44	0.15	0.41	1.00	0.42	0.62	0.46	0.85
0.09	0.41	1.24	0.88	0.51	0.16	0.33	1.80	0.42	0.64	0.52	1.08
0.08	0.41	1.02	0.95	0.52	0.15	0.33	1.58	0.43	0.65	0.51	1.08
0.09	0.41	1.20	0.90	0.51	0.16	0.33	1.50	0.42	0.63	0.57	1.17
0.00	0.54	–	–	0.62	0.11	0.28	1.62	0.46	0.62	0.67	4.56
0.09	0.37	1.23	0.92	0.53	0.16	0.32	1.62	0.43	0.64	0.53	1.27
0.11	0.41	1.35	0.91	0.56	0.15	0.29	1.69	0.45	0.66	0.48	1.17
0.26	0.51	3.40	1.28	0.61	0.12	0.27	2.19	0.44	0.65	0.57	1.27
0.15	0.52	1.15	0.94	0.48	0.17	0.35	1.09	0.45	0.63	0.36	1.56
0.23	0.78	3.57	0.86	0.49	0.19	0.32	1.22	0.47	0.62	0.55	1.94
0.10	0.53	1.12	1.06	0.45	0.15	0.40	1.07	0.43	0.62	0.48	1.04
	–	–	–	–	–	–	–	–	–	–	
0.16	0.61	1.45	0.97	0.47	0.16	0.37	1.41	0.42	0.62	0.71	1.13

Table 1. Continued

Name	Pristane/ Phytane	API Gravity (°)	Weight% S*	Saturate $\delta^{13}C$ (‰)	Aromatic $\delta^{13}C$ (‰)	C_{19}/C_{23}**	C_{22}/C_{21}**	$C_{24}Tet/C_{23}$†
Williams 2976 no. 1	1.65	39.19	0.12	−31.07	−30.24	0.06	0.21	0.10
Windham 10 no. 1	1.44	61.23	0.00	−30.8	–	0.51	0.18	0.19
Windham 164 no. 1	1.72	41.86	0.13	−30.63	−30.08	0.05	0.21	0.10
Zorns no. 3W	–	55.04	0.00	−27.82	–	–	–	–

*Weight% S = wt.% sulfur.
**C_{19}/C_{23}, C_{22}/C_{21} = tricyclic terpane ratios.
†$C_{24}Tet/C_{23}$ = C_{24} tetracyclic terpane/C_{23} tricyclic terpane.
††C_{35}/C_{34}, C_{33}/C_{32} = hopane ratios.
‡C_{29} S/R = C_{29} sterane maturity ratio.
‡‡C_{29} $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ = C_{29} sterane maturity ratio.
¶TAS = triaromatic steroid ratio $[(C_{21} + C_{22})/\{C_{21} + C_{22} + (C_{26}-C_{28})\}]$.
¶¶TOC = total organic carbon.

(0.008 in.) × 0.50 μm 100% dimethylpolysiloxane capillary column is used to resolve both light hydrocarbons and the higher molecular weight hydrocarbons up to n-C_{44}; (2) a constant flow of hydrogen carrier gas is used during the entire gas chromatographic run; and (3) the injector temperature is 300°C, with oven programming at 35°C for 20 min, 8°C/min, to 300°C, 0.5–325°C, and held for 20 min. Components are detected by an FID held at 330°C. A blank run immediately follows all whole oil and whole extract analyses. Oil samples are shaken or mixed to insure sample homogeneity especially for waxy crude oils, then prepared for analysis by an weighing and the addition of internal standards consisting of 1-hexene (elutes just before n-C_6) and squalane (in between n-C_{26} and n-C_{27}). All weight percent values were determined from the 1-hexene standard. The amount of standard added is approximately 0.5 μL. The results are the weight percent of an integrated compound per whole oil weight. The peak response of the internal standard at its known weight percent is compared to identified peaks to quantify results in weight percent of oil.

Gas Chromatography–Mass Spectrometry

Biomarkers in Fort Worth Basin oils and condensates were analyzed using the maltene fraction (apshaltenes precipitated) on an HP 6890 GC connected to a JEOL GCMate double-focusing magnetic sector mass spectrometer. The GC was equipped with a ZB-1701 60-m (196-ft) (length) × 0.31-mm (0.01-in.)-internal-diameter fused silica column with 0.25 μm film thickness (bonded phase 14% cyanopropylphenyl, 86% dimethylpolysiloxane). The GC oven starting temperature was 50°C and was programmed to rise from 50 to 150°C at 5°C/min and then from 150 to 300°C at 3°C/min and held for 9 min at 300°C. The mass/charge (*m/z)* 191.1800, *m/z* 217.1956, *m/z* 253.1956, and *m/z* 231.1174 ions were monitored.

RESULTS

Natural-Gas Properties

Gas composition data are summarized in Table 2. The gases are dominantly methane, with gas wetness $[(\sum C_2-C_5/\sum C_1-C_5) \times 100]$ values ranging from 3 to 43% and nonhydrocarbon contents less than 7% for all but two samples that are 11 and 21%. Methane $\delta^{13}C$ values range from −41.1 to −47.8‰ethane $\delta^{13}C$ values range from −29.5 to −36.0‰and propane $\delta^{13}C$ values range from −26.9 to −31.7‰Gas maturity, expressed as equivalent vitrinite reflectance (R_o), ranges from approximately 0.7 to 1.2% R_o (Figure 3). Gases produced from the Barnett and a few samples from the Boonsville show the highest maturity. The one Caddo gas sample is slightly less mature than the Barnett gases, and the Strawn gases are less mature than the Barnett, the Caddo, and some of the Boonsville gases. The name Boonsville is of local usage in the Boonsville field and refers to gases produced from the Pennsylvanian Bend conglomerate. The Boonsville gases encompass the complete range of maturities observed. Gas wetness decreases as gas maturity increases (Prinzhofer et al., 2000) (Figure 4).

Gammacerane/ hopane	Norhopane/ hopane	C_{35}/C_{34}[††]	C_{33}/C_{32}[††]	% C_{27} Sterane	% C_{28} Sterane	% C_{29} Sterane	C_{27} Diasterane/ C_{27} Sterane	C_{29} S/R[‡]	C_{29} αββ/ (ααα + αββ)[‡‡]	TAS[¶]	Terpane/ Sterane
0.13	0.42	1.04	0.69	0.59	0.13	0.28	1.43	0.42	0.65	0.47	1.27
	–	–	–	–	–	–	–	–	–	1.00	
0.15	0.61	1.72	1.02	0.50	0.19	0.32	1.40	0.45	0.62	0.49	2.03
	–	–	–	–	–	–	–	–	–	–	–

Oil Bulk Properties

Oils were sampled from two areas within the Fort Worth Basin, the western Fort Worth and the Newark East areas (Figure 1). Analyses show the oils to be low sulfur (<0.10–0.40%) and of moderate to high API gravities (34–62°, Table 1; Figure 5). Sulfur content decreases as oil thermal maturity and API gravity increase. Saturated and aromatic hydrocarbon $\delta^{13}C$ values range from −32.1 to −30.0 and −31.2 to −28.0‰ respectively, and hydrocarbons become relatively enriched in ^{13}C as thermal maturity increases and mixing occurs (Figure 6).

High-Resolution Gas Chromatography

High-resolution, whole-oil GC was performed on all oils and on extracts from two outcrop samples and seven cuttings samples from two wells in Montague County. Pristane/phytane (Pr/Ph) ratios range from 1.25 to 2.01 and plot in the marine shale region of the Pr/Ph vs. sulfur diagram (Figure 7) (after Chung et al., 1992). In general, an increase in Pr/Ph ratio exists with an increase in thermal maturity. Jarvie et al. (2001) differentiated shale, carbonate, and kukersite organic facies by the analysis of C_7 light hydrocarbons. Our study further shows that terrigenous and carbonate oils plot in the same region of the branched + cyclic (B) versus n-C_7 (N) versus toluene + methylcyclohexane (A) NBA triangular plot (Figure 8a). When oils are plotted on the methylcyclohexane (M) versus toluene (T) versus n-C_7 (N) MTN triangular plot (Figure 8b), the terrigenous and carbonate oils are differentiated. The Fort Worth Basin oils plot in the shale and carbonate + terrigenous regions of the NBA plot, and mixtures are apparent (Figure 8). All but two of the samples that plot in the MTN terrigenous field were collected in the Newark East area. Mixtures of oils generated from terrigenous and shale sources were collected from both the Newark East and western Fort Worth Basin areas. Light hydrocarbon analysis was not performed on outcrop and cuttings samples.

The n-C_{19} peaks in the whole-oil GCs in our samples are larger than the adjacent n-C_{18} or n-C_{20} peaks, but are less pronounced or not observed in outcrop and cuttings samples. The enhanced n-C_{19} response is not observed in the saturated fraction GCs, but a partially resolved shoulder on n-C_{19} identified as the regular isoprenoid i-C_{21} is observed and is most likely the compound that coelutes with n-C_{19} in the whole-oil GCs.

Gas Chromatography–Mass Spectrometry

Biomarkers were analyzed by gas chromatography–mass spectrometry (GCMS) for 137 oil samples, 2 Barnett Shale outcrop samples, and 7 well-cuttings samples, and results for 74 oils are summarized in Table 1. The triaromatic steroid maturity parameter (TAS = $[C_{21} + C_{22}]/[\sum C_{21} - C_{28}]$; Mackenzie et al., 1981) was used to evaluate the thermal maturity of Fort Worth Basin oils. The $C_{21} + C_{22}$ triaromatic steroids are more stable than the higher molecular weight triaromatic compounds and, thus, increase in concentration relative to the higher molecular weight triaromatic compounds as thermal maturity increases. Only the samples with triaromatic steroid ratios less than 0.61 were used to interpret organic facies and source rock characteristics,

Table 2. Gas Composition from Fort Worth Basin Production Wells*

Well Identification	Formation	Field Name	N_2	O_2/Ar	CO_2	H_2S	Hydrogen	Methane
Caswell 1	Barnett Shale	Newark East	1.39	0.20	0.31	0.00	0.73	77.82
Cole Trust C 1	Barnett Shale	Newark East	0.98	0.15	2.68	0.00	0.00	93.05
Jerry North 1	Barnett Shale	Newark East	7.56	1.97	1.35	0.00	0.00	77.02
Peterson 1	Barnett Shale	Newark East	1.05	0.21	2.25	0.00	0.00	90.90
Beamon 2	Boonsville conglomerate	Morris	3.19	0.17	0.79	0.00	0.00	79.05
Beamon 3	Boonsville conglomerate	Boonsville	4.86	0.32	0.60	0.00	0.00	79.48
Casey 1	Boonsville conglomerate	Boonsville	2.47	0.16	0.61	0.00	0.00	78.86
Collins 3	Boonsville conglomerate	Boonsville	3.16	0.28	0.68	0.00	0.00	77.08
Craft TWB 2	Boonsville conglomerate	Cap Yates	2.56	0.48	0.78	0.00	0.00	54.14
Crawford 2	Boonsville conglomerate	Risch East	2.21	0.26	0.48	0.00	0.00	75.66
D. O. Lawson 3	Boonsville conglomerate	Boonsville	2.42	0.21	0.66	0.00	0.00	72.07
Della Christian WB 3	Boonsville conglomerate	Morris	2.73	0.30	0.54	0.00	0.00	69.41
E. L. Seagraves 3	Boonsville conglomerate	Risch East	1.27	0.17	0.34	0.00	0.00	65.05
E. L. Seagraves 4	Boonsville conglomerate	Boonsville	2.05	0.06	0.56	0.00	0.00	78.30
Glenn George 2	Boonsville conglomerate	Morris	2.73	0.40	0.69	0.00	0.00	67.32
Glenn George 3	Boonsville conglomerate	Boonsville	2.21	0.08	0.71	0.00	0.00	74.41
Grace 1	Boonsville conglomerate	Weiler	2.85	0.18	0.51	0.00	0.00	77.74
Hatchel 2	Boonsville conglomerate	Boonsville	2.13	0.17	1.01	0.00	0.00	67.43
J. D. Parr 2	Boonsville conglomerate	Morris	1.79	0.00	0.65	0.00	0.00	78.97
McConnell 2A	Boonsville conglomerate	McConnell	2.37	0.25	0.57	0.00	0.00	66.88
McConnell 6	Boonsville conglomerate	Morris	16.41	4.39	0.65	0.00	0.00	52.38
Mildred A. Durham 14	Boonsville conglomerate	Boonsville	2.35	0.14	0.64	0.00	0.00	69.88
North 2	Boonsville conglomerate	Newark East	0.80	0.08	1.47	0.00	0.00	82.75
Perkins 1	Boonsville conglomerate	Boonsville	2.34	0.31	0.65	0.00	0.00	66.86
Raney 6	Boonsville conglomerate	Boonsville	3.34	0.26	0.75	0.00	0.00	77.77
Scott 1	Boonsville conglomerate	Boonsville	2.27	0.04	0.69	0.00	0.00	75.48
T. G. Rogers 2	Boonsville conglomerate	Boonsville	4.92	0.73	0.31	0.00	0.16	76.62
T. H. Zorns 3W	Boonsville conglomerate	Newark East	1.72	0.35	1.25	0.00	0.00	79.51
Tarrant County Waterboard unit 1 no. 3	Boonsville conglomerate	Cap Yates	2.72	0.20	0.56	0.00	0.00	71.05
Tarrant County Waterboard unit 6 no. 4	Boonsville conglomerate	Cap Yates	2.39	0.27	0.62	0.00	0.00	69.77
W. W. A. Murphy 4	Boonsville conglomerate	Boonsville	1.85	0.15	0.87	0.00	0.00	78.40
Bogy A 2	Caddo	Morris	4.84	0.33	0.36	0.00	0.00	79.16
A. D. Huff 1	Strawn	Kenkirk	4.89	0.17	0.30	0.00	0.00	81.34
Aaron Hull 3	Strawn	Jack County regular	6.01	0.38	0.43	0.00	0.00	77.17

*In mole percent.
**Wetness = sum (ethane – pentane)/sum (methane – pentane).

because at higher maturities (TAS > 0.61), the pentacyclic terpanes show evidence of thermal degradation (Table 1; Figure 9). From the *m/z* 191 chromatogram, the C_{19}/C_{23} tricyclic, C_{24} tetracyclic/C_{23} tricyclic, C_{22}/C_{21} tricyclic, norhopane/hopane, C_{33}/C_{32} and C_{35}/C_{34} hopane, and gammacerane/C_{31} hopane ratios were evaluated to assess organic matter type, source rock facies, redox conditions, and salinity during source rock deposition. Sterane distributions and diasterane ratios (diasterane/sterane) were evaluated from the *m/z* 217 and 218 chromatograms to assess source rock facies and organic matter type. The triaromatic steroid ratio was measured

Ethane	Propane	n-Butane	i-Butane	n-Pentane	i-Pentane	Neopentane	Wetness**	i-Butane/ n-Butane	Methane $\delta^{13}C$ (‰)	Ethane $\delta^{13}C$ (‰)	Propane $\delta^{13}C$ (‰)
11.34	4.96	1.56	0.92	0.29	0.37	0.00	20.30	0.59	−47.59	−32.71	−29.19
2.56	0.02	0.25	0.26	0.02	0.03	0.00	3.17	1.04	−41.13	−32.7	–
7.77	2.20	0.86	0.70	0.20	0.23	0.00	13.52	0.81	−44.18	−29.52	–
4.40	0.42	0.32	0.34	0.04	0.05	0.00	5.75	1.06	−41.82	−29.63	–
7.53	5.39	1.83	0.95	0.42	0.39	0.00	17.28	0.52	−46.61	−33.54	−31.01
6.63	4.76	1.65	0.85	0.33	0.33	0.00	15.60	0.52	−46.93	−33.42	−30.87
8.36	5.13	2.16	1.21	0.38	0.41	0.02	18.38	0.56	−45.99	−33.11	−29.8
8.79	5.67	2.00	1.08	0.46	0.49	0.02	19.53	0.54	−45.73	−32.71	−30.23
15.50	15.43	4.77	2.52	1.54	1.38	0.04	43.48	0.53	−45.69	−34.55	−30.03
9.16	7.06	2.58	1.24	0.58	0.52	0.00	21.95	0.48	−46.13	−34.77	−31.73
11.46	7.61	2.56	1.49	0.53	0.61	0.03	25.49	0.58	−46.77	−32.89	−27.91
11.14	9.26	3.04	1.55	0.79	0.73	0.02	27.78	0.51	−47.61	−34.51	−30.17
16.11	10.85	2.93	1.72	0.60	0.62	0.03	34.04	0.59	−45.03	−33.97	−29.88
9.33	5.44	2.18	1.12	0.37	0.37	0.00	19.75	0.51	−45.27	−34.23	−29.99
12.28	9.42	3.35	1.54	0.83	0.80	0.02	29.90	0.46	−47.2	−33.46	−29.55
9.90	7.10	2.67	1.17	0.65	0.60	0.02	23.25	0.44	−47.13	−33.84	−29.49
8.88	5.52	2.23	1.06	0.41	0.36	0.00	19.45	0.48	−46.93	−36.02	−31.13
10.69	8.62	4.15	1.83	1.36	1.33	0.04	29.55	0.44	−46.62	−32.99	−29.52
8.48	5.33	2.36	1.25	0.46	0.51	0.02	19.12	0.53	−46.51	−33.08	−30.74
11.65	10.79	3.45	1.77	0.90	0.81	0.02	30.72	0.51	−46.97	−35.55	−31
11.04	9.26	2.87	1.49	0.61	0.57	0.02	33.60	0.52	−46.31	−34.74	−30.38
10.59	9.59	3.13	1.58	0.82	0.74	0.02	27.81	0.50	−46.14	−34.97	−30.68
9.51	2.92	1.01	0.79	0.23	0.27	0.02	15.52	0.78	−44.35	−30.54	−26.89
13.52	9.89	2.99	1.57	0.71	0.66	0.00	30.73	0.53	−47.79	–	–
7.77	5.82	2.14	1.00	0.46	0.46	0.00	18.76	0.47	−47.26	−32.9	−30.23
9.54	6.88	2.38	1.10	0.56	0.51	0.02	22.11	0.46	−47.33	−33.79	−29.54
7.48	5.14	2.03	1.01	0.58	0.55	0.00	18.17	0.50	−46.76	−32.77	−29.24
10.64	3.21	1.79	0.96	0.22	0.24	0.00	18.01	0.54	−46.18	−32.52	−27.97
10.42	9.03	2.89	1.50	0.64	0.60	0.00	26.35	0.52	−46.95	−34.58	−30.36
11.10	9.38	2.98	1.65	0.71	0.68	0.02	28.13	0.55	−45.91	−34.32	−29.03
9.45	4.63	2.15	1.18	0.44	0.47	0.03	19.10	0.55	−44.84	−33.09	−28.57
7.14	4.43	2.00	1.02	0.28	0.28	0.00	16.18	0.51	−45.72	−33.01	−30.31
5.50	4.14	2.06	1.02	0.22	0.25	0.00	14.01	0.50	−47.26	−33.79	−31.26
5.39	5.37	2.48	1.39	0.53	0.53	0.02	17.02	0.56	−47.39	−34.23	−30.9

from the *m/z* 231 fragmentogram and used to evaluate thermal maturity.

The C_{19}/C_{23} tricyclic terpane ratio is low for Fort Worth Basin oils, outcrop, and cuttings samples (0.01–0.39; Figure 10). Cuttings samples show values as high as 0.50. The C_{24} tetracyclic/C_{23} tricyclic ratio ranges from 0.02 to 0.63 for the highest maturity oil samples, and outcrop and cuttings samples range from 0.07 to 0.38 (Figure 10). The C_{22}/C_{21} tricyclic terpane ratio values are between 0.30 and 0.81 for oils and 0.31 and 0.57 for outcrop and cuttings samples. The pentacyclic terpanes are also used to interpret source rock

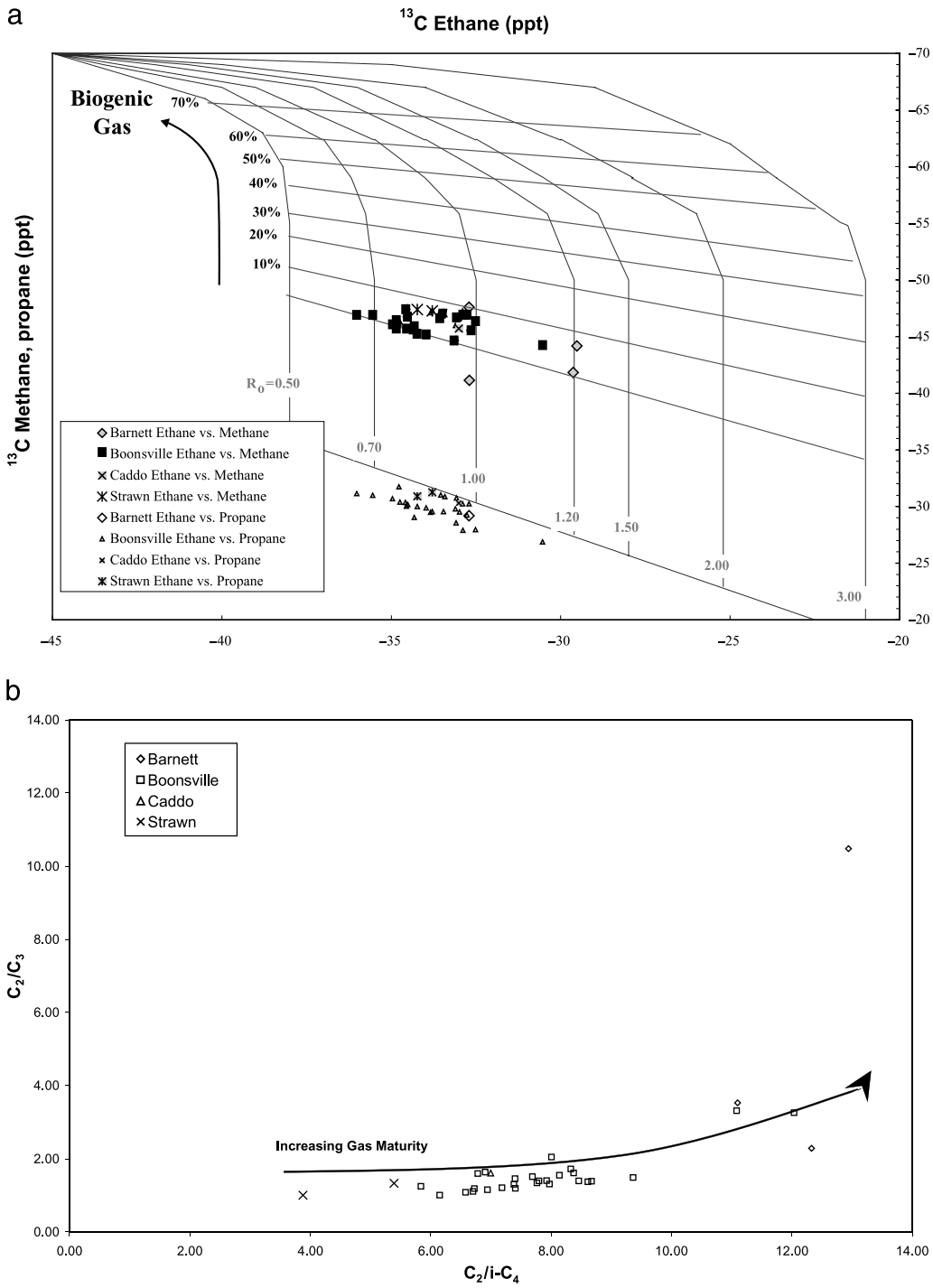


Figure 3. (a) $\delta^{13}C$ ethane versus $\delta^{13}C$ methane and $\delta^{13}C$ propane for estimating gas maturity and biogenic gas content. Gas maturity is expressed as equivalent vitrinite reflectance. Fort Worth Basin gases were cogenerated with oil and contain little or no biogenic gas (M. Schoell, 2002, personal communication). (b) C_2/i-C_4 versus C_2/C_3 compositional plot demonstrating that Barnett gases are highest maturity (modified from Prinzhofer et al., 2000).

facies, redox conditions, and salinity during source rock deposition. The oil C_{29} norhopane/hopane ratio ranges from 0.31 to 0.72 and the C_{31}R/hopane ratio ranges from 0.21 to 0.50 (Figure 11). The C_{35}/C_{34} hopane and C_{33}/C_{32} hopane ratios increase as thermal maturity increases, with values exceeding 1.42 at highest maturities for C_{35}/C_{34} and 1.54 for C_{33}/C_{32} (Figure 11). Outcrop and cuttings samples show the C_{35}/C_{34} ratio from 0.46 to 0.76 and the C_{33}/C_{32} hopane ratio from 0.50 to 0.74. Gammacerane/hopane ratio is less than 0.10 for samples for low-maturity samples (TAS < 0) and increases to nearly 2.49 at higher maturities. Outcrop and cuttings samples range from 0.02 to 0.09 (Table 1).

The sterane/hopane ratio for Fort Worth Basin oils ranges from 0.38 to 2.12 for oils and is less than 0.74 for

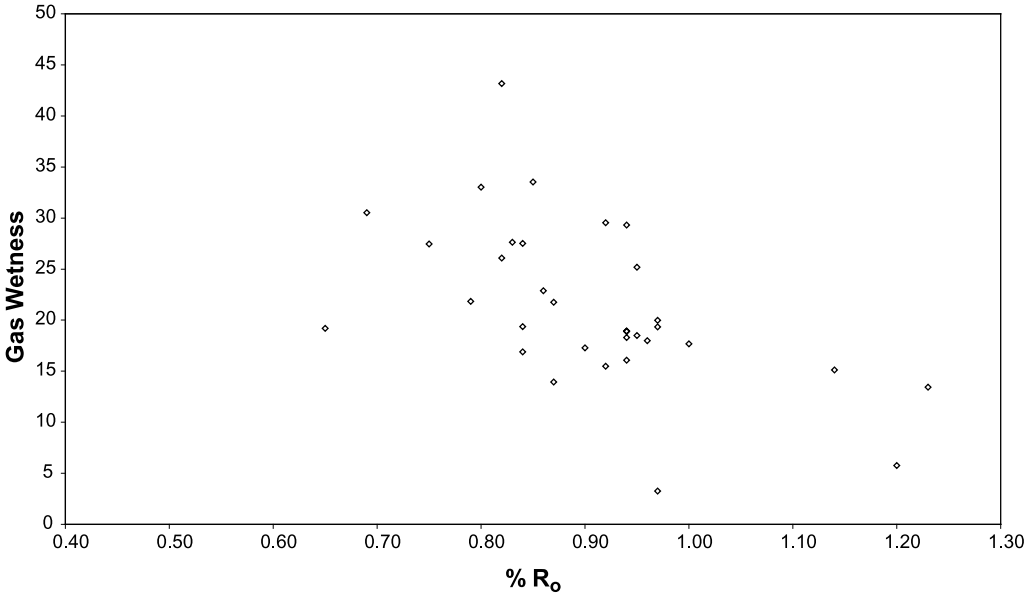


Figure 4. Gas wetness ($\sum C_2-C_5/\sum C_1-C_5$) versus gas maturity expressed as equivalent % R_o from Figure 3. Gas wetness decreases as gas maturity increases.

all outcrop and cuttings samples analyzed (Figure 12). The variation in sterane/hopane ratios with increases in thermal maturity is small. A slight predominance exists in C_{29} relative to C_{27} steranes for the lower maturity oil samples, with C_{29} predominance persisting as thermal maturity increases (Figure 13). The diasterane/regular sterane ratio ranges from 0.78 to 9.59 for oils (Figure 14). Outcrop and cuttings samples range from 0.65 to 3.35.

DISCUSSION

The Barnett Shale is the primary source rock for oils and gases in the Fort Worth Basin, based on isotopic, biomarker and light hydrocarbon geochemical analysis, thermal-maturity trends, and the areal extent of the formation (Henry, 1982; Jarvie et al., 2001). In our study, detailed geochemical analyses were performed, oil-source rock correlation was confirmed, and the characteristics of

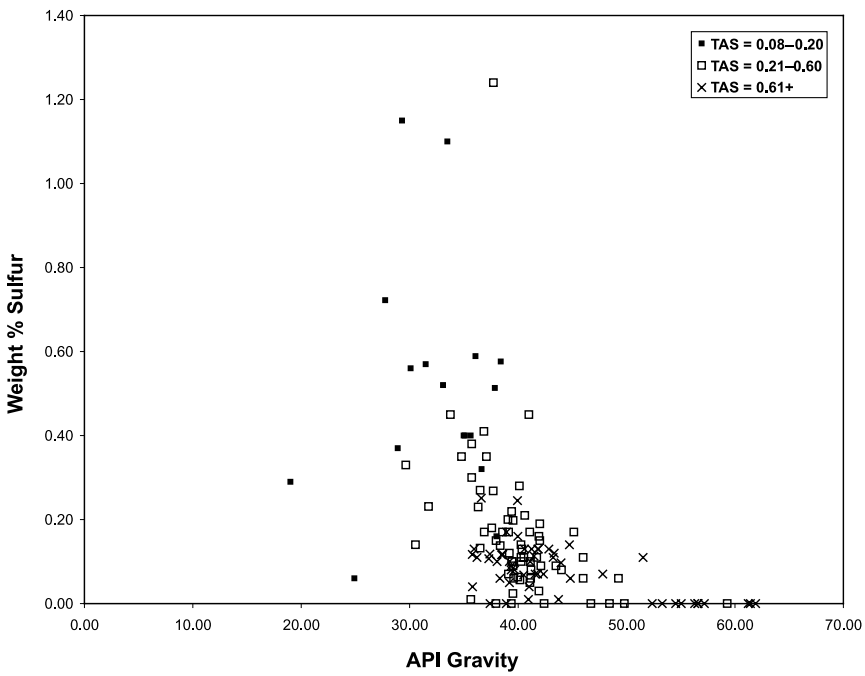


Figure 5. Oil API gravity versus weight percent sulfur with oil thermal maturity annotated showing sulfur content decreases as API gravity and thermal maturity increase. TAS = triaromatic steroid ratio.

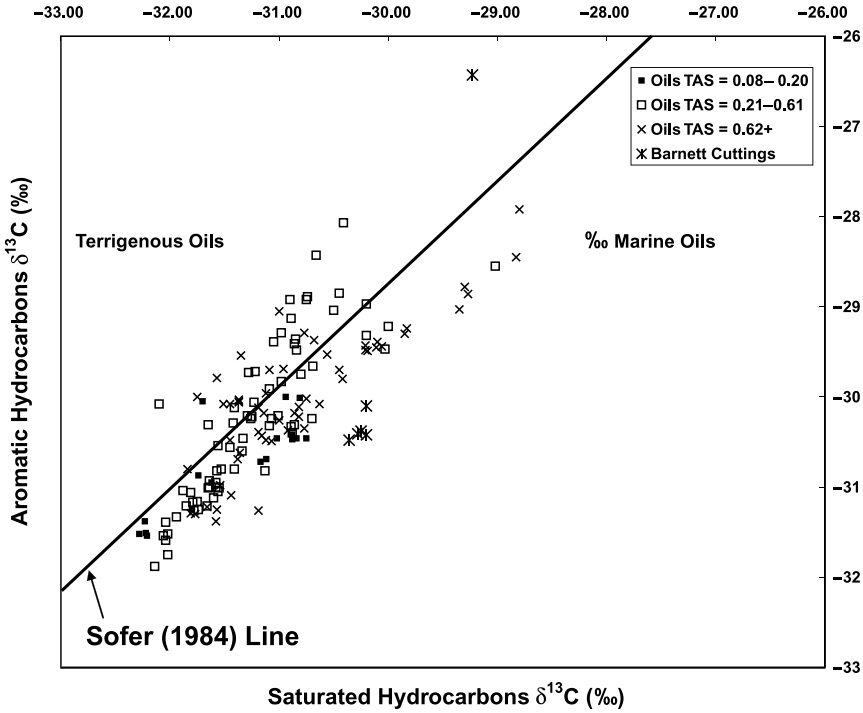


Figure 6. Saturated vs. aromatic hydrocarbon $\delta^{13}C$ shows ^{13}C enrichment with increased thermal maturity. Cuttings and oil samples show similar stable carbon isotopic values. Sofer (1984) line is shown for reference.

the Barnett facies that generated the oils were inferred from oil analysis. Because the range of thermal maturities observed for the oils is great, interpretation of source rock characteristics from oil biomarkers was attempted only for samples (TAS < 0.61) that do not show overwhelming effects from thermal degradation. Samples with TAS values above 0.61 show thermal degradation of the hopanes, and at higher maturities, the steranes are also affected. The effect of thermal alteration on oil API gravity, sulfur (Figure 5) (Baskin and Peters, 1991), saturated and aromatic hydrocarbon $\delta^{13}C$ (e.g., Figure 6) (Sofer, 1984; Hughes et al., 1985), and biomarker

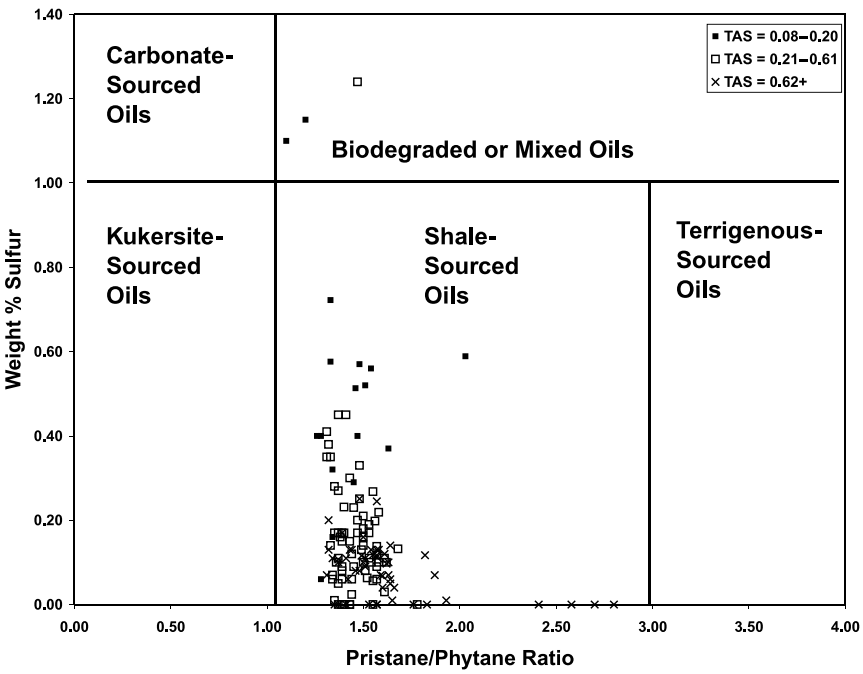


Figure 7. Pristane/phytane ratio versus weight percent sulfur shows that Fort Worth Basin oils plot in the marine shale source region (modified from Chung et al., 1992). TAS = triaromatic steroid ratio.

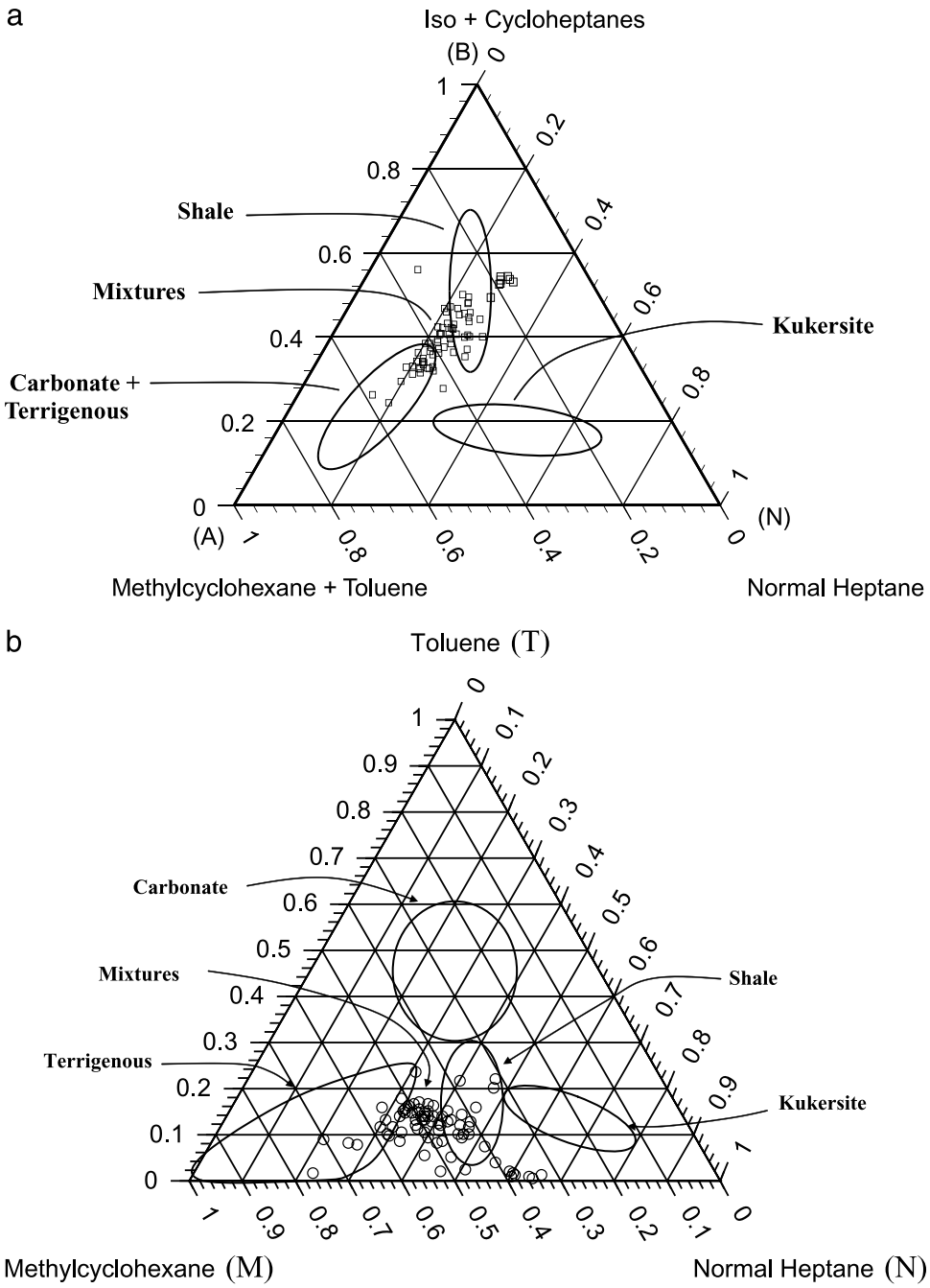


Figure 8. (a) n-C_7/branched + cyclic/toluene + methylcyclohexane (NBA) C_7 light hydrocarbon triangular plot showing shale, kukersite, and carbonate + terrigenous facies after Jarvie et al. (2002) and Fort Worth Basin oils showing association with the shale and carbonate + terrigenous light hydrocarbon facies with mixtures also apparent. (b) Methylcyclohexane/toluene/n-C_7 (MTN) plot that differentiates carbonate and terrigenous facies and shows that Fort Worth Basin oils plot in the shale and terrigenous fields with mixtures also apparent, but not in the carbonate field.

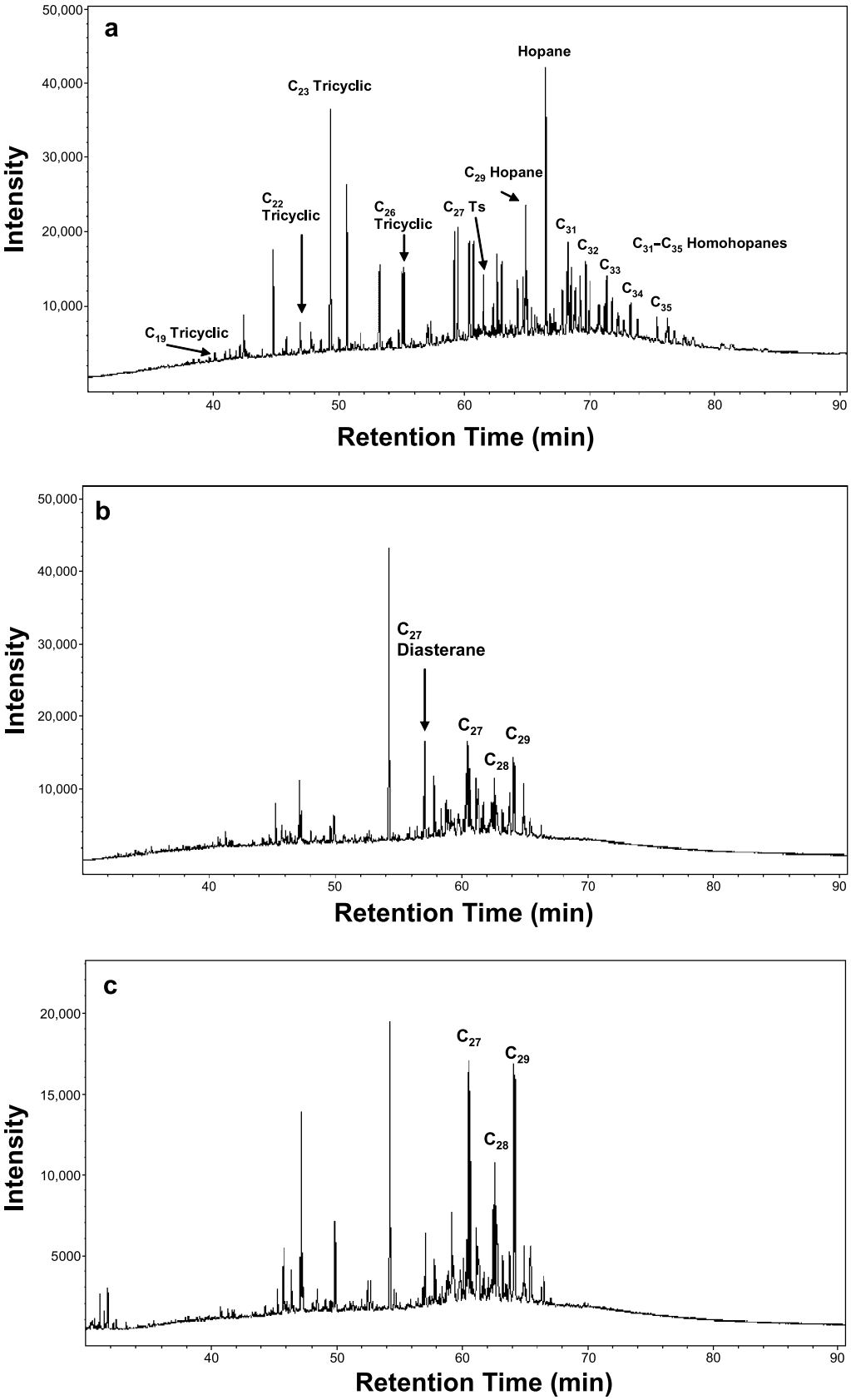
parameters (Seifert and Moldowan, 1978; Mackenzie, 1984; Rullkötter et al., 1984; Curiale, 1986, 1992; Sakata et al., 1988; Peters et al., 1990; Peters and Moldowan, 1991, 1993; Peters, 2000) has been discussed elsewhere.

Source Facies and Organic Matter Type from Oils

Mello et al. (1988a, b) and Peters and Moldowan (1993) summarized some characteristic of marine- and nonmarine-sourced oils. Geochemical evidence indicates that oils and condensates from the Fort Worth Basin originated from a shale source rock containing type II organic matter deposited under normal-marine salinities and dysoxic conditions. The principal lines of evidence supporting conclusions about the origin of the organic matter are summarized below.

Pr/Ph ratio and sulfur content have been used as an indicator of organic matter type, with Pr/Ph < 1 indicating type I, II, or II-S organic matter deposited in an anoxic environment, Pr/Ph 1–3 indicating type II

Figure 9. (a) Oil *m/z* 191 GCMS trace demonstrating tricyclic terpane and hopane distribution typical for petroleum derived from a marine organic matter source. (b) Oil *m/z* 217 trace demonstrating sterane distribution typical for petroleum derived from a Paleozoic marine source. (c) Oil *m/z* 218 GCMS trace demonstrating αββ sterane distribution. (d) Barnett Shale cuttings extract *m/z* 191 GCMS trace demonstrating tricyclic terpane and hopane distribution typical for petroleum derived from a marine organic matter source. Note the similarity to oil *m/z* 191 trace. (e) Barnett Shale cuttings extract *m/z* 217 trace demonstrating sterane distribution typical for petroleum derived from a Paleozoic marine source. Note the similarity to oil *m/z* 217 trace. (f) Barnett Shale cuttings *m/z* 218 GCMS trace demonstrating αββ sterane distribution similar to what is observed for oils.



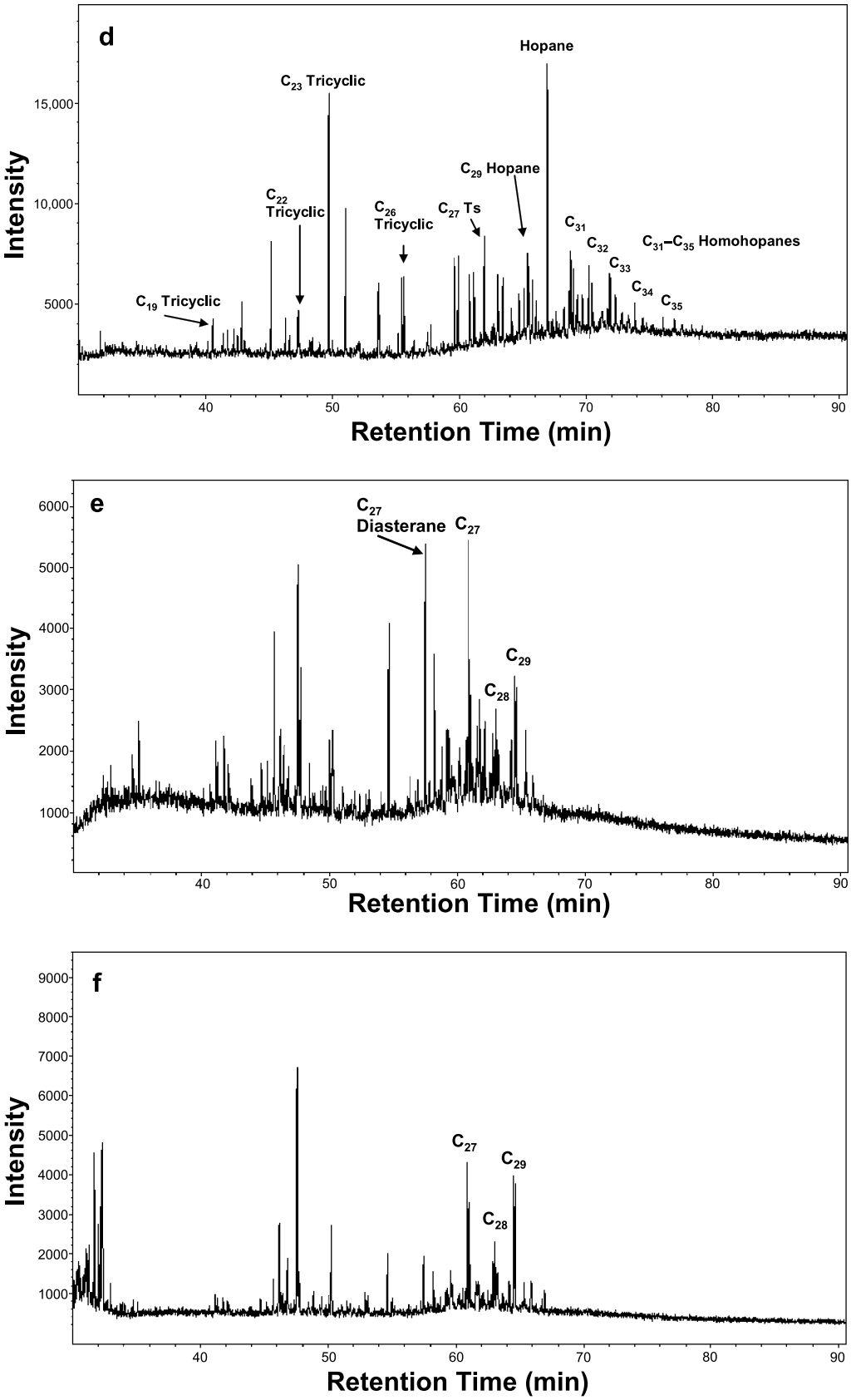


Figure 9. Continued.

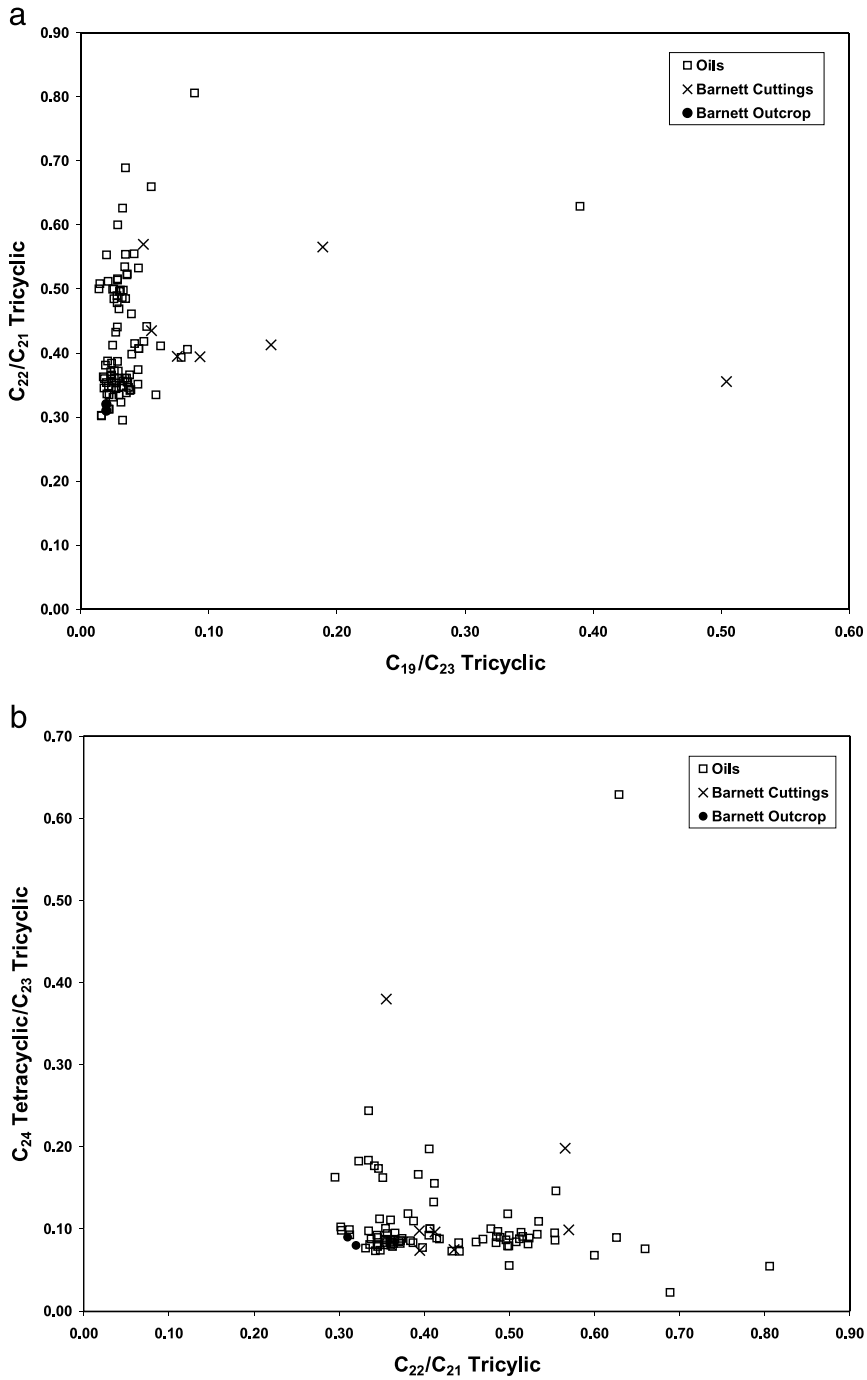


Figure 10. (a) Tricyclic terpane C_{19}/C_{23} versus C_{22}/C_{21} plot showing correlation of Fort Worth Basin oils to Barnett Shale outcrop and cuttings extracts. Data are typical for petroleum generated from marine shale source. (b) Tricyclic terpane C_{22}/C_{21} versus C_{24} tetracyclic/C_{23} tricyclic plot showing correlation of Fort Worth Basin oils to Barnett Shale outcrop and cuttings extracts. Tricyclic terpane data from cuttings demonstrate there is variation in Barnett Shale organic facies. Plots include oils with TAS < 0.61 (n = 97).

organic matter, and Pr/Ph > 3 indicating type III organic matter (Volkman and Maxwell, 1986). Fort Worth Basin oils show Pr/Ph ratios between 1 and 2. Marine shales generate low-sulfur oils (<1%), and carbonate oils have sulfur contents of 1% or more, although biodegradation can result in elevated sulfur content (Mello et al., 1988a, b). The sulfur content of Fort Worth Basin oils is less than 0.5% (Figure 7).

The hopane/sterane ratio for source rocks containing marine organic matter is generally less than 3, whereas rocks containing terrigenous organic matter show values between approximately 5 and 30 (Moldowan et al., 1985; Mello et al., 1988a, b; Isaksen, 1991). Hopanes originate from prokaryotic organisms (mainly bacteria) and are more abundant in nonmarine environments or where bacterial reworking of organic matter is significant. Steranes originate from eukaryotic organisms (mainly algae and higher plants). The sterane/hopane ratio used in this study is generally less than 3.5 for marine oils. In the Fort Worth Basin oils, the

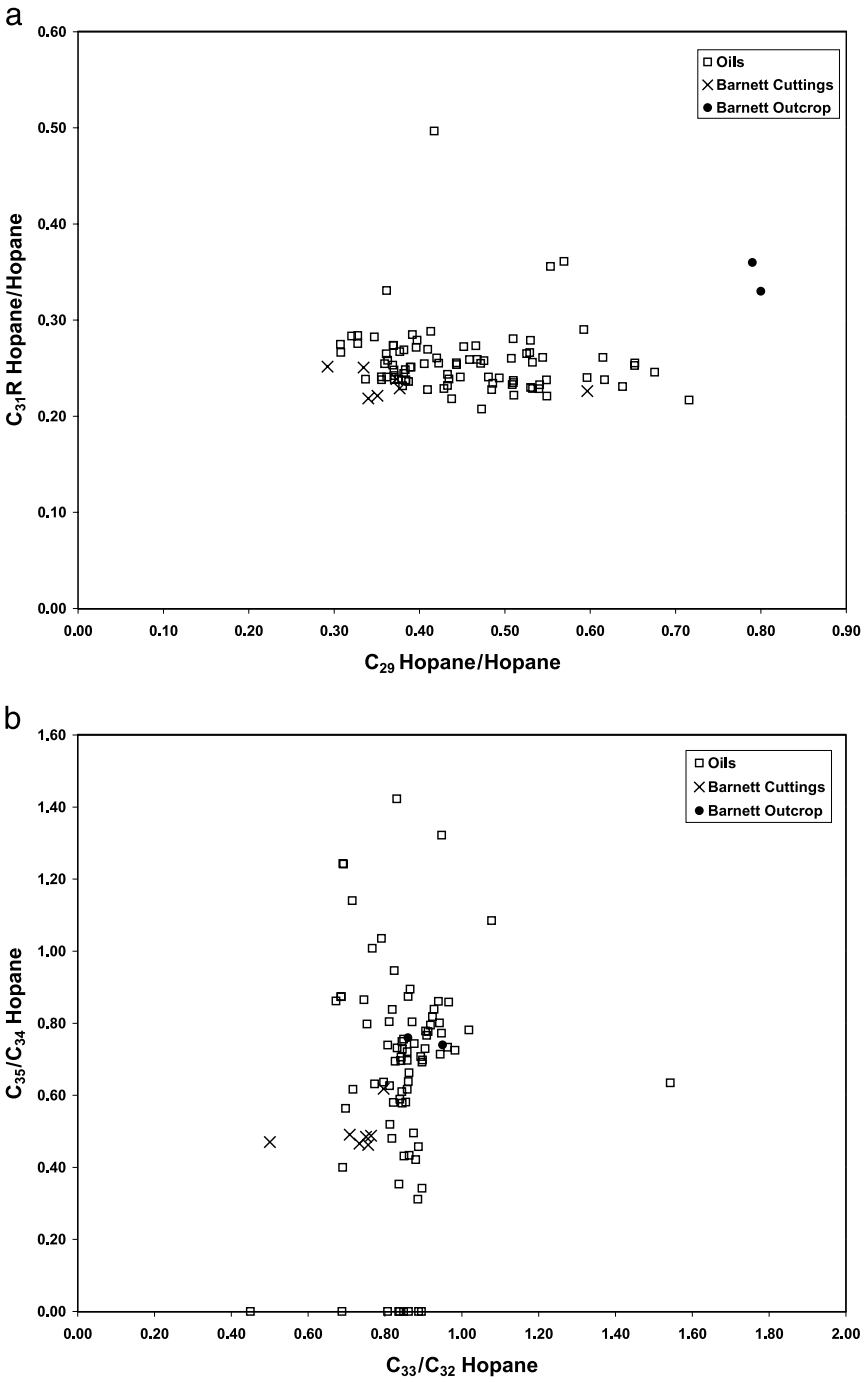
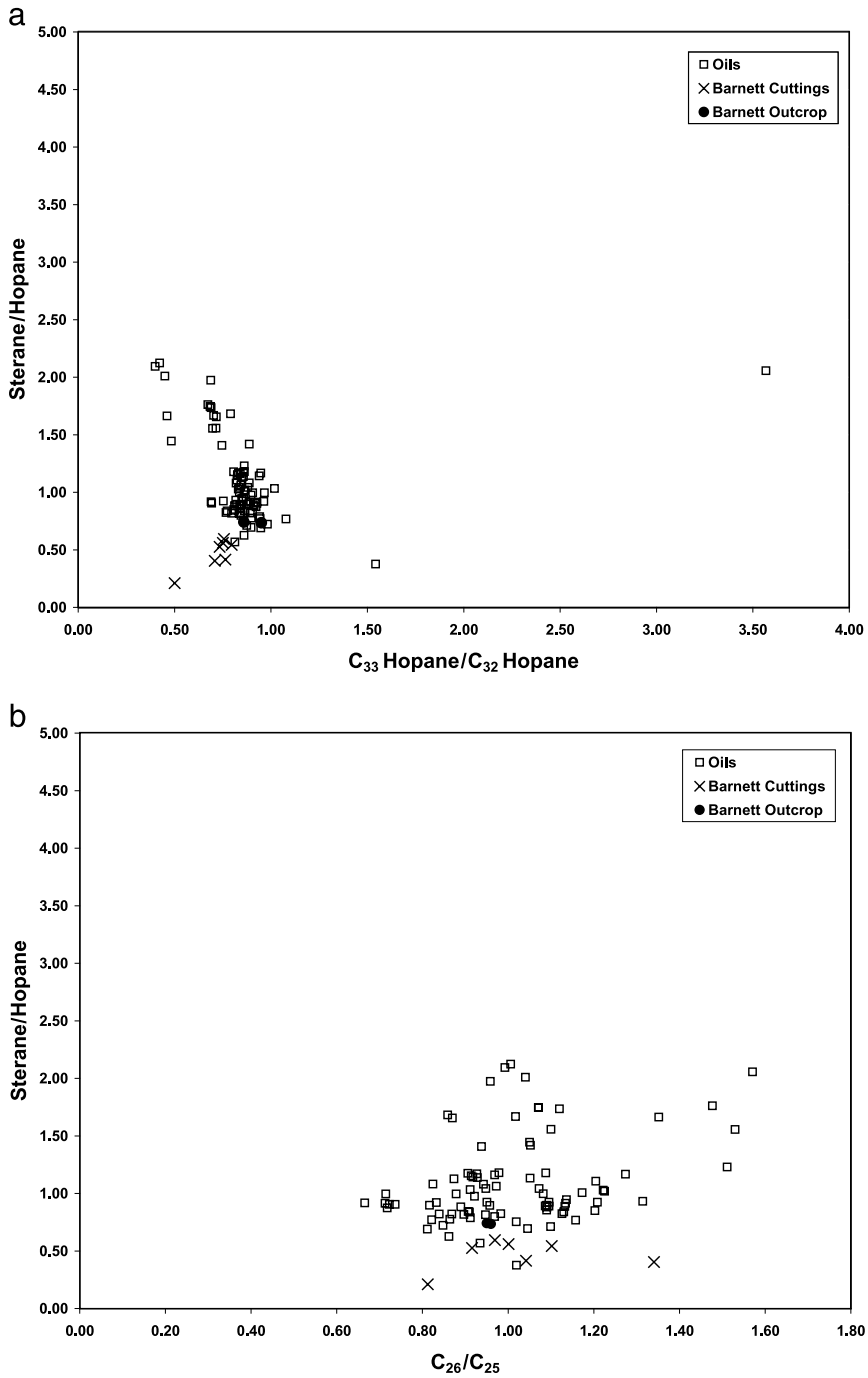


Figure 11. (a) Hopane C_{29}/hopane versus C_{31}R/hopane ratio demonstrating correlation between Fort Worth Basin oils and Barnett outcrop and cuttings extracts. This data range is typical for oils generated from a marine shale source. (b) Hopane C_{33}/C_{32} versus C_{35}/C_{34} demonstrating correlation between Fort Worth Basin oils and Barnett outcrop and cuttings extracts. Plots include oils with TAS < 0.61 (n = 97).

sterane/hopane ratio is less than 2.5, suggesting a marine origin (Figure 12).

The steranes are valuable as indicators of organic matter type in source rocks (see Peters and Moldowan, 1993). Huang and Meinshein (1979) observed that C_{27} sterols predominate in marine organic matter, whereas C_{29} sterols predominate in terrigenous organic matter. Mackenzie et al. (1983) and Moldowan et al. (1985) demonstrated that sterane distributions in oils correlate with those in their source rocks, and this is observed for oils from the Fort Worth Basin (Figure 13). However, as Volkman (1986) stressed, significant overlap exists in the sterane distributions of oil from marine and nonmarine shales. Furthermore, Moldowan et al. (1985) and Grantham (1986) showed that C_{29} steranes predominate in Paleozoic marine source rocks. For oils of the Fort Worth Basin (TAS < 0.61), C_{29} regular steranes predominate, indicating that marine organic matter is an important contributor for these oils derived from a Paleozoic source rock (Moldowan et al., 1985; Grantham, 1986).

Figure 12. (a) Hopane C_{33}/C_{32} versus sterane/terpane ratio demonstrating correlation between Fort Worth Basin oils and Barnett outcrop and cuttings extracts. (b) Tricyclic C_{26}/C_{25} terpane ratio versus sterane/terpane ratio demonstrating correlation between Fort Worth Basin oils and Barnett outcrop and cuttings extracts.



Oils generated from marine organic matter have low C_{19}/C_{23} tricyclic terpane ratios; in contrast, oils generated from mainly terrigenous sources have ratios of about 1 or greater. The C_{19} and C_{20} tricyclic diterpanes appear to be derived predominantly from higher plants, with C_{19} as the predominant compound (Reed, 1977; Simoneit, 1977; Alberdi et al., 2001), and the extended tricyclic terpanes appear to have bacterial and algal sources (Ourisson et al., 1982; Moldowan et al., 1983; Zumberge, 1983; Aquino Neto et al., 1983). The C_{19}/C_{23} ratios for Fort Worth Basin oils thus suggest limited terrigenous input (Figure 10).

Redox conditions during source rock deposition were evaluated using the Pr/Ph ratio (Didyk et al., 1978) and the homohopane distribution (Peters and Moldowan, 1991), with salinity conditions being derived from gammacerane content (Moldowan et al., 1985; Fu Jiamo et al., 1986). The combined Pr/Ph ratios (>1) and the C_{35}/C_{34} and C_{33}/C_{32} homohopane ratios (approaching 1) are interpreted to indicate that the source rock

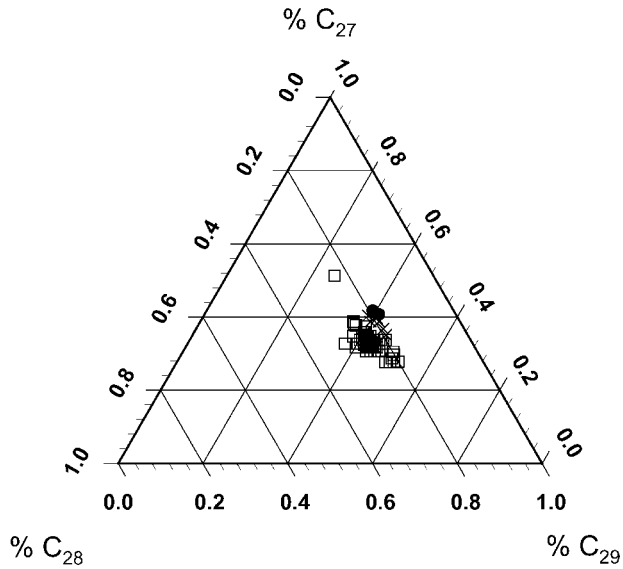


Figure 13. Weight percent C_{27}, C_{28}, and C_{29} steranes showing correlation between Fort Worth Basin oils and Barnett Shale outcrop and cuttings. The C_{29} sterane predominance for oils, outcrop, and cuttings samples is typical for marine-derived Paleozoic oils.

for oils in the Fort Worth Basin was deposited in oxic to dysoxic conditions (Figures 7, 11) (Moldowan et al., 1992; Peters and Moldowan, 1993). The low gammacerane/hopane ratios for Fort Worth Basin oils (Table 1) are typical of source rocks deposited under normal salinity conditions, whereas large amounts of gammacerane in petroleum indicate saline and highly reducing depositional conditions (Moldowan et al., 1985; Fu Jiamo et al., 1986). Biomarker data (C_{26} S + R/C_{27} Ts) also indicate that strong upwelling conditions contributed to high primary productivity in the Fort Worth Basin, perhaps resulting in high-TOC Barnett Formation shales (Holba et al., 2003) (Figure 9). Upwelling conditions are also indicated by the presence of phosphate minerals in the Barnett Shale (Hickey and Henk, 2007; Loucks and Ruppel, 2007). A source rock containing marine organic matter deposited under upwelling, normal salinity, and dysoxic environmental conditions is consistent with what is known about the regional setting for the Barnett Shale.

Although the biomarker data support a dysoxic marine shale source, the stable carbon isotope data and light hydrocarbon data suggest that some of the petroleum in the Fort Worth Basin was generated from terrigenous organic matter (Figures 6, 8). All oil samples showing a mixed shale plus terrigenous or terrigenous light hydrocarbon signature are interpreted to be mixtures of Barnett Shale–derived oil with condensate from a postulated terrigenous organic matter-dominated facies of the Barnett Shale or other source rock within the Fort Worth Basin. This is based on previous work that demonstrated that light hydrocarbons could be used to differentiate marine shale, marine carbonate, and Ordovician kukersite-sourced oils in the Williston Basin (Jarvie et al., 2001, 2002) and the work of this study that demonstrated that Tertiary terrigenous-sourced oils could be differentiated from these oils using light hydrocarbons (Figure 8). The results of this study suggest that Jarvie et al. (2001) are differentiating organic matter type, which is controlled in part by source rock lithology instead of strictly source rock lithology. In as much as a terrigenous source is indicated only by the presence of light hydrocarbons, we suggest that there is shale facies within the Barnett or another source unit in the basin containing dominantly terrigenous kerogen that contributed condensates, but no higher molecular weight hydrocarbons that might alter the marine-shale biomarker signature. This assumes that the light hydrocarbon signature from Paleozoic terrigenous kerogen is similar to that of Tertiary terrigenous kerogen. An alternative explanation is that a particular facies within the formation contains both marine and terrigenous organic matter that imparts a mixed light hydrocarbon signature, or that increased thermal maturity results in changes in light hydrocarbon distribution. Jarvie et al. (2002) demonstrated the utility of integrating light hydrocarbon and biomarker analyses to identify mixtures of shale- and carbonate-sourced oils when only one of the oils is the contributing biomarker to the mixture. All but two oils indicating the presence of terrigenous-sourced light hydrocarbons are from the Newark East area, where thermal maturity is higher than in the western area of the basin (Pollastro et al., 2003).

Peters et al. (1986) showed that only 66% of oils from a suite of marine and nonmarine crude oils were correctly separated using stable carbon isotopes, but that 100% of the oils could be correctly distinguished statistically when biomarkers were combined with stable carbon isotopes. This demonstrates that although stable carbon isotopes are useful, they should not be used alone to interpret organic matter type and would provide misleading results if used exclusively in this study. The biomarker and light hydrocarbon evidence for the oils analyzed in this study suggest that any terrigenous-sourced petroleum occurs as condensate.

Source Rock Lithology

Source rock lithology can be interpreted from the distribution of terpanes and steranes in oils. For Fort Worth Basin oils, the C_{22}/C_{21} tricyclic ratios for the Fort Worth

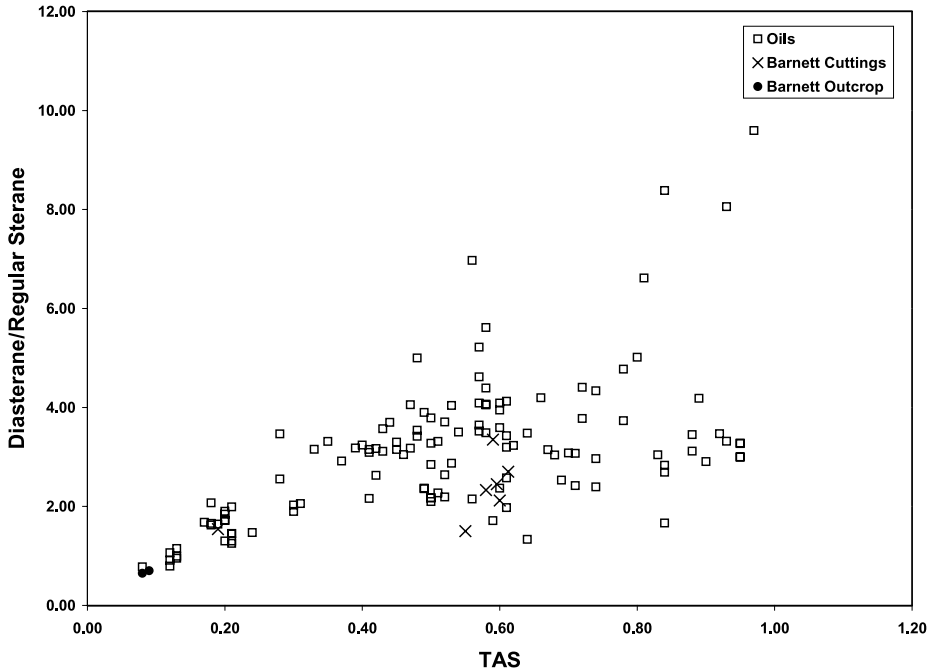


Figure 14. Correlation of diasterane/sterane ratio for Barnett outcrop and oil samples is good for oils with triaromatic steroid ratio less than 0.61. Diasterane/sterane ratio increases as oil thermal maturity increases.

Basin oils (<0.25) are typical of oils being generated by a shale source rock (Figure 10). In comparison, data published by Zumberge (1984) and Palacas et al. (1984) and summarized in Peters et al. (2005) indicate that the C_{22}/C_{21} tricyclic ratio for carbonate source rocks is 0.5 or greater. Additionally, a marine shale source is indicated by the norhopane/hopane ratios (Figure 11), which are characteristic of shales, but not of carbonate- and evaporite-sourced oils (Zumberge, 1984; Connan et al., 1986; Clark and Philp, 1987; Fan Pu et al., 1987; ten Haven et al., 1988; Peters and Moldowan, 1993).

The oils in the Fort Worth Basin contain significant amounts of diasteranes (Figure 14), which appear to form through the interaction of sterenes with clay mineral surfaces in source rocks (Rubinstein et al., 1975; Sieskind et al., 1979). Thus, the presence of significant amounts of diasteranes relative to regular steranes in oils has been used as evidence for petroleum generation from an argillaceous source rock, whereas low concentrations are considered to indicate a source rock lacking clay minerals (Hughes, 1984; Mello et al., 1988a, b). The increase in the diasterane/sterane ratio with an increase in thermal maturity is consistent with previous studies (Seifert and Moldowan, 1978).

Correlation with the Barnett Shale

Oils are generated from a particular source rock or correlated with a source rock when there is significant overlap between the geochemical characteristics of the oils and source rock solvent extracts. In this study, the Fort Worth Basin oils are interpreted to be generated primarily from the Barnett Shale because of the demonstrated similarity in geochemical characteristics. The Pr/Ph, C_{19}/C_{23} and C_{22}/C_{21} tricyclic, C_{24} tetracyclic/C_{23} tricyclic, C_{33}/C_{32} terpane, C_{35}/C_{34} terpane, and gammacerane/hopane ratios for the oils and rock extracts, for example, are nearly identical, and there is significant overlap in other geochemical parameters supporting this conclusion (Table 1; Figures 7, 9 –14). Given that oils originate from thick, laterally extensive pods of source rock, whereas rock samples represent discrete points of such pods, it is unlikely that the composition of any single rock sample will exactly reflect the averaged geochemical composition of a crude-oil sample. In this case, the correspondence between oil and rock geochemistry is good.

Correlation between the Barnett Shale and oils from the Fort Worth Basin was also demonstrated using hierarchical cluster analysis (HCA) of 95 oils (Zumberge, 1987) (Figure 15). The highest maturity oils were not used in the HCA analysis because some of the parameters used in the analysis could not be determined. The C_{19}/C_{23}, C_{22}/C_{21}, C_{24}/C_{23}, and C_{26}/C_{25} tricyclic ratios, C_{24} tetracyclic/C_{23} tricyclic ratio, C_{33}/C_{32}, C_{28}/hopane, C_{29}/hopane, C_{31}R/hopane, gammacerane/C_{31}R hopane ratios, the % C_{27}, C_{28}, C_{29} steranes, the C_{28}/C_{29} sterane ratio, and the saturated and aromatic hydrocarbon $\delta^{13}C$ values were used in the HCA analysis. Two general oil groups were differentiated, with the outcrop and cuttings

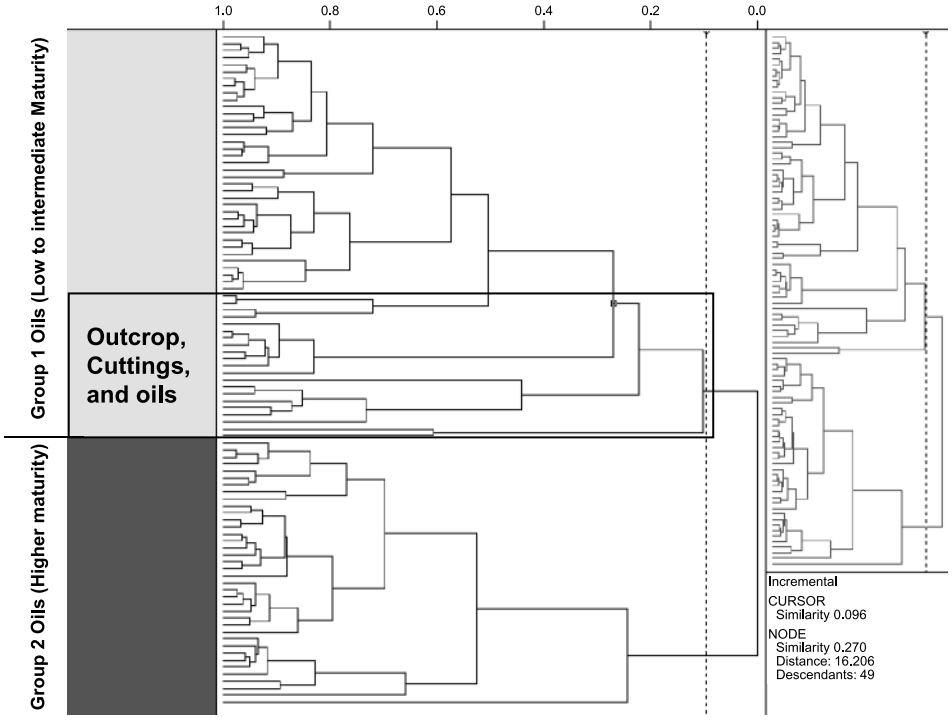


Figure 15. Hierarchical cluster analysis of Fort Worth Basin oils, outcrop, and cuttings samples showing two general oil groups can be differentiated statistically, and that oils in group 1 correlate with outcrop and cuttings samples. Although the parameters used in the HCA analysis are not strongly dependent on thermal maturity, the oils in group 2 show higher TAS values than those in group 1, suggesting that group 2 oils may be mixtures of petroleum.

samples showing the best correlation with the oils in group 1. Group 1 oils are low- to intermediate-maturity oils, whereas group 2 oils are intermediate- and higher maturity oils. Because the parameters used in the HCA analysis are not influenced by thermal-maturity effects except at the high levels of thermal alteration, the samples should be differentiated strictly on facies relationships. The thermal-maturity overprint on the HCA results is interpreted to mean the mixing of oils has occurred and is a significant process in the Fort Worth Basin.

Geochemical variability in the cuttings and outcrop solvent extracts demonstrate that multiple Barnett Shale geochemical facies exist, with some samples showing better correlation to produced oils than others. Generation from different source facies may account for some of the geochemical variability observed. The variability in oil geochemistry can also be attributed, in part, to the range of thermal maturities represented by the oils. However, we cannot rule out the mixing of oils from different Barnett Shale facies or the contribution of oil from other source rocks in the basin such as the Pennsylvanian Smithwick Shale or other source units as alternative explanations for the geochemical variability. The HCA analysis seems to support this interpretation. The generation of oil from the Smithwick (or other sources) or mixing of oils generated from the Barnett and the Smithwick might explain some of the oil geochemical variability observed, but until the Smithwick and other sources are investigated in more detail, this remains a hypothesis.

Gas Geochemistry

Gas molecular and isotopic composition demonstrates that Fort Worth Basin gases are of thermogenic origin with minor biogenic input (Figure 3; M. Schoell, 2002, personal communication). The gas maturities determined from isotope analysis support thermal generation of oil and gas from the Barnett Shale, with some gas possibly generated by cracking of oil. The estimated gas maturity from isotope analysis is consistent with Barnett Shale thermal maturity based on the equivalent % R_o estimated from the gas isotope data. Stratigraphic significance to the distribution of gas exists. Based on the complete range of maturity values exhibited by their contained gases, reservoirs of the Boonsville conglomerate of the Pennsylvanian Bend Group (Figure 2) were probably the first to receive gas generated by the Barnett (or other) source rocks and then continued to accumulate gas throughout the generation period. Except for the reservoirs within the Barnett, the Boonsville reservoirs are closest stratigraphically to the gas source. The Strawn Formation (Figure 2) is the youngest reservoir sampled. The Caddo Pool Formation, stratigraphically below the Strawn, received higher maturity gas than the

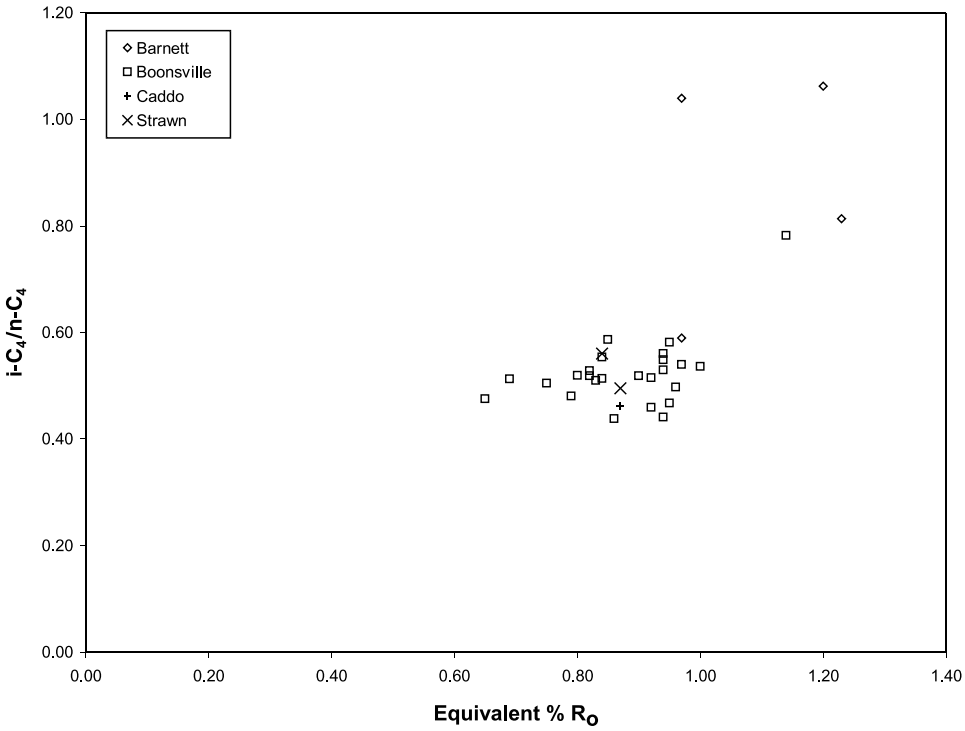


Figure 16. i-C_4/n-C_4 ratio is highest for Barnett Shale–reservoired gases and one Boonsville gas. These gases also show the highest maturity. The higher i-C_4/n-C_4 ratio appears to indicate the onset of oil cracking within the Barnett Shale, and that i-C_4 is a significant butane product of the cracking of retained petroleum in the Barnett Shale. Increased i-C_4 in Barnett Shale gases may be caused by the interaction of retained petroleum with clay minerals during cracking.

Strawn, although not as high as the Barnett or the highest maturities observed in the Boonsville reservoirs. More samples of gases from the Caddo are required to further confirm this trend. Excluding the Boonsville, gases appear to have filled the shallower reservoirs first, starting with the Strawn and then the Caddo, with the highest maturity gas remaining in the Barnett Shale. We cannot rule out contributions of gas from sources other than the Barnett, such as the Smithwick, but Barnett is interpreted to be the primary gas source based on oil-source relationships.

The inverse correlation of gas wetness with thermal maturity further supports the conclusions based on isotope data: gases generated at higher thermal maturities tend to be drier when compared to low-maturity gases. The presence of gases of all maturities in the Boonsville indicates that it may have acted as a primary reservoir with episodic expulsion from the Boonsville to the Strawn and Caddo, which would account for the gas-maturity distribution. Alternatively, the gas-maturity distribution may just reflect complex migration pathways available during petroleum generation or generation from multiple sources.

Two phenomena potentially explain the increase in i-C_4/n-C_4 (isobutane/normal butane) gas ratio at highest gas maturities (Figure 16). The highest maturity gases are in the Barnett Shale, with the exception of one gas sample from the Boonsville. Isobutane is less stable than normal butane (e.g., Prinzhofer et al., 2000) and, thus, should decrease relative to ethane or normal butane as thermal maturity increases. The increase in i-C_4/n-C_4 (isobutane/normal butane) with maturity appears to indicate the onset of oil cracking within the Barnett Shale, causing a pulse of i-C_4 (isobutane) in the Barnett reservoired gases that possibly resulted from the interaction of retained petroleum with clay minerals during oil cracking (Tannenbaum and Kaplan, 1985). A second possibility is that gases in the Boonsville, Caddo, and Strawn reservoirs represent mixtures of gases generated from more than one source facies, whereas the Barnett gases represent the generation from a single source facies. More extensive gas sampling and analysis is required to further test these hypotheses.

CONCLUSIONS

In all, 137 oils, 34 gases, and 9 source rock extracts were analyzed as part of our study to understand the origin of hydrocarbons in the Fort Worth Basin. Geochemical composition of the oils indicates the generation from a marine shale source rock deposited under dysoxic, strong upwelling, normal salinity conditions. Detailed biomarker and light hydrocarbon geochemistry demonstrate that the marine Mississippian Barnett Shale is the main source rock, although contributions from

other sources, such as the Smithwick Shale, are possible. Light hydrocarbon analyses reveal a significant terrigenous-sourced condensate input to some reservoirs, resulting in terrigenous and mixed marine-terrigenous light hydrocarbon signatures for many oils. Biomarker data, however, do not indicate terrigenous organic matter input. This study demonstrates the importance of integrating biomarker and light hydrocarbon data to define petroleum source rocks and also highlights the need to understand the significance of light hydrocarbon variations, especially in Paleozoic petroleum systems. Biomarker analysis alone would not have allowed for the identification of the source facies containing dominantly terrigenous organic matter. Cuttings analysis indicates that Barnett Shale organic facies are variable, and that variable oil compositions are expected in the Fort Worth Basin.

The gases of the Fort Worth Basin are thermogenic in origin, with minor contribution from biogenic sources. Gas-maturity data support the cogeneration of hydrocarbon gases with oil from the Barnett Shale, with some gas also resulting from oil cracking. Gases appear to be stratigraphically segregated with younger reservoirs containing less mature gas and older reservoirs containing more mature gas. The exception is the Pennsylvanian Strawn Group that contains gases representing the complete range of maturities observed. The increase in i-C_4/n-C_4 (isobutane/normal butane) with maturity appears to indicate the onset of oil cracking within the Barnett Shale, resulting in a pulse of i-C_4 (isobutane) in the Barnett reservoired gases. The higher i-C_4/n-C_4 (isobutane/normal butane) in Barnett gases is interpreted to result from the interaction of retained petroleum with clay minerals during gas generation. Alternatively, the gases reservoired in the Boonsville conglomerate of the Pennsylvanian Bend Group, Caddo Pool Formation, and Strawn Group may represent mixtures of gases generated from more than one source facies or source unit. Given the limited number of gas samples in this study, more research is required to further confirm these observations.

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