

Composition, Distribution, and Origin of Fruitland Formation and Pictured Cliffs Sandstone Gases, San Juan Basin, Colorado and New Mexico*

Andrew R. Scott¹
W.R. Kaiser¹
Walter B. Ayers, Jr.²

NMOCD CASE #11996
PENDRAGON ENERGY
EXHIBIT

N-20

1. Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas
2. Formerly Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas. Now with Taurus Exploration Inc., Birmingham, Alabama

ABSTRACT

One of the most active gas plays in the United States, the Fruitland Formation in the San Juan basin, contains an estimated 43 to 49 TCF ($1,217 \times 10^9$ to $1,387 \times 10^9$ m³) of coal gas in place. The Pictured Cliffs Sandstone, which underlies the Fruitland Formation, is a mature gas play that has produced more than 3 TCF (85×10^9 m³) of natural gas. We have studied the composition of gases from these units to evaluate gas origin, migration, and possible communication between formations. Gas analyses from more than 470 Fruitland and 5,500 Pictured Cliffs wells were used. Histograms, ternary diagrams, and maps were made to evaluate variations among gases by producing lithology (coal and/or sandstone), formation, pressure regime, and regional occurrence.

The distribution of Fruitland coal gases is controlled by basin hydrology and coal rank. Gases produced from coalbeds in the overpressured area of the basin are chemically drier (C_1/C_{1-5} values greater than 0.97) and contain more carbon dioxide (commonly greater than 6%) than coal gases from the underpressured area (C_1/C_{1-5} values generally less than 0.94 and carbon dioxide content less than 3%). The wettest coal gases coincide with the liquid hydrocarbon-generating stage (vitrinite reflectance values from 0.50% to 0.78%) of the hydrogen-rich Fruitland coal. Gases from underpressured Fruitland coalbeds, Fruitland sandstone, and Pictured Cliffs Sandstone have similar compositions, indicating that gas composition alone cannot be used to determine gas origin in all parts of the basin. Analysis of gas composition suggests that Pictured Cliffs Sandstone gases may be derived from both the underlying Lewis Shale and locally from overlying Fruitland coalbeds.

The abrupt transition of gas composition across the overpressured/underpressured boundary, methane and carbon dioxide $\delta^{13}C$ values, and isotopic values of bicarbonate from formation water suggest that some Fruitland coalbed methane is biogenic in origin. Desorption of carbon dioxide from coal surfaces and exsolution from formation water as pressure decreases during production may account for the high carbon dioxide content (greater than 10%) of some coal gases in the northern part of the basin.

INTRODUCTION

Fruitland coalbeds and sandstones and Pictured Cliffs sandstones in the San Juan basin contain significant amounts of nonassociated natural gas. Fruitland coalbeds alone contain an estimated 43 to 49 TCF ($1,217 \times 10^9$ to $1,387 \times 10^9$ m³) of gas in place (Ambrose and Ayers, 1991), and annual production in 1990 is predicted to exceed 200 BCF (5.660×10^9 m³). Cumulative gas production from Pictured

Cliffs Sandstone reservoirs through 1988 was 3.1 TCF (87.7×10^9 m³). Ultimate recovery is estimated to exceed 4.5 TCF (127.4×10^9 m³) (R. Hugman, 1990, pers. comm.).

Pictured Cliffs shoreline sandstones overlie and intertongue with the marine Lewis Shale, and the base of the Pictured Cliffs Sandstone conventionally is placed at the base of an upward-coarsening sequence (Figure 1). The Pictured Cliffs Sandstone is overlain by the coal-bearing Fruitland Formation, which represents the continental facies deposited landward of the shoreline deposits. Temporary landward shifts of the paleoshoreline during an overall

* Published by permission of the Director, Bureau of Economic Geology, The University of Texas at Austin.

marine regression during the Late Cretaceous resulted in intertonguing of upper Pictured Cliffs sandstones (UP1 in Figure 1) with the Fruitland Formation in the northern part of the basin (Ambrose and Ayers, 1991). The Fruitland Formation is overlain conformably by the Kirtland Shale throughout most of the basin, but the Ojo Alamo Sandstone unconformably overlies or truncates the Fruitland Formation in the east (Ambrose and Ayers, 1991).

Fruitland and Pictured Cliffs gases are predominantly methane with variable amounts of heavier hydrocarbons (ethane, propane, butane, and pentane), carbon dioxide, and nitrogen. Natural gases are generated from organic matter during thermal maturation through biogenic, early thermogenic, and late thermogenic processes. Catagenesis is the process by which organic material is altered, primarily as the result of increasing temperature, to produce thermogenic gases and liquid hydrocarbons (Hunt, 1979). Biogenic methane is produced at relatively low temperature through the metabolic activity of methanogenic bacteria (methanogenesis). Nonassociated gases in Fruitland coalbeds, Fruitland sandstones, and Pictured Cliffs sandstones have been interpreted to be mainly thermogenic in origin (Rice, 1983). Early thermogenic gases are formed before and during the main stage of oil generation. Heavier hydrocarbons, including chemically wet gas and oil, are derived from the organic material when thermal maturation reaches the oil-generating stage. Dry thermogenic gases are released from terrestrial organic matter or are generated by the cracking of heavier hydrocarbons formed during the oil-generating stage in sapropelic or hydrogen-rich organic matter as temperature increases with burial depth.

Carbon dioxide can be generated by bacterial activity and during catagenesis. Methanogenic bacteria are capable of metabolizing organic acids through the process of acetate fermentation to produce carbon dioxide and methane (Carothers and Kharaka, 1980; Whiticar and others, 1986). Carbon dioxide also is derived from oxygen-bearing functional groups of the organic matter and is released during decarboxylation at relatively low levels of thermal maturity (Stach and others, 1975) before significant quantities of liquid hydrocarbons and thermogenic gases are generated. At higher temperature, decarboxylation of organic acids can generate both carbon dioxide and methane (Carothers and Kharaka, 1980). Molecular nitrogen in Fruitland and Pictured Cliffs gases probably is derived from the oxidation of ammonia (Rohrback and others, 1983) evolved from organic matter during catagenesis.

Variation in composition among gases produced from Pictured Cliffs sandstones, Fruitland sandstone and coal gases, or regionally within one unit, may prove useful in establishing gas origin and migration pathways and in performing cost analyses. Understanding the origin of gases is important in developing exploration strategies by allowing more favorable drilling sites to be selected based on gas-migration pathways. Furthermore, nonhydrocarbon components may be corrosive (carbon dioxide), and inert

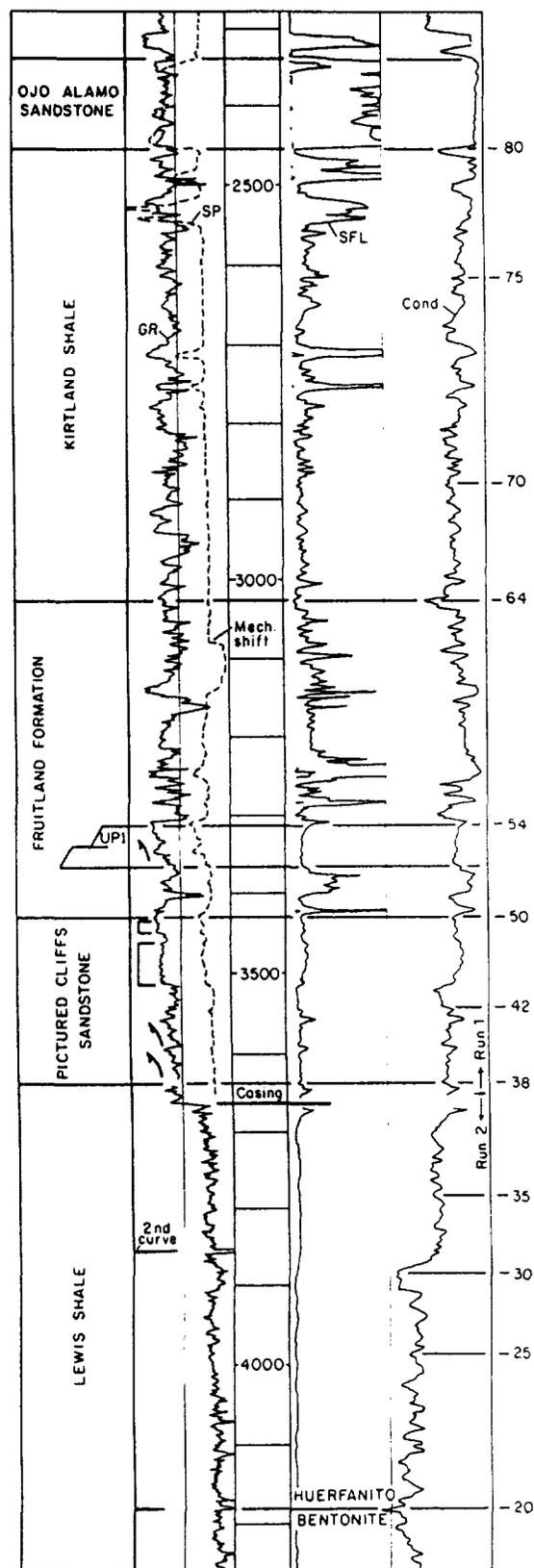


Figure 1. Type log of Upper Cretaceous stratigraphy in the San Juan Basin. An upper Pictured Cliffs sandstone (UP1) intertongues with the Fruitland Formation. From Ayers and others (1991).

gases (nitrogen) may significantly lower the heat content of the gas; both must be removed before the gas can enter the pipeline system.

The objectives of this study were to (1) determine any significant differences in gas composition among Fruitland coalbed, Fruitland sandstone, and Pictured Cliffs sandstone reservoirs; (2) determine any regional variations in gas composition among the same reservoir types; (3) compare Fruitland coal-gas composition with coal rank and basin hydrodynamics to evaluate factors controlling gas composition; and (4) determine if minor variations in gas composition can be used to determine the origin of these gases and possibly their migration pathways.

METHODOLOGY

Gas analyses from more than 5,500 Pictured Cliffs Sandstone wells and about 470 Fruitland Formation wells were used in this study. These data were obtained from pipeline companies, published reports, and Gas Research Institute cooperative wells. Gas samples generally were collected from the meter run, downstream from production equipment, or from the wellhead in nonproducing wells; collecting samples directly from the meter reduces the possibility of air contamination. Samples were analyzed with a gas chromatograph using a silica column.

Completion lithologies (sandstone and/or coal) for Fruitland wells were confirmed by the operator or were determined from completion reports and geophysical logs. If logs were unavailable for a well, then equivalent perforation intervals on well logs from adjacent wells were used to determine lithology. Wells whose producing zone and producing lithology could not be determined were designated as Basin Fruitland coal completions based on information provided by Dwight's Coal Bed Methane Report (1990a, 1990b). Wells were omitted if gases were commingled, if the producing lithology was uncertain, or if production could have been from both coalbeds and sandstone. For Pictured Cliffs Sandstone completions, a limited number of wells were examined to verify that the perforation interval actually was in the Pictured Cliffs Sandstone.

Gas contents discussed in this report are given in mole percent. The ratio of methane (C_1) to total hydrocarbons (C_{1-5}) was used to determine a gas-dryness index. We define gas dryness according to the following ranges in C_1/C_{1-5} values:

Dryness	C_1/C_{1-5}
Very dry	>0.99
Dry	0.94–0.99
Wet	0.86–0.94
Very wet	<0.86

These gas-dryness ranges are similar to those reported by Hanson (1990).

Isotopic data for methane, carbon dioxide, and water were collected from published reports. Bicarbonate is the dominant species in Fruitland Formation water, and $\delta^{13}C$ values for total dissolved carbonate species will herein be referred to as bicarbonate $\delta^{13}C$ values. All isotopic values are relative to the PDB (Peedee belemnite) standard.

COMPOSITION AND DISTRIBUTION OF FRUITLAND AND PICTURED CLIFFS GASES

Previous studies have suggested that Fruitland Formation and Pictured Cliffs sandstone gas composition and distribution are controlled by coal rank and source rock type (Rice and others, 1988, 1989). Furthermore, overpressuring in the Fruitland Formation was inferred to represent fossil geopressure associated with basin subsidence and thermal maturation, rather than basin hydrodynamics (Decker and Horner, 1987). However, our study suggests that compositional variations in Fruitland coal gases and regional distribution of the gases result from both thermal maturity and basin hydrology. The Fruitland Formation is a regional aquifer in which recharge occurs in the north, where thick northwest-trending coalbeds crop out along the Hogback monocline (Kaiser and others, 1991a). Because of vertical confinement and basinward pinchout of coalbeds and/or localized faulting (Ambrose and Ayers, 1991), the Fruitland is regionally overpressured in the northern part of the basin (Figure 2) (Kaiser and others, 1991a).

Fruitland coal rank ranges from subbituminous to low-volatile bituminous (Figure 3). Low-volatile bituminous coal occurs locally in the northern part of the basin. From this area of high maturity, coal rank decreases abruptly toward the northern basin margin. Along the Hogback monocline high-volatile C to high-volatile A bituminous isoreflectance lines parallel the basin margin. Southward, isoreflectance lines generally parallel the basin's structural contours. Ambrose and Ayers (1991) hypothesize the existence of a northwest-trending structural hingeline consisting of a normal fault zone downthrown on the northeast. Significantly, offset of coalbeds across this fault zone, and the southwestward pinchout of coalbeds, may have inhibited the southwestward migration of fluids derived from the thermally more mature area in the north. This hingeline would explain the closely spaced isoreflectance contours in the north (Figure 3, vitrinite reflectance values greater than 0.65%), as well as the southwestern boundary of overpressuring.

Previous studies have concluded that Fruitland coal gases are chemically distinct from Fruitland sandstone and Pictured Cliffs sandstone gases (Rice and others, 1988, 1989). Differences in gas composition between sandstone and coal reservoirs were inferred to result from different organic matter sources—Type III terrestrial kerogen in coalbeds produced chemically dry gas, whereas dispersed Type III kerogen in adjacent shale generated wetter gas. However, these studies were based on relatively few

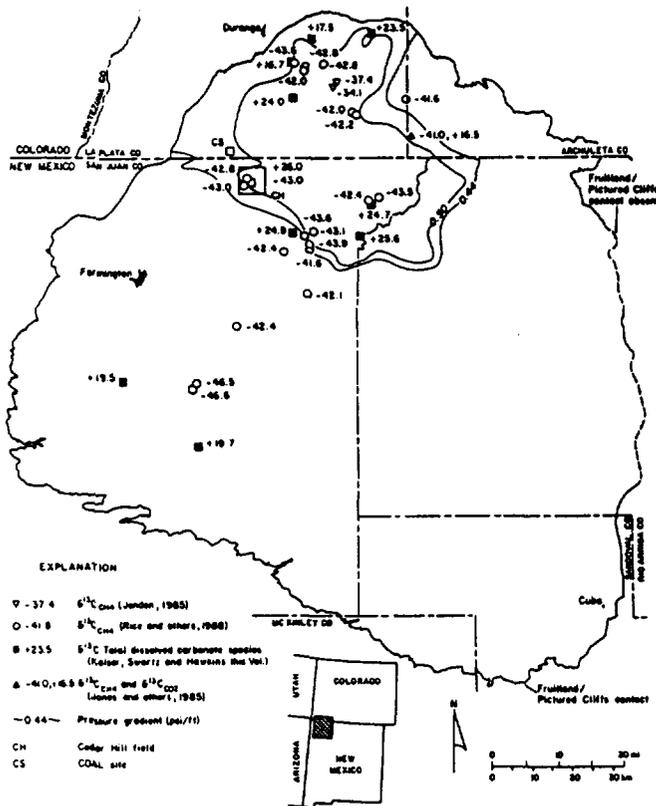


Figure 2. Regional pressure gradient and distribution of $\delta^{13}\text{C}$ values of methane and carbon dioxide produced from Fruitland coalbeds and $\delta^{13}\text{C}$ values of total dissolved carbonate species in Fruitland Formation waters, San Juan basin. The Fruitland is overpressured relative to hydrostatic pressure in the north (pressure gradient of 0.50 psi/ft); underpressured areas have pressure gradients less than 0.44 psi/ft.

samples, and extrapolation of their conclusions throughout the basin is not justified or supported by a regional database. In this study we show that gas composition varies more with coal rank and pressure regime than with producing lithology.

Carbon dioxide, ethane, and nitrogen were evaluated to characterize variations in gas composition among Fruitland coal, Fruitland sandstone, and Pictured Cliffs sandstone. These three components, rather than methane, were selected so that minor variations in gas composition could be recognized. If methane had been used as an end member, gas compositional data points would have clustered in one corner of the ternary diagram. Furthermore, a good correlation is apparent between methane content and these three components (Figure 4) and between ethane and heavier gas components (C_{3-5} hydrocarbons).

Coal gases from the overpressured part of the basin follow gas compositional trend A, which has a correlation coefficient of .99 (Figure 4a). These gases are composed predominantly of methane and carbon dioxide and only minor amounts of other hydrocarbon gases. Sandstone and coal gases from the northern part of the basin follow different trends. However, pressure and hydrochemical

data indicate that Fruitland sandstones and coalbeds in the overpressured area are in regional hydraulic communication (Kaiser and others, 1991a, 1991b). Therefore, differences between sandstone and coal gas compositional trends in the north probably reflect the way gases are stored in, and released from, these reservoirs rather than noncommunication between reservoirs.

Fruitland coal and sandstones gases from the underpressured area generally follow trend B (correlation coefficient of .91; Figure 4b), which suggests possible communication between sandstone and coal in the southern part of the basin.

The relatively minor variation in coal-gas composition with time (Hale and Firth, 1988) suggests that the length of production should not be a major factor affecting gas compositional data and that gas compositional trends recognized in this study probably are valid.

Fruitland Formation Gases

Previous studies attributed the presence of wet gases produced from Fruitland coals to unspecified completion practices rather than to production directly from the coal (Rice and others, 1988, 1989). However, our study indicates that Fruitland coal is the source of wet coal gas. Further-

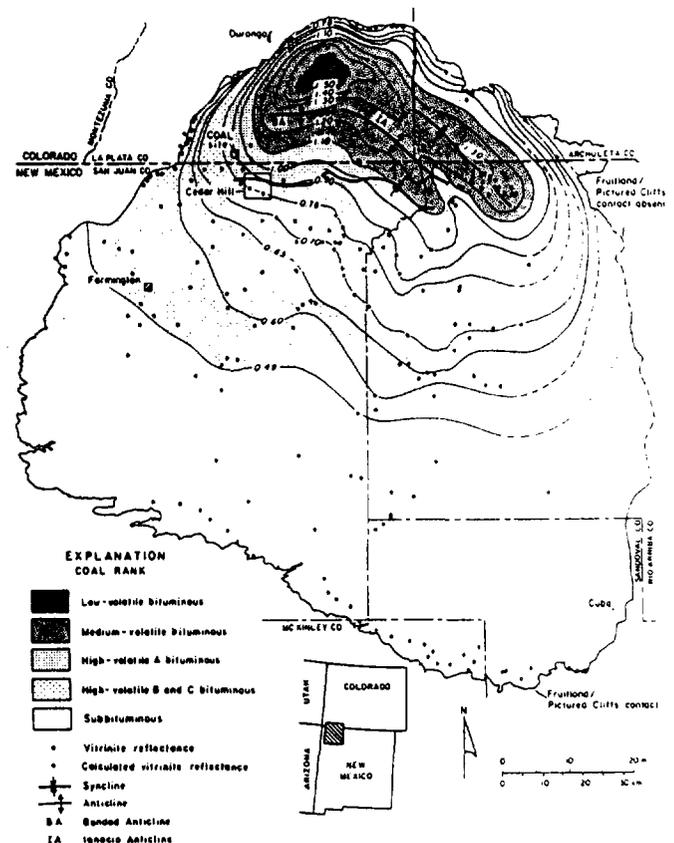


Figure 3. Fruitland Formation coal rank map. From Scott and others (1991). Structural axes are from the structure map of the Huerfanito Bentonite Bed (Ayers and others, 1991).

basin (Figure 5). The ethane content of sandstone gas ranges from less than 1% to nearly 11%, with gases from the underpressured region containing significantly more ethane than those from the overpressured region (Table 1, Figure 5).

Gases from overpressured and underpressured sandstone reservoirs have similar ranges of carbon dioxide content (Table 1). However, sandstone gases in the north generally contain more than 1% carbon dioxide (Figure 6) and have a mean carbon dioxide content of 2.2%.

Ternary diagrams of Fruitland sandstone gas composition reflect the relatively high ethane content (Figure 7). Gases from overpressured sandstones and UP1 have similar gas compositions and generally contain more carbon dioxide and less ethane than gases from underpressured Fruitland sandstones. Gases from some wells completed in sandstone but exhibiting coal-decline production behavior (Kaiser and others, 1991a) have proportionately higher carbon dioxide and/or nitrogen contents (Figure 7), indicating that these sandstones may have derived at least some gas from adjacent coalbeds. However, other wells with coal-decline production behavior do not follow this trend.

Fruitland Coal Gases

Analysis of Fruitland coal gases showed that although many coal gases are chemically dry, a significant number

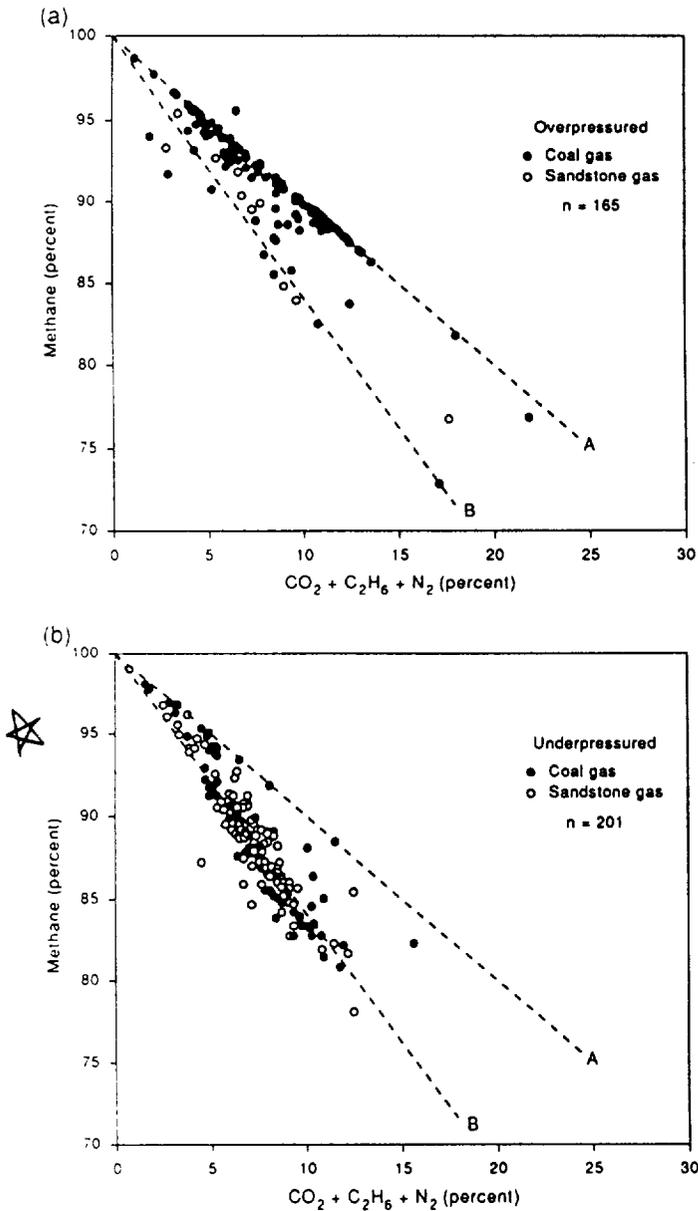


Figure 4. Methane content vs sum of carbon dioxide, ethane, and nitrogen content in Fruitland coal gas and Fruitland sandstone gas in (a) overpressured and (b) underpressured areas of the San Juan basin.

more, Fruitland coal and sandstone gas compositions are similar in the southern part of the basin, indicating that gas composition alone cannot be used to determine gas origin in this area.

Fruitland Sandstone Gases

Gases produced from Fruitland sandstone have values of C_1/C_{1-5} ranging from 0.80 to 1.00, with a mean of 0.90 (Table 1). Sandstone gases from the underpressured area are wetter than those from the overpressured area (mean C_1/C_{1-5} values of 0.90 and 0.94, respectively). Wet gases (C_1/C_{1-5} values commonly less than 0.91) occur in a northwest-trending band in the west-central part of the

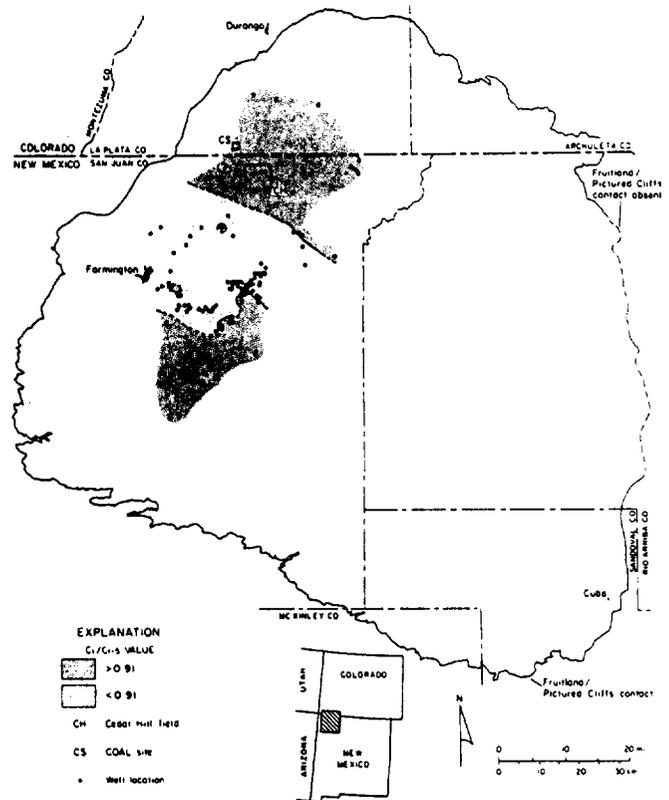


Figure 5. C_1/C_{1-5} values of Fruitland sandstone gases, San Juan basin.

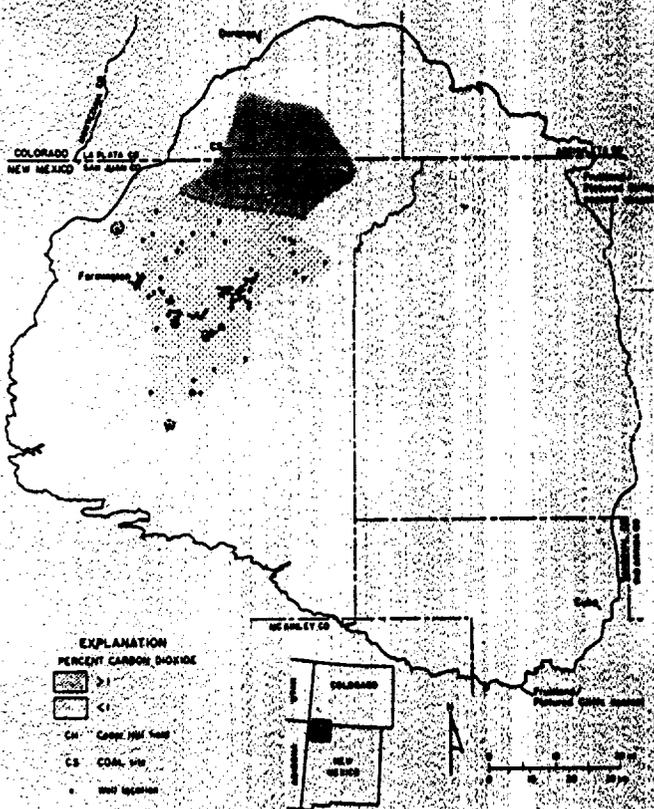


Figure 6. Carbon dioxide content of Fruitland sandstone gases, San Juan basin.

are chemically wet. The range of C_1/C_{1-5} values (0.77 to 1.00) is similar to that of Fruitland sandstone gases (Table 1). A west-northwest-trending band of relatively wet coal gases (Figure 8) occurs in the northern part of the underpressured southern basin. Coal gases from the overpressured area are chemically drier (mean C_1/C_{1-5} value of 0.98) than those from underpressured areas, which have a mean C_1/C_{1-5} value of 0.92. However, gases from underpressured coal and sandstone have similar values of mean C_1/C_{1-5} (0.92 and 0.90, respectively). Ternary diagrams also indicate that gases from overpressured coalbeds are generally drier and have significantly more carbon dioxide than gases from underpressured coalbeds, which are characterized by a higher proportion of ethane (Figure 9). Coal gases from the transition zone, located between overpressured and underpressured areas, have compositions between those of the two pressure regimes.

Carbon dioxide content in Fruitland coal gases ranges from less than 1% to more than 13% (Table 1). Coal gases with the highest carbon dioxide content (greater than 10%) are from the north-central part of the basin (Figure 10), which is further characterized by very dry gases (C_1/C_{1-5} values of 1.00) and highly productive coalbed methane wells. From here, carbon dioxide content decreases gradually northwestward and very abruptly southward. Coal gases in the south generally contain less than 1% carbon dioxide. Coal gases typically contain more carbon dioxide

than either underpressured or overpressured sandstone gases (Table 1).

Histograms of coal-gas composition indicate major differences between overpressured and underpressured gases (Figure 11). Underpressured coal gases generally have C_1/C_{1-5} values less than 0.93 and carbon dioxide content less than 2%. Furthermore, gases from overpressured, thermally more mature coalbeds are significantly drier (C_1/C_{1-5} values generally greater than 0.97) and have more carbon dioxide (greater than 3%) than gases produced from underpressured coalbeds. The compositions of gases produced from underpressured coalbed and sandstone reservoirs are similar—both have relatively high ethane and generally minor carbon dioxide and nitrogen contents (Figures 7b and 9c). Histograms of coal and sandstone gases from the underpressured part of the basin are similar; these gases are chemically wet to very wet and contain only minor carbon dioxide (Figure 12).

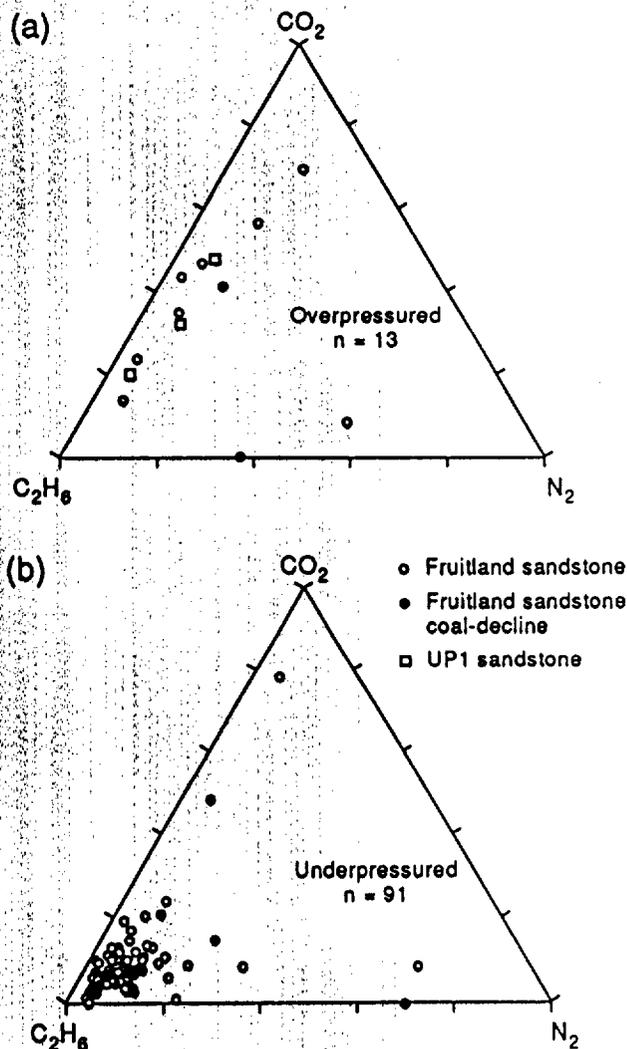


Figure 7. Ternary diagrams of ethane, carbon dioxide, and nitrogen composition of gases produced from Fruitland sandstone, Fruitland sandstone showing coal-decline behavior, and Pictured Cliffs sandstones. a. Overpressured area. b. Underpressured area.

Table 1. Composition of natural gases in Fruitland sandstone, Fruitland coalbeds, and Pictured Cliffs sandstones, San Juan basin.

Component	Fruitland Sandstone			Fruitland Coal			Pictured Cliffs Sandstone
	All (n = 101)	UP* (n = 91)	OP ⁺ (n = 10)	All ⁺⁺ (n = 288)	UP* (n = 111)	OP ⁺ (n = 157)	All (n = 1,553)
<i>C</i> ₁ / <i>C</i> ₁₋₅							
x	0.90	0.90	0.94	0.96	0.92	0.98	0.88
S	0.04	0.03	0.04	0.05	0.04	0.03	0.04
C	0.04	0.04	0.05	0.05	0.05	0.03	0.04
min	0.80	0.80	0.86	0.77	0.83	0.85	0.75
max	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ethane (%)							
x	5.7	6.2	3.8	2.5	4.8	1.1	6.7
S	2.0	1.86	2.00	2.69	2.35	1.70	1.83
C	0.35	0.30	0.53	1.08	0.49	1.55	0.27
min	0.3	0.3	0.6	0	<0.1	0	<0.5
max	10.7	10.7	6.4	11.9	9.7	8.5	14.8
Carbon dioxide (%)							
x	0.8	0.5	2.2	4.5	1.4	6.4	0.7
S	0.73	1.86	0.87	3.90	1.54	3.71	0.64
C	0.93	0.31	0.41	0.87	1.10	0.58	0.91
min	0	0	<0.1	<0.1	<0.1	0.2	<0.1
max	3.4	3.4	3.2	13.5	11.4	13.5	10.1
Nitrogen (%)							
x	0.8	0.6	1.8	0.7	0.8	0.7	0.7
S	1.28	0.90	2.95	1.56	1.32	1.79	0.52
C	1.60	1.50	1.64	2.23	1.65	2.56	0.72
min	0.1	0.1	0.3	0	0	0	0
max	9.7	8.5	9.7	13.3	11.2	13.3	5.3

x = Arithmetic mean.

S = Standard deviation.

C = Coefficient of variation.

* UP = Underpressured area.

+ OP = Overpressured area.

++ Includes 20 samples from transition zone.

Pictured Cliffs Sandstone Gases

Fruitland sandstone, Fruitland coal, and Pictured Cliffs Sandstone gases can have similar C_1/C_{1-5} values (Figures 13 and 14), indicating that gas composition alone cannot be used to determine gas origin in all areas of the basin. Pictured Cliffs gases show a normal distribution of C_1/C_{1-5} values (Figure 14) from 0.75 to 1.00 (mean 0.88); they may contain nearly 15% ethane (Table 1). The wettest Pictured Cliffs gases occur in the southeast (Figure 15). Elongate trends of relatively dry gas (C_1/C_{1-5} values greater than 0.85) parallel depositional strike in the southeastern corner of the basin, suggesting that localized variations in gas composition may be the result of (1) migration effects across shale/sandstone contacts, which would enrich the gases in methane relative to other components (Leythaeuser

and others, 1979); or (2) migration of chemically dry gases southeastward through more permeable sandstone.

The ranges of carbon dioxide and nitrogen contents of Pictured Cliffs Sandstone gases also are similar to those in Fruitland sandstone gases. However, Fruitland coal gases generally are chemically drier and contain more carbon dioxide than Pictured Cliffs Sandstone gases (Table 1). Carbon dioxide content of Pictured Cliffs Sandstone gases generally is less than 1% (Figure 16). Carbon dioxide content is highest in the Cedar Hill field area (Figures 10 and 16); gases from the western part of the basin are chemically drier and contain more carbon dioxide (Figures 15 and 16). These areas of high carbon dioxide content may represent reservoir communication between Pictured Cliffs sandstones and Fruitland coalbeds and/or commingled production from the respective strata.

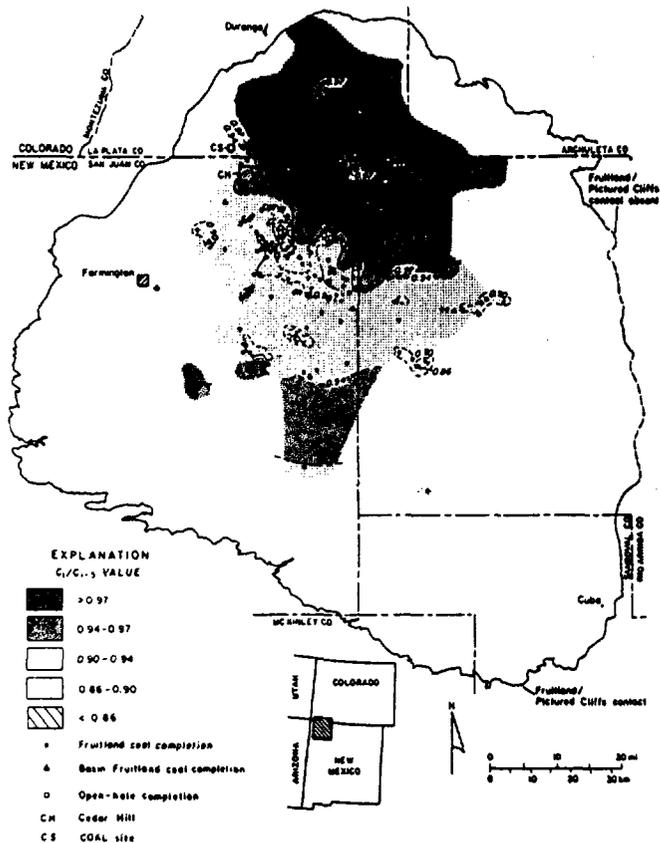


Figure 8. C_1/C_{1-5} values of Fruitland coal gases, San Juan basin.

RELATIONSHIP OF COAL-GAS COMPOSITION TO THERMAL MATURITY AND PRESSURE REGIME

Previous studies did not consider the influence of basin hydrodynamics on coal-gas composition (Rice and others, 1988, 1989). Interpretations of coal-gas composition and origin were based on the assumption that coal rank alone controlled gas composition. Coal typically is composed of type III kerogen, which traditionally is considered to be a major source of chemically dry gas; therefore, Fruitland coalbeds were assumed to generate only very dry gases (C_1/C_{1-5} values greater than 0.99; Rice and others, 1988; Figure 7 in Rice and others, 1989). However, Hanson (1990) reported that although many desorbed coal gases are dry to very dry, some are wet to very wet, with gas wetness depending on coal rank and maceral composition. Furthermore, Fruitland coal is hydrogen rich and may be the source of condensate produced from the coals (Rice and others, 1989).

Thermogenic gases, formed during catagenesis, become chemically drier with increasing temperature. Predictably, gases from the thermally more mature coals in the northern part of the basin are chemically dry to very dry. However, regional distribution of these gases (Figure 8) suggests that coal rank is not the only factor controlling the chemical composition of the gas. The eastern boundary of chemically dry coal gases crosses coal rank trends (Figure 3).

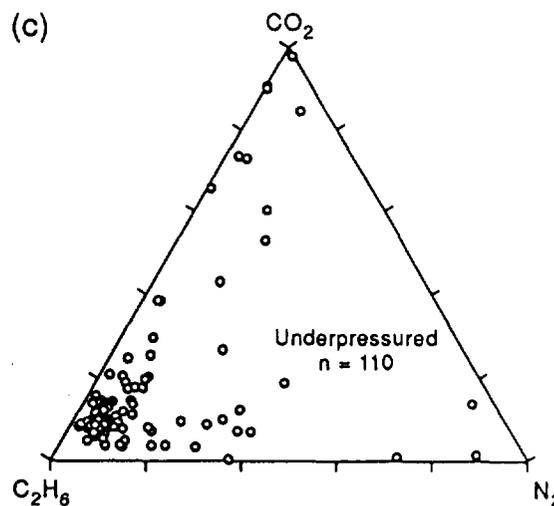
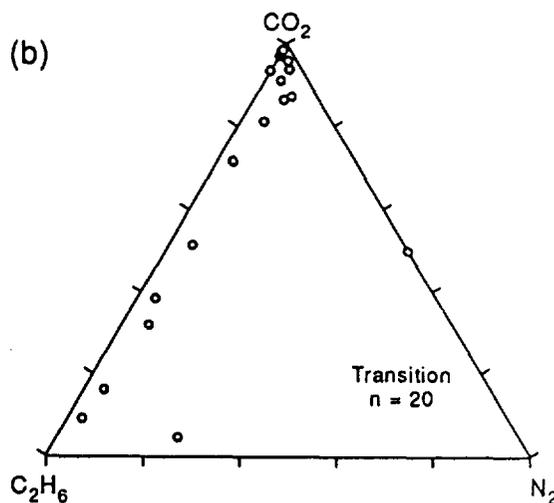
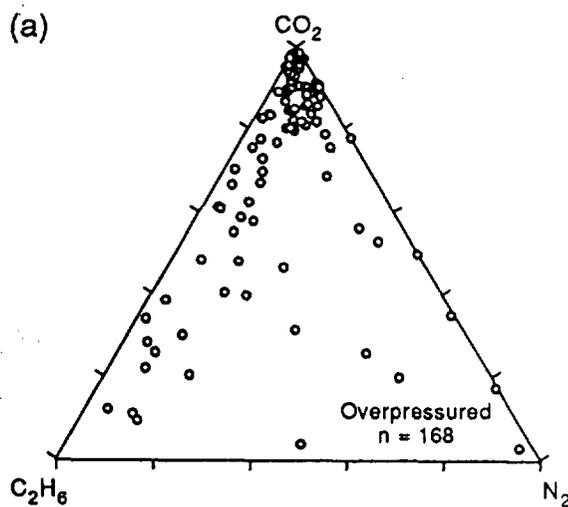


Figure 9. Ternary diagram of ethane, carbon dioxide, and nitrogen composition of Fruitland coal gases. a. Overpressured area. b. Transition zone between overpressuring and underpressuring. c. Underpressured area.

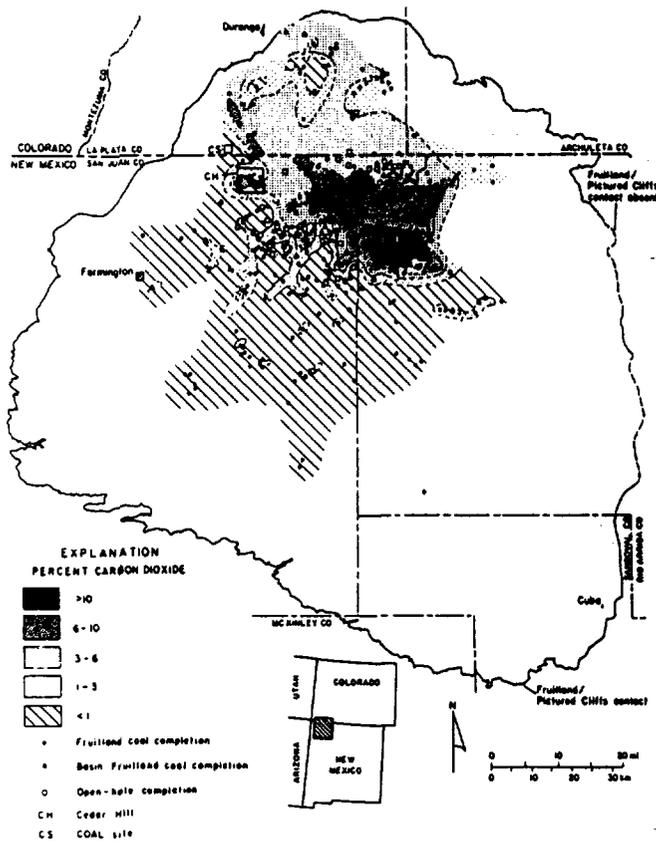


Figure 10. Carbon dioxide content of Fruitland coal gases, San Juan basin. Highest carbon dioxide content (greater than 6%) coincides with highest bottom-hole pressures (greater than 1,600 psi; Kaiser and others, 1991a) and regional overpressure (see Figure 16).

Furthermore, a gradational contact between very dry and wet coal gases paralleling vitrinite reflectance trends would be expected if coal rank alone controlled gas composition. Instead, the transition from very dry (C_1/C_{1-5} value of 1.00) to wet (C_1/C_{1-5} value of 0.87) coal gases is abrupt, occurring over a distance of less than 1.5 miles (2 km) along some parts of the overpressure/underpressure boundary (Figure 8). In fact, gas-composition trends coincide with the pressure regime in the Fruitland Formation (Kaiser and others, 1991a) rather than with coal rank (Figures 2 and 3). Therefore, basin hydrology is believed to be a major factor controlling coal-gas composition. Basinward migration of sufficient quantities of methane in Fruitland Formation waters could explain the presence of chemically dry gases along the overpressure/underpressure boundary, and some migration probably has occurred. However, methane is not very soluble in water, and large volumes of water moving through the coal would be required to transport significant amounts of methane. Furthermore, simple migration of methane from higher rank coals southward in formation water does not explain gas and water isotopic data. These isotopic data and the origin of the gases will be discussed below.

Previous studies have suggested that carbon dioxide content in coal gas decreases with increasing coal rank (Rice and others, 1988, 1989, 1990). However, Fruitland coal gases with the highest carbon dioxide content occur in the northern part of the basin where coal rank is high-volatile A bituminous. Gases from low- and medium-volatile bituminous coals in the north generally have lower carbon dioxide content (less than 3%) than some lower rank coals. However, carbon dioxide content does not follow vitrinite isorefectance contours in that area (Figures 3 and 10). Carbon dioxide content coincides more with formation pressure (Kaiser and others, 1991a) and regional overpressure in the Fruitland than with coal rank (Figures 2,

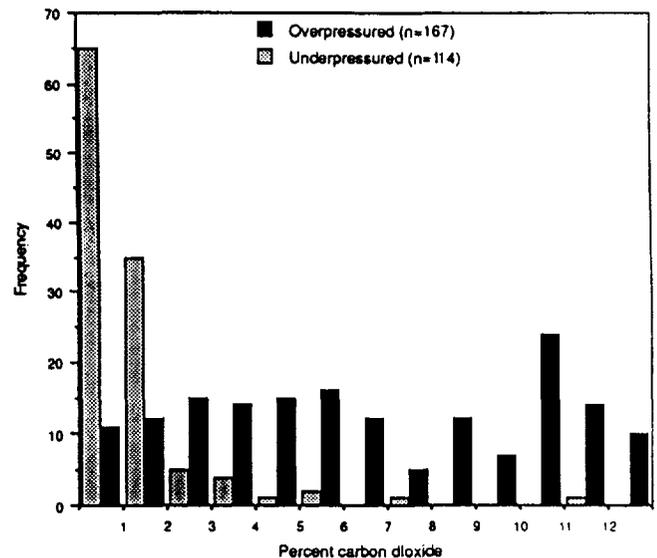
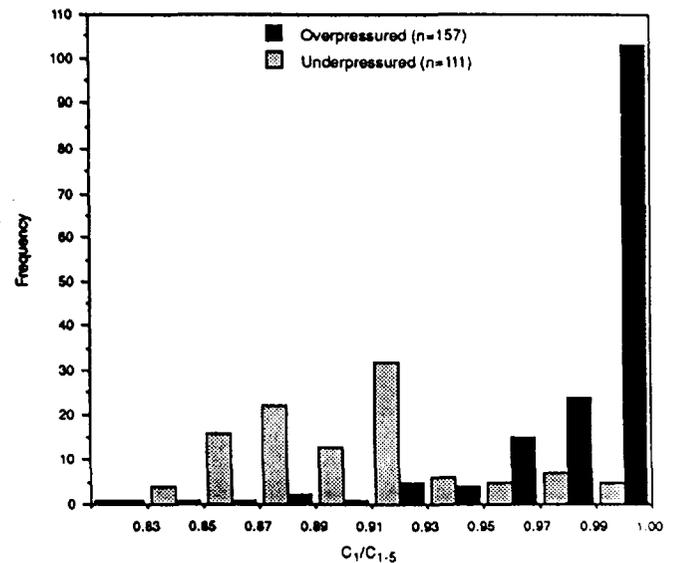


Figure 11. Histograms of C_1/C_{1-5} values and carbon dioxide content of gases from underpressured and overpressured Fruitland coalbeds, San Juan basin. Bimodal distribution of carbon dioxide in overpressured gases primarily reflects high carbon dioxide content of samples from the north-central part of the basin.

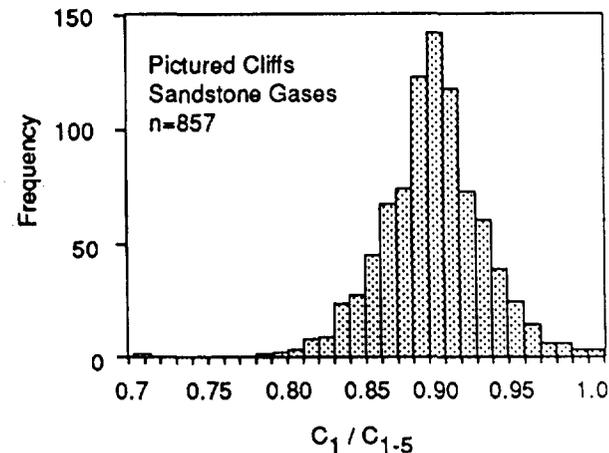
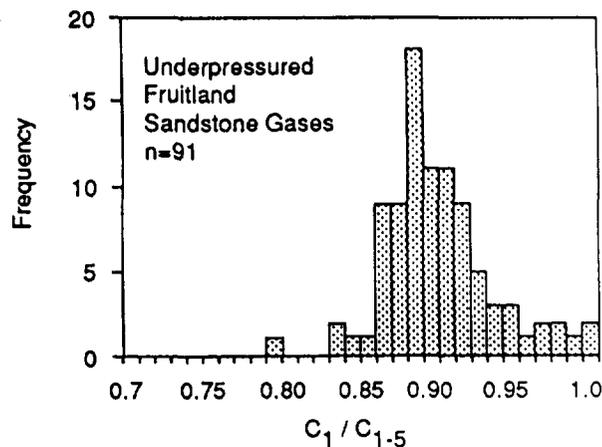
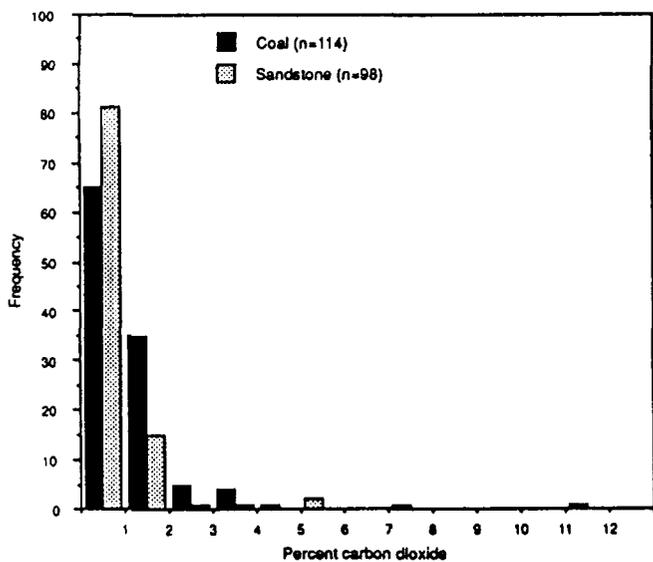
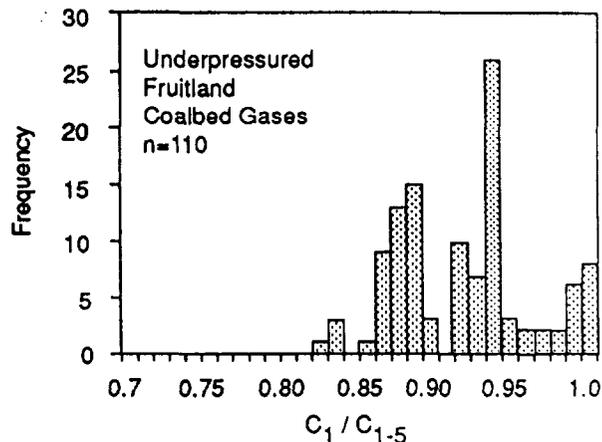
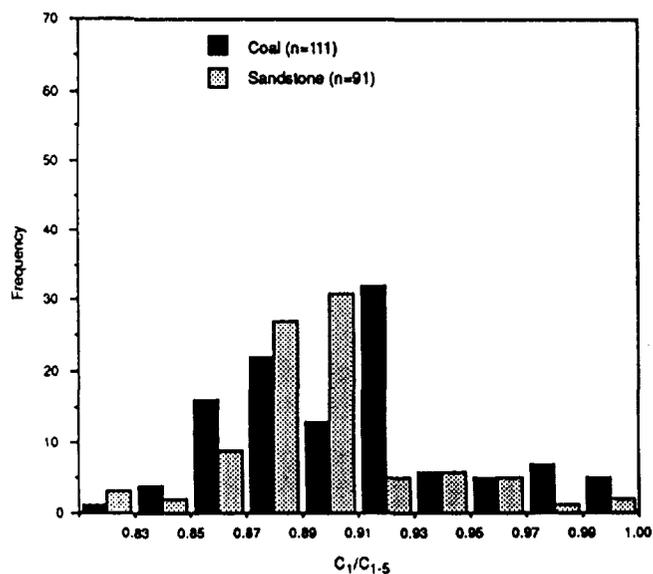


Figure 12. Histograms of C_1/C_{1-5} values and carbon dioxide content of gases from underpressured Fruitland coal and sandstone, San Juan basin.

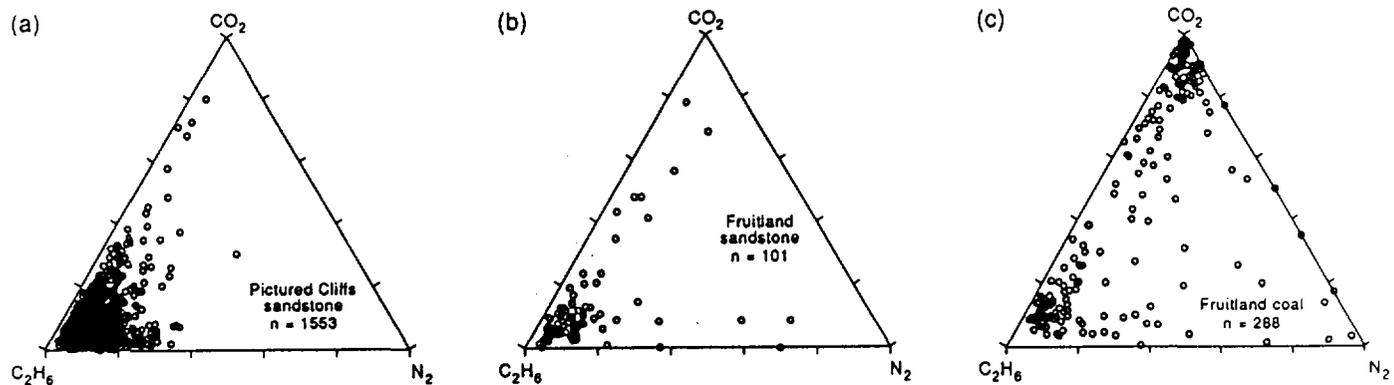


Figure 13. Ternary diagrams of ethane, carbon dioxide, and nitrogen composition of Pictured Cliffs and Fruitland gases.

3, and 10), indicating that carbon dioxide content in coal gases is controlled by both basin hydrology and coal rank.

ORIGIN OF FRUITLAND COALBED AND PICTURED CLIFFS SANDSTONE GASES

Fruitland Coal Gases

The quantity and composition of gas in a coalbed are determined by coal rank, formation pressure, ash content, and maceral composition. Rank and maceral composition, particularly the relative abundance of hydrogen-rich organic material, also control the types of gases produced from the coal. Coal generates progressively more thermogenic methane and less carbon dioxide and nitrogen during catagenesis, and the methane storage capacity of coal increases with rank; the density of methane molecules adsorbed onto coal surfaces can resemble that of liquid methane (Creedy, 1988).

Previous studies of gas wetness and carbon isotopic values of methane have suggested that most of the gas produced from the Fruitland Formation is thermogenic in

origin; only a few gas samples in the southern basin were believed to be of possible biogenic origin (Rice and others, 1988, 1989). However, the distributions of carbon dioxide content and C_1/C_{1-5} values for Fruitland coal gases do not support these conclusions. Geochemical studies (Rice and others, 1989; Law and others, 1990) and the distribution of wet gases in the Fruitland Formation suggest that wet gases are indigenous to the coal. Although most of the gas produced from Fruitland coalbeds probably has a thermogenic origin, mixing of thermogenic and biogenic gases can better explain gas compositional distributions and $\delta^{13}C$ isotopic signatures of methane, total dissolved carbonate, and carbon dioxide found in the Fruitland Formation.

Coal traditionally has been thought of as a major source of dry gas, having little potential for generation of liquid hydrocarbons. However, hydrogen-rich coal is capable of generating liquid hydrocarbons (Khorasani, 1987). Furthermore, coals composed predominantly of vitrinite may contain submicroscopic particles of hydrogen-rich organic matter within the vitrinite. These particles would not be identified during microscopic study of the kerogen, leading to the interpretation that coal composed predominantly of vitrinite has little potential to generate wet gas (Bertrand, and others, 1986, and references therein). Results of Rock-Eval pyrolysis of Fruitland coals (Rice and others, 1989; Law and others, 1990) indicate that they are

Figure 14 (left). Histograms of gases from underpressured Fruitland coalbeds, Fruitland sandstones, and Pictured Cliffs sandstones. Pictured Cliffs gas data used in this histogram are from the same part of the basin as Fruitland gas data.

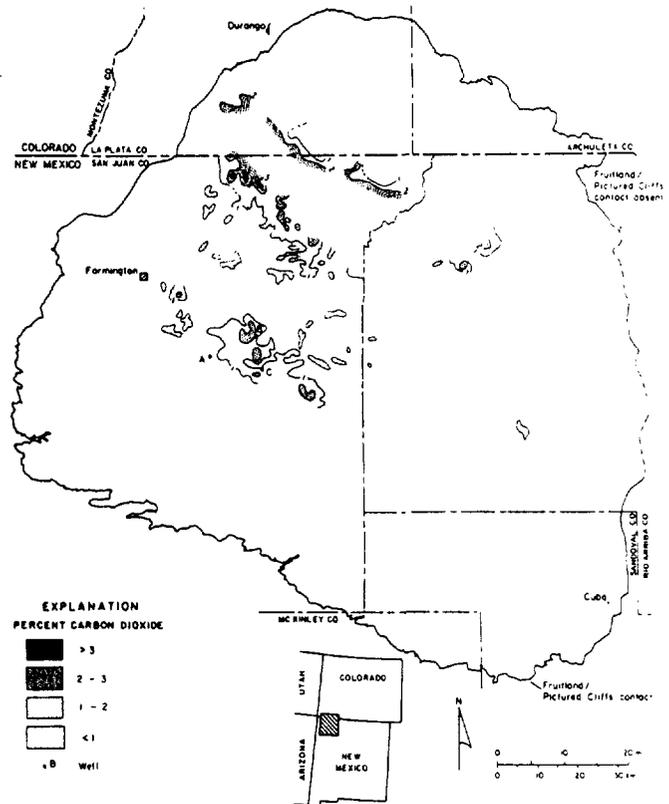
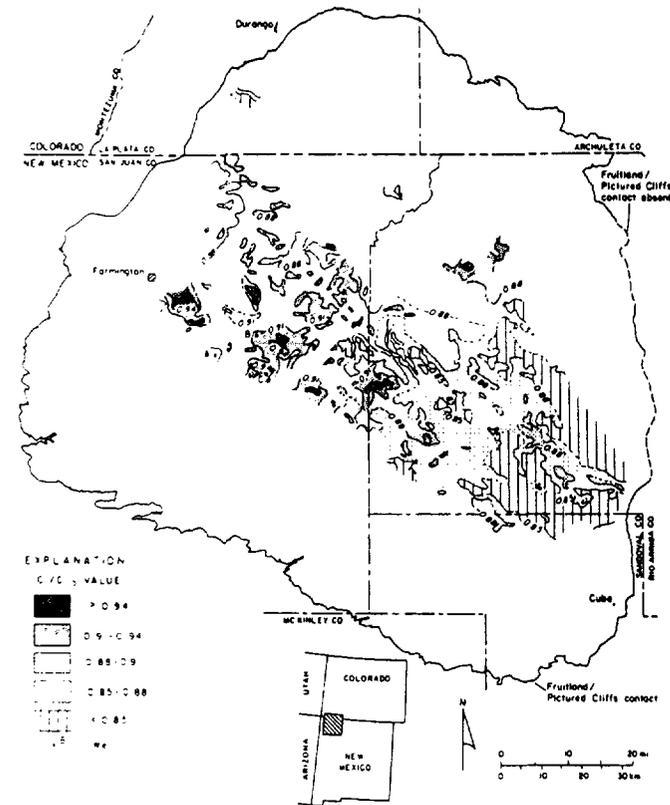


Figure 15. Distribution of C_1/C_{1-5} values of Pictured Cliffs Sandstone gases, San Juan basin, based on gas analyses from more than 5,500 wells.

Figure 16. Carbon dioxide distribution in Pictured Cliffs Sandstone gases, San Juan basin, based on gas analyses from more than 5,500 wells.

hydrogen rich and have moderate potential for generating liquid hydrocarbons. Saturated-hydrocarbon distributions on gas chromatograms of Fruitland coal and carbonaceous shale extracts are similar to condensates produced from Fruitland coalbeds, indicating that the condensates originated from the coals (Rice and others, 1989). From these observations, Fruitland coalbeds are capable of producing wet gas, and areas of wet coal gas in the southern part of the basin are directly related to coal rank.

The generation of dry thermogenic gas from coal typically begins at vitrinite reflectance values of 0.7% (Meissner, 1987), which coincides with the southwestern limit of dry coal gases (Figure 8), suggesting that dry gases in the northern San Juan basin are thermogenic in origin, as suggested previously (Rice and others, 1988, 1989). However, if Fruitland coalbed methane is entirely thermogenic, $\delta^{13}\text{C}$ values of methane should become less negative (-55% to -15%) with increasing thermal maturation (Schoell, 1983; Jenden, 1985). Instead, the isotopic signature of methane from Fruitland coal varies little throughout the basin and does not change significantly with coal rank (Figure 2). Either the process of thermogenic gas generation from coal is significantly different than gas generation from other types of organic matter, resulting in a relatively narrow range of $\delta^{13}\text{C}$ methane values over a wide range of coal ranks, or Fruitland coal gases may be mixtures of thermogenic and biogenic gases.

By comparison, biogenic methane $\delta^{13}\text{C}$ values range from less than -90% to -40% (Jenden, 1985), indicating that biogenic and thermogenic gases can have overlapping methane $\delta^{13}\text{C}$ isotopic values in the range of -55% to -40% . Biogenic gases generated by carbonate reduction and/or acetate dissimilation can produce both chemically very dry gas (C_1/C_{1-5} values of 1.00) and isotopically heavy bicarbonate (Carothers and Kharaka, 1980). Furthermore, bacterial alteration of chemically wet gas can remove nearly all heavier gas components, leaving a chemically dry gas that resembles thermogenic gas (James and Burns, 1984). Therefore, the composition and distribution of coal gases and the isotopic composition of bicarbonate from formation water were considered in addition to methane $\delta^{13}\text{C}$ values to determine the origin of Fruitland coalbed methane.

Regional variations in carbon dioxide content and chemical composition (C_1/C_{1-5} values) of coal gases coincide with regional overpressure in the Fruitland, indicating a relationship between basin hydrology and gas composition (Figures 2, 8, and 10). Waters from the northern, overpressured area of the basin are dominantly sodium bicarbonate, characterized by high alkalinity and low chloride content (Kaiser and others, 1991a). $\delta^{13}\text{C}$ values for the bicarbonate are isotopically heavy, ranging from $+16.7\%$ to $+26.0\%$ (Kaiser and others, 1991a). These values are consistent with Jones and others' (1985) reported $\delta^{13}\text{C}$ values of $+16.2\%$ and $+16.8\%$ for carbon dioxide produced from the Glover No. 1 well in southwestern Archuleta

County, Colorado. Isotopically heavy values such as these can be derived from dissolution of isotopically heavy carbonate cement and/or bacterial activity.

Dissolution of isotopically heavy carbonate cement could produce the range of bicarbonate isotopic values found in Fruitland Formation waters. Carbonate cement occurs within Fruitland coal cleats (Tremain and others, 1991, and this volume), but the coal and/or adjacent sandstones contain insufficient carbonate cement to account for the large amount of carbon dioxide in some coal gases. Dissolution of large quantities of isotopically very heavy carbonate cement ($\delta^{13}\text{C}$ greater than or equal to $+26\%$) would be required to explain the $\delta^{13}\text{C}$ values of total dissolved carbonate found in Fruitland Formation waters (maximum $+26.0\%$). Furthermore, carbonate dissolution would have to be demonstrated; precipitation of isotopically heavy carbonate in the cleat system may have occurred rather than dissolution of carbonate cement. Presently, these waters, under in situ conditions, are supersaturated with respect to all carbonate minerals. Therefore, bacterial degradation of organic acids and/or reduction of carbon dioxide by methanogenic bacteria may have produced the isotopically heavy carbon dioxide and bicarbonate in the Fruitland Formation.

A combination of thermogenic and biogenic gases can explain both methane $\delta^{13}\text{C}$ values and the heavy isotopic signature of total dissolved carbonate species in Fruitland Formation waters. Methanogenic degradation of short-chained organic acids through acetate dissimilation would produce both positive $\delta^{13}\text{C}$ values for total dissolved carbonate and methane depleted in ^{13}C by 74% to 65% relative to the bicarbonate at present in situ formation temperatures of 30°C to 54°C (Friedman and O'Neil, 1977). Furthermore, acetate dissimilation probably is the major source of biogenic gas in fresh-water environments (Whiticar and others, 1986, and references therein). Biogenic carbonate reduction of carbon dioxide also produces isotopically heavy bicarbonate and isotopically light methane. A mixture of 85% thermogenic methane ($\delta^{13}\text{C}$ of -42%) and 15% biogenic methane ($\delta^{13}\text{C}$ of -48%) would produce methane with an average isotopic value of -43% . The $\delta^{13}\text{C}$ value of the corresponding bicarbonate would be $+23\%$, assuming a fractionation factor of 71% between the biogenic methane and bicarbonate. These isotopic values are similar to isotopic ranges seen in Fruitland coal gases and formation waters (Figure 2). The less positive $\delta^{13}\text{C}$ values of total dissolved carbonate ($+16.7\%$ and $+17.5\%$) in the northwestern part of the basin (Figure 2) may indicate dilution of isotopically heavy bicarbonate by fresh ground water containing isotopically light bicarbonate derived from atmospheric and/or soil sources.

Although the carbon in biogenic methane is derived from carbon dioxide or organic material, the hydrogen originates from formation waters. Methanogenic bacteria using carbon dioxide as a carbon source derive all the hydrogen for methane formation from the water, whereas

acetate-fermenting bacteria derive only about 25% of the hydrogen from water (Whiticar and others, 1986). Therefore, carbon- and hydrogen-isotope fractionation during methanogenesis results in the generation of isotopically light biogenic methane that is depleted in ^{13}C and in deuterium (D). Because of the enrichment of ^{12}C and ^1H in the methane, formation waters become progressively enriched in ^{13}C and D and become isotopically heavier. The close correlation of δD with $\delta^{13}\text{C}$ in Fruitland Formation waters (Figure 17a) also suggests that some Fruitland coalbed methane is biogenic in origin (Kaiser and others, 1991a), particularly in that no correlation was found between δD and salinity to suggest mixing of fresh and connate waters. Furthermore, Fruitland Formation waters generally plot above the meteoric water line (Figure 17b), suggesting isotopic exchange between hydrogen gas and formation water (Kaiser and others, 1991a).

northern part of the basin where coal rank is higher; thermogenic gas from lower rank coals may have $\delta^{13}\text{C}$ values similar to biogenic methane.

The presence of biogenic methane in coal gases is supported in part by studies of gas desorption from Fruitland coal, which reported that desorbed methane from coal samples was isotopically heavier than methane produced from nearby wells (Rice and others, 1988). This suggests that $\delta^{13}\text{C}$ values of produced gases could represent a mixture of biogenic methane, occurring as free or dissolved gas in the cleat system, and thermogenic methane desorbed from the coal surfaces. The presence of free gas in some wells may be indicated by a geometric mean value of 195 MCFD (5,518 m^3/day) for initial production that is significantly larger than a mean value of 93 MCFD (2,632 m^3/day) for maximum annual production (Kaiser and others, 1991b).

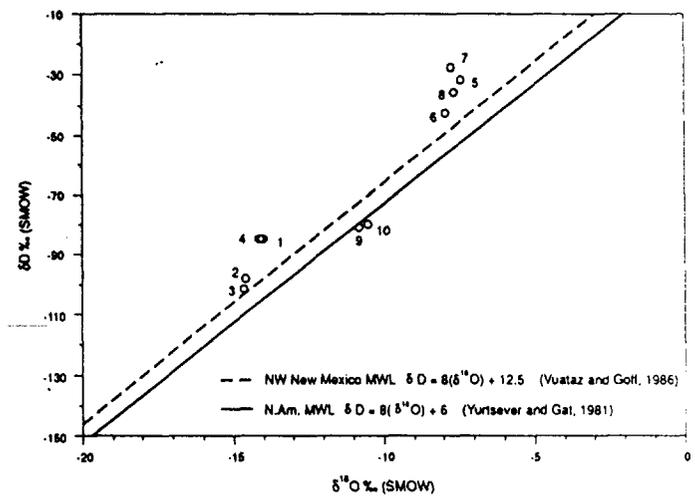
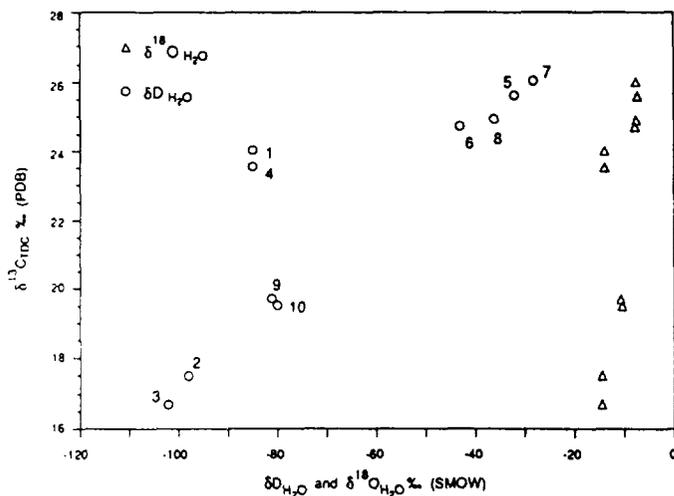


Figure 17. Stable-carbon isotope values for Fruitland Formation water. a. Formation water δD and $\delta^{18}\text{O}$ values increase with increasing $\delta^{13}\text{C}$ values. b. Northern and southern waters plot above the meteoric water line (MWL), suggesting isotopic exchange with hydrogen gases. From Kaiser and others (1991a).

Adsorption of methane onto coal particle surfaces is controlled by the amount of methane in the gas phase (Puri and Yee, 1990). Therefore, as the concentration of biogenic methane increases in the cleat system, methane will be adsorbed, assuming the maximum methane storage capacity has not been reached. If the concentration of biogenic methane is insufficient for adsorption to occur, methane remains as free gas in the cleat system or is dissolved in the formation water. As pressure decreases during production, adsorbed biogenic methane would be released together with thermogenic methane. During initial production, the gas would have a relatively large biogenic component (isotopically light methane), whereas subsequently desorbed gas would become progressively enriched in thermogenic methane (isotopically heavier). If this hypothesis is correct, $\delta^{13}\text{C}$ values of the produced methane should become less negative with time, as the relative proportions of the two gases change. The change in methane $\delta^{13}\text{C}$ values with time would be most pronounced in the

Rice and others (1988, 1989) suggested that dry coal gases in the southern San Juan basin may be biogenic in origin; the light isotopic signature of the methane ($\delta^{13}\text{C}$ values of -46.6‰ to -46.5‰) results from acetate dissimilation instead of carbonate reduction during methanogenesis. $\delta^{13}\text{C}$ values of $+19.5\text{‰}$ and $+19.7\text{‰}$ for bicarbonate in Fruitland water produced from two wells in this area support the conclusion that the gases are biogenic. However, some relatively dry gases in the southwestern part of the basin may be of early thermogenic origin, as suggested by Rice and others (1989).

As shown in Figure 10, coal gases in the overpressured area of the basin may contain significant amounts of carbon dioxide (greater than 3%). This area of high carbon dioxide content coincides with highest bottom-hole pressures, regional overpressure in the Fruitland, and medium- to high-volatile A bituminous coal. High production rates and large quantities of carbon dioxide (locally greater than 10%) in the gases produced from coalbeds in this area may

be a function of several factors, including (1) presence of thick coalbeds (which increase the resource) and folds (which increase fracture porosity and permeability in the coal; Ayers and Zellers, 1991), (2) coal rank, which may control the amount of carbon dioxide and organic acids in the system, (3) a general southeastward movement of aqueous transported organic compounds, bicarbonate, and methane, (4) permeability controls restricting lateral flow, and (5) bacterial degradation of organic compounds to produce significant amounts of isotopically heavy carbon dioxide and isotopically light biogenic methane.

Carbon dioxide is very soluble in water, and a significant proportion of the isotopically heavy carbon dioxide produced by acetate dissimilation probably was dissolved in formation waters; bicarbonate may have been subsequently transported southeastward (basinward). Because formation pressure increases basinward, progressively more carbon dioxide could be dissolved, and total alkalinity would increase. As reservoir pressure is reduced during production, carbon dioxide exsolves from the formation water and is produced with the gas. Therefore, the large proportion of carbon dioxide in coal gases from the over-pressured area is a result of carbon dioxide desorption from coal surfaces and exsolution from formation waters as reservoir pressures decrease during production.

Pictured Cliffs Sandstone Gases

Previous studies suggest that Pictured Cliffs Sandstone gases were derived from Fruitland coalbeds (Choate and others, 1984; Rice and Threlkeld, 1986) or from dispersed type III kerogen in the underlying Lewis Shale (Rice and others, 1988, 1989, 1990). Significant quantities of early thermogenic gas can be generated from type III organic material at low levels of thermal maturity (Galimov, 1988). Methane $\delta^{13}\text{C}$ values of Pictured Cliffs Sandstone gases (-44.3‰ to -39.1‰ ; Rice, 1983; Rice and others, 1988) suggest that Pictured Cliffs Sandstone gases are thermogenic in origin. Although significant volumes of Pictured Cliffs gas probably were derived from the underlying Lewis Shale, some could have migrated from overlying Fruitland coalbeds, and mixing of gases from these two sources is possible.

The wettest Pictured Cliffs Sandstone gases (C_1/C_{1-5} values less than 0.88) occur in the southeast corner of the basin (Figure 15). These wet gases may reflect lower levels of thermal maturity and/or differences in kerogen type. The fact that the highest nitrogen contents in Pictured Cliffs Sandstone gases also occur in this area may reflect gases derived predominantly from sapropelic organic material (containing more nitrogen-rich proteins relative to terrestrial organic matter) in the Lewis Shale. Alternatively, the wet gases in the southeast may represent gases derived only from the Lewis Shale, whereas Pictured Cliffs gases from other parts of the basin may represent a mixture of gases that migrated into the sandstone reservoirs from adjacent coalbeds and from the Lewis Shale.

Choate and others (1984) suggested that Pictured Cliffs reservoirs are sourced by Fruitland coalbeds, where pressure differences between the two formations result in downward migration of chemically drier coal gases. Relatively dry (C_1/C_{1-5} values greater than 0.88) sandstone gases occur in the northwestern part of the basin where thick basal coalbeds rest directly on top of Pictured Cliffs sandstones. Dip-elongate bands of coal are not as thick or abundant in the southeast (Ambrose and Ayers, 1991). The driest Pictured Cliffs gases (C_1/C_{1-5} values greater than 0.91), which occur in a dip-elongate band in eastern San Juan County, may result from completion practices (dual completion in Fruitland coalbeds and Pictured Cliffs Sandstone) or from downward migration from Fruitland coalbeds. This trend of dry gas coincides with dip-elongate bands of basal Fruitland coalbeds that may exceed 20 ft (6 m) in thickness (Ambrose and Ayers, 1991). The fact that C_1/C_{1-5} values of coal gases in western Rio Arriba County are similar to those from underlying Pictured Cliffs Sandstone gases also suggests possible local communication between the two reservoirs.

Hydraulic communication between basal Fruitland coalbeds and Pictured Cliffs Sandstone in the west-central part of the basin also is indicated by similar water chemistries and hydraulic heads (Kaiser and others, 1991a). However, the similarity of underpressured Fruitland coalbed and Pictured Cliffs Sandstone C_1/C_{1-5} values (Figures 9c, 13, and 14) and gas-composition distribution (Figures 8, 10, 15, and 16) indicate that gas composition alone does not necessarily distinguish coalbed from sandstone gases in parts of the southern basin. More detailed analytical methods, including methane, hydrogen, and carbon isotopic analyses and isotopic analyses of the wet gas components of both Fruitland and Pictured Cliffs gases on a basinwide scale, probably are required to establish the origin and migration pathways of Pictured Cliffs Sandstone gases.

CONCLUSIONS

1. Wet coal gases (C_1/C_{1-5} values less than 0.94) in the southern part of the San Juan basin probably are indigenous to the hydrogen-rich Fruitland coal and, therefore, do not result from completion practices and/or migration of gas from adjacent shale. Chemically dry to very dry coal gases in some parts of the southern basin most likely are biogenic in origin, although some early thermogenic methane may be present.

2. The similar composition of Pictured Cliffs Sandstone, Fruitland sandstone, and underpressured Fruitland coal gases in the southern part of the basin make determination of gas origin, based on gas composition alone, difficult or impossible. However, minor differences in carbon dioxide content and gas wetness in some areas may allow coal gases to be distinguished from sandstone gases locally.

3. Basin hydrology and coal rank control Fruitland coal-gas composition. The effect of basin hydrology on coal gas

composition is evidenced by the abrupt transition from carbon dioxide-rich, chemically dry to very dry gases in the northern, overpressured part of the basin to carbon dioxide-poor, chemically wet gases in the southern, underpressured area.

4. Bacterial degradation of organic acids by acetate dissimilation and/or the microbial reduction of carbon dioxide are required to produce the isotopically heavy bicarbonate ($\delta^{13}\text{C}$ values of +16.7‰ to +26‰) found in Fruitland Formation waters. The presence of free and dissolved biogenic methane in the coal cleat system and/or biogenic methane adsorbed onto coal particle surfaces may explain the relatively constant $\delta^{13}\text{C}$ methane values in the northern part of the basin, reported in earlier studies.

5. The large amounts of carbon dioxide in gases produced from coalbeds in the overpressured part of the basin may result from a combination of factors. Isotopic data suggest that much of the carbon dioxide in Fruitland coal gas is biogenic in origin but that some may originate from the formation water. We suggest that bacterially generated carbon dioxide was dissolved in formation waters and transported basinward. As reservoir pressure is reduced during production, carbon dioxide exsolves from the formation water and mixes with carbon dioxide, methane, and other gases desorbed from the coal.

6. Pictured Cliffs Sandstone gases are thermogenic in origin and probably were derived from the underlying Lewis Shale and, possibly, from overlying thick, basal Fruitland coalbeds in the western part of the basin. The wettest Pictured Cliffs gases, which occur in the southeast, may reflect a change in source-rock type (greater marine influence) and/or indicate gases derived entirely from the Lewis Shale. Chemically drier Pictured Cliffs gases elsewhere may represent a mixture of gases derived from both overlying coal and underlying shale.

ACKNOWLEDGMENTS

We thank Jeff Peace and George Lippman of El Paso Natural Gas Company, Brent W. Hale of Northwest Pipeline Corporation, Tom Hemler of Jerome P. McHugh and Associates, and Ernie Busch of the New Mexico Oil Conservation Commission for providing the gas data used in this study. Carol M. Tremain of the Colorado Geological Survey and Ernie Busch provided cumulative Fruitland coalbed methane production estimates. We also thank William B. Hanson of Amoco Production Company and Peter D. Jenden of Chevron Production Research for their valuable comments concerning coal-gas chemistry. Drafting was provided by the cartographic staff of the Bureau of Economic Geology under the direction of R.L. Dillon. We thank Tucker F. Heintz for reviewing the manuscript. This publication was authorized by the Director, Bureau of Economic Geology, The University of Texas at Austin. Research was funded by the Gas Research Institute under contract no. 5087-214-1544.

REFERENCES

- Ambrose, W.A., and Ayers, W.B., Jr., 1991, Geologic controls on coalbed occurrence, thickness, and continuity, Cedar Hill field and the COAL site, in Ayers, W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 47-68.
- Ayers, W.B., Jr., and Zellers, S.D., 1991, Geologic controls on Fruitland coal occurrence, thickness, and continuity, Navajo Lake area, San Juan Basin, in Ayers, W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 69-94.
- Bertrand, Philippe, Behar, Françoise, and Durand, Bernard, 1986, Composition of potential oil from humic coals in relation to their petrographic nature: *Organic Geochemistry*, v. 10, nos. 1-3, p. 601-608.
- Carothers, W.W., and Kharaka, Y.K., 1980, Stable carbon isotopes of HCO_3^- in oil-field waters—Implications for the origin of CO_2 : *Geochimica et Cosmochimica Acta*, v. 44, no. 2, p. 323-332.
- Choate, R., Lent, J., and Rightmire, C.T., 1984, Upper Cretaceous geology, coal, and the potential for methane recovery from coalbeds in San Juan Basin—Colorado and New Mexico, in Rightmire, C.T., Eddy, G.E., and Kirr, J.N., eds., *Coalbed methane resources of the United States: AAPG Studies in Geology, Series 17*, p. 185-222.
- Creedy, D.P., 1988, Geologic controls on the formation and distribution of gas in British coal measure strata: *International Journal of Coal Geology*, v. 10, no. 1, p. 1-31.
- Decker, A.D., and Horner, D.M., 1987, Origin and production implications of abnormal coal reservoir pressure, in *The 1987 Coalbed Methane Symposium Proceedings—University of Alabama, Tuscaloosa, November 16-19, 1987: School of Mines and Energy Development, Gas Research Institute, and U.S. Mine Safety and Health Administration*, p. 51-62.
- Dwight's Oil and Gas Reports, 1990a, Natural gas well production histories: Colorado Statewide Coal Bed Methane Report, v. 1, 373 p.
- Dwight's Oil and Gas Reports 1990b, Natural gas well production histories: New Mexico Statewide Coal Bed Methane Report, v. 1, 853 p.
- Friedman, Irving, O'Neil, J.R., and Fleischer, Michael, 1977, Compilation of stable carbon isotope fractionation factors of geochemical interest: USGS Professional Paper 440-KK, 12 p.
- Galimov, E.M., 1988, Sources and mechanisms of formation of gaseous hydrocarbons in sedimentary rocks, in Schoell, M., ed., *Origin of methane in the earth: Chemical Geology*, v. 71, nos. 1-3, p. 77-95.
- Hale, B.W., and Firth, C.H., 1988, Production history of the San Juan Unit No. 6 well, northern San Juan basin, New Mexico, in Fassett J.E., ed., *Geology and coal-bed methane resources of the northern San Juan basin, Colorado and New Mexico: Rocky Mountain Association of Geologists Guidebook*, p. 199-204.
- Hanson, W.B., 1990, Chemistry of western interior USA coal-bed gases based upon desorption of subsurface coal samples (abs.): AAPG Bulletin, v. 74, no. 8, p. 1326.
- Hunt, J.M., 1979, *Petroleum geochemistry and geology*: San Francisco, W.H. Freeman and Co., 617 p.
- James, T.A., and Burns, B.J., 1984, Microbial alteration of subsurface

- natural gas accumulations: AAPG Bulletin, v. 68, no. 8, p. 957-960.
- Jenden, P.D., 1985, Analysis of gases in the earth's crust: Gas Research Institute Rept. GRI-85/0106, 110 p.
- Jones, A.H., Kelkar, S., Bush, D., Hanson, J., Rakop, K., Ahmed, U., Holland, M., Tibbitts, G., Owen, L.B., and Bowman, K.C., 1985, Methane production characteristics of deeply buried coalbed reservoirs: Gas Research Institute, Final Rept. GRI-85/0033 (February 1982-December 1984), 176 p.
- Kaiser, W.R., Ayers, W.B., Jr., Ambrose, W.A., Laubach, S.E., Scott, A.R., and Tremain, C.M., 1991b, Geologic and hydrologic characterization of coalbed methane production, Fruitland Formation, in Ayers W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 273-301.
- Kaiser, W.R., Swartz, T.E., and Hawkins, G.J., 1991a, Hydrology of the Fruitland Formation, San Juan Basin, in Ayers, W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 195-241.
- Khorasani, G.K., 1987, Oil-prone coals of the Walloon Coal Measures, Surat Basin, Australia, in Scott, A.C., ed., 1987, Coal and coal-bearing strata—Recent advances: Geological Society Special Publication 32, p. 303-310.
- Law, B.E., Anders, D.E., and Michael, G.E., 1990, Use of Rock-Eval pyrolysis and vitrinite reflectance data in characterizing type and maturity of organic matter in coal, upper Cretaceous Fruitland Formation, San Juan Basin, New Mexico and Colorado (abs.): AAPG Bulletin, v. 74, no. 8, p. 1333.
- Leythaeuser, D., Schaefer, R.G., Cornford, C., and Weiner, B., 1979, Generation and migration of light hydrocarbons (C₂-C₇) in sedimentary basins: Organic Geochemistry, v. 1, p. 191-204.
- Meissner, F.F., 1987, Mechanisms and patterns of gas generation and expulsion—Migration and accumulation associated with coal measures Green River and San Juan Basins Rocky Mountain region, USA, in Doligez, Brigitte, ed., Migration of hydrocarbons in sedimentary basins: Paris, Éditions Technip, p. 79-112.
- Puri, R., and Yee, D., 1990, Enhanced coalbed methane recovery: Society of Petroleum Engineer Paper 20732 [presented at SPE Annual Technical Conference and Exhibition, September 23-26, New Orleans, Louisiana].
- Rice, D.D., 1983, Relation of natural gas composition to thermal maturity and source-rock type in San Juan Basin, northwestern New Mexico and southwestern Colorado: AAPG Bulletin, v. 67, no. 8, p. 1199-1218.
- Rice, D.D., Clayton, J.L., and Pawlewicz, M.J., 1989, Characterization of coal-derived hydrocarbons and source-rock potential of coal beds, San Juan Basin, New Mexico and Colorado, U.S.A.: International Journal of Coal Geology, v. 13, p. 597-626.
- Rice, D.D., and Threlkeld, C.N., 1986, Comparison of natural gases produced from Upper Cretaceous Fruitland Formation coal beds and adjacent sandstone reservoirs, San Juan basin, New Mexico and Colorado (abs.): AAPG Bulletin, v. 70, no. 5, p. 638.
- Rice, D.D., Threlkeld, C.N., Vuletich, A.K., and Pawlewicz, M.J., 1988, Identification and significance of coal-bed gas, San Juan Basin, northwestern New Mexico and southwestern Colorado, in Fassett, J.E., ed., Geology and coal-bed methane resources of the northern San Juan basin, Colorado and New Mexico: Rocky Mountain Association of Geologists Guidebook, p. 51-59.
- Rice, D.D., Threlkeld, C.N., Vuletich, A.K., and Pawlewicz, M.J., 1990, Nonassociated gas potential of San Juan Basin considerable: Oil & Gas Journal, v. 88, no. 33 (August 13), p. 60-61.
- Rohrback, B.G., Peters, K.E., Sweeney, R.E., and Kaplan, I.R., 1983, Ammonia formation in laboratory simulated thermal maturation—Implications related to the origin of nitrogen in natural gas, in Bjørøy, M., ed., Advances in organic geochemistry, 1981: New York, John Wiley and Sons, p. 819-823.
- Schoell, Martin, 1983, Genetic characterization of natural gases: AAPG Bulletin, v. 67, no. 12, p. 2225-2238.
- Scott, A.R., Kaiser, W.R., and Ayers, W.B., Jr., 1991, Thermal maturity of Fruitland coal and composition and distribution of Fruitland Formation and Pictured Cliffs sandstone gases, in Ayers, W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 243-270.
- Stach, E., Mackowsky, M.T., Teichmüller, M., Taylor, G.H., Chandra, D., and Teichmüller, R., 1975, Stach's text book of coal petrology, 2d ed.: Stuttgart, Gebrüder Borntraeger, 428 p.
- Tissot B., and Welte, D., 1978, Petroleum formation and occurrence: Berlin, Springer-Verlag, 521 p.
- Tremain, C.M., Laubach, S.E., and Whitehead, N.H., III, 1991, Coal fracture (cleat) patterns in Upper Cretaceous Fruitland Formation, San Juan Basin, Colorado and New Mexico, in Ayers, W.B., Jr., and others, Geologic and hydrologic controls on the occurrence and producibility of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute, Topical Rept. GRI-91/0072 (August 1987-July 1990), p. 97-117.
- Whiticar, M.J., Faber, E., and Schoell, M., 1986, Biogenic methane formation in marine and freshwater environments. CO₂ reduction vs. acetate fermentation—Isotope evidence: Geochimica et Cosmochimica Acta, v. 50, no. 5, p. 693-709.
- Yurtsever, Y., and Gat, J.R., 1981, Atmospheric waters, in Gat, J.R., and Gonfiantini, R., eds., Stable isotope hydrology—Deuterium and oxygen-18 in the water cycle: International Atomic Energy Agency Technical Report Series 210, p. 103-142.
- Vuataz, F.D., and Goff, F., 1986, Isotope geochemistry of thermal and nonthermal waters in the Valles Caldera, Jemez Mountains: Journal of Geophysical Research, v. 91, p. 1835-1854.